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# Quantitative Analytical Chemistry (QUANCHEM)

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School of Sciences

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**Lesson 1. Introduction to Analytical Chemistry**

1. Analytical chemistry vs. Chemical analysis.
2. Current relevance of Analytical Chemistry.
3. Analytical cases.
4. Classification of analytical methods of analysis.
5. Stages in the analytical procedure.
6. Techniques, methods and protocols.
7. Sampling and preparation.

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**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.

**Wilhelm Ostwald, 1894. Nobel prize awarded on 1909.**

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**Analysis**

<p><b>Qualitative</b></p> <p><u>Recognition and identification</u> of the different components</p> <p><b>What's?</b></p>	<p><b>Quantitative</b></p> <p><u>Determination (quantification)</u> of the content of each of the components</p> <p><b>How much?</b></p>
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**Sequential steps in chemical analysis**

Analytical Chemistry involves the:


- separation
- identification
- determination

of the relative amounts of the components of a given sample.

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**Classification of Analytical Methods**

<p><b>Chemical or Classic</b></p> <ul style="list-style-type: none"> <li>• Qualitative analysis</li> <li>• Gravimetric analysis</li> <li>• Volumetric analysis (titrimetry)</li> </ul>	<p><b>Physicochemical or Instrumental</b></p> <ul style="list-style-type: none"> <li>• Spectroscopic</li> <li>• Electrochemical</li> <li>• Radiochemical</li> <li>• Thermal...</li> </ul>
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**Classical Methods vs. Instrumental Methods**

The **classical methods** have in common the fact that they are based on chemical reactions in **equilibrium**.

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

In **gravimetric analysis**, quantification is done by transforming the species in an insoluble product of high purity and defined stoichiometry, which is then **weighed**.

**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**.

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


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Gravimetry

**Chemical precipitation:**

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

**Electrodeposition:**  
 passage of current through the solution and weighting of the deposit formed at the cathode.

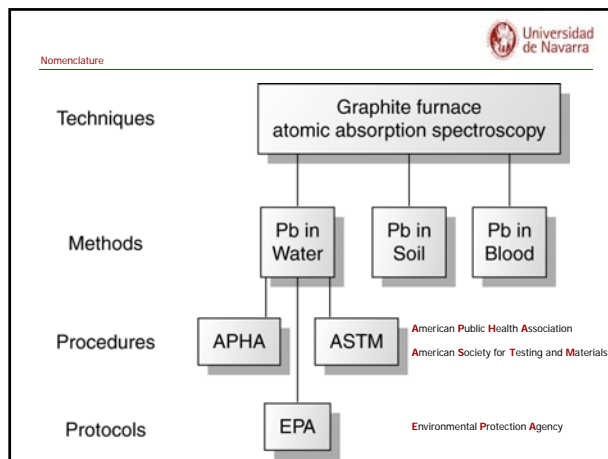


**Volatilization**

**Physical:** weight loss upon heating

**Chemical:** CO<sub>2</sub> evolved from a calcite

**Gravimetric Analysis**



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Nomenclature

Techniques: Graphite furnace atomic absorption spectroscopy

Methods: Pb in Water, Pb in Soil, Pb in Blood

Procedures: APHA, ASTM

Protocols: EPA

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, work objectives, rationale, 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
  - a) Hypothesis to be verified
  - b) Why is it necessary or interesting to conduct the study
  - c) Relevant information existing about it and search methodology used
  - d) Usefulness of the results obtained and the field of application or generalization of these
3. If any, description of the risks to participants and control systems provided
4. Type design : randomized , observational , etc. . .
5. Description of treatment or intervention being studied
6. Inclusion and exclusion criteria
7. Calendar of study
8. What are the variables of measurement that will be studied , elementary (primary objective) and secondary
9. Method of allocation to each group ( randomized , randomized by strata , etc. ) as well as other mechanisms to control bias : for example, double-blind study
10. Planned sample size and justification of it.
11. If a pilot study was conducted: description and results
12. Notebook data collection
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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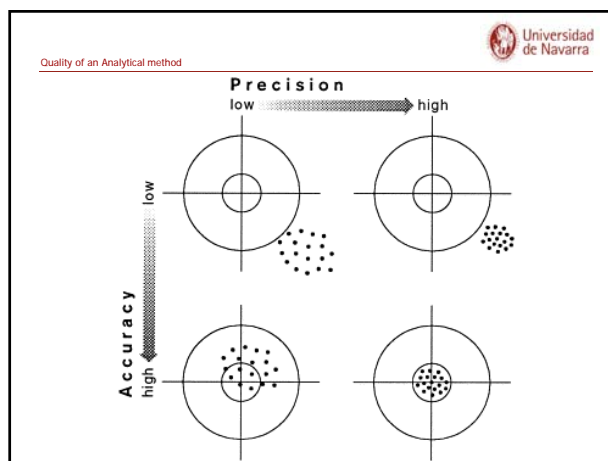
Figures of merit of an Analytical Method

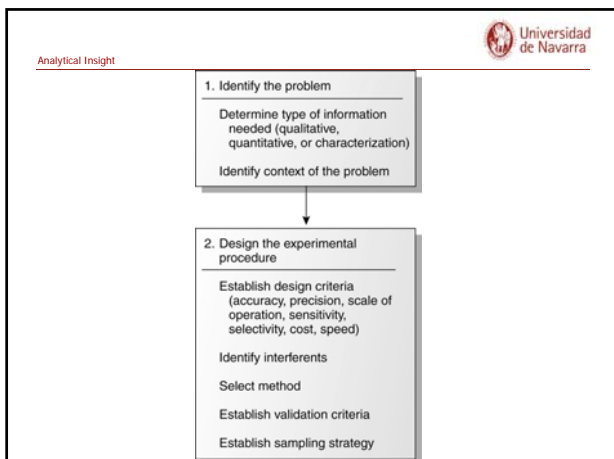
**SENSITIVITY:**  
minimum quantity or concentration which can be determined

**ACCURACY:**  
proximity of a measurement to its true value

**SELECTIVITY:**  
interference of a chemical species in the identification/determination of another

**PRECISION:**  
Concordance between two or more numerical results when obtained in an identical manner





- Stages of the Analytical Process
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.
- 

- Gross sample collection
- **LIQUIDS:** aliquot
  - **GASES:** The problem is in the storage and transport
  - **SOLIDS:**
    - **Fragments or particles:** random selection of batches
    - **Compact:** specimens and filings

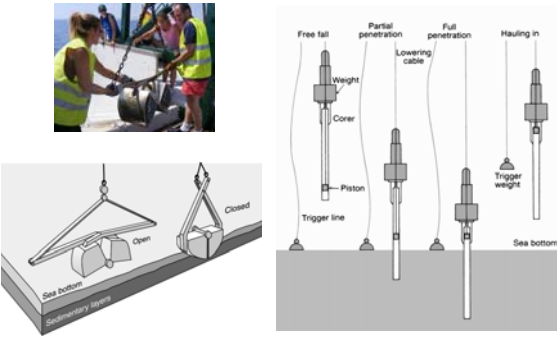
Collection of marine samples: Niskin bottles

April 1997

March 1998




Collecting marine sediments: dredges and specimens





Solid sample collection

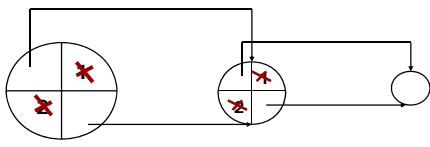





Reduction of size of sample

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**.

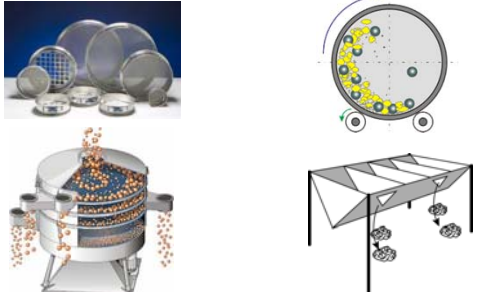
Quartered system






Reduction of size of sample


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 (CO<sub>2</sub> 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
  - H<sub>2</sub>O (cold or hot)
  - HCl diluted
  - HCl concentrated
  - HNO<sub>3</sub> diluted
  - HNO<sub>3</sub> concentrated
  - Aqua regia (3 HCl + 1 HNO<sub>3</sub>)



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.
5. Heat treatment of precipitates.
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 of Analysis

**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




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	Colloidal suspension	Crystalline suspension
$10^{-8}$ cm	$10^{-7} - 10^{-4}$ cm	$> 10^{-4}$ cm

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



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 *concentración de los reactivos*
- 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:

**Relative Supersaturation:**  $\frac{Q-S}{S}$

**Q:** concentration of the solute at any instant  
**S:** equilibrium solubility




RS and Particle Size

The **particle size** of a precipitate **varies inversely** with the average relative supersaturation during the time when the reagent is being introduced.

$$a A + r R \rightarrow \downarrow A_a R_r$$

- **Large R.S.:** precipitate tends to be **colloidal** (small particle size)
- **Small R.S.:** **crystalline** precipitate more likely (large particle size)



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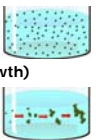
Nucleation (N) vs. Particle Growth (PG)

**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**



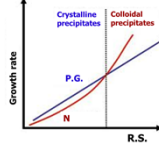
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Nucleation (N) vs. Particle Growth (PG)

If nucleation (N) is predominant:  
 ⇨ large number of small size particles

When particle growth (PG) becomes predominant:  
 ⇨ smaller number of larger particles is produced

**N increases exponentially with R.S.**  
**PG varies linearly with R.S.**



R.S. can be minimized:

- High T (S increases)
- Dilute solutions (reduces Q)
- Slow addition of the precipitating agent with good stirring (minimizes Q)

$$\frac{Q - S}{S}$$

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Colloids

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**

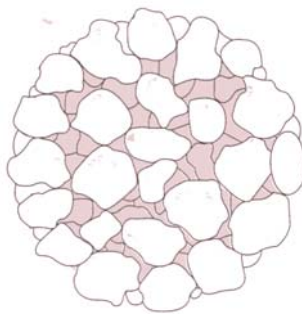
**EMULSOID**  
 Lyophilic (H<sub>2</sub>O: hydrophilic); Fe, Al

**SUSPENSOID**  
 Lyophobic (H<sub>2</sub>O: hydrophobic); AgCl  
 110°C: total loss of H<sub>2</sub>O

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Specific Surface Area of Colloids

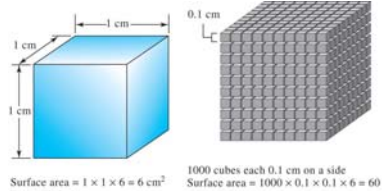
A coagulated colloid continues to expose a large surface area to the solution from which it is formed



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Specific Surface Area of Colloids

Surface area per unit mass of solid (cm<sup>2</sup> g<sup>-1</sup>)



Surface area = 1 × 1 × 6 = 6 cm<sup>2</sup>  
 Surface area = 1000 × 0.1 × 0.1 × 6 = 60 cm<sup>2</sup>

1000 cubes each 0.1 cm on a side

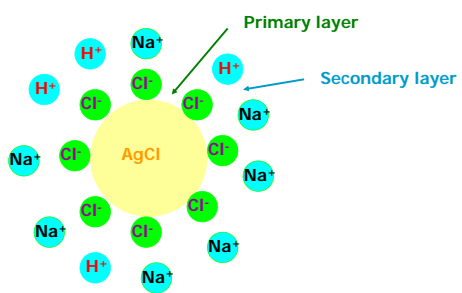
**Crystalline precipitate: 0.1 - 001 cm**  
 m=2g ⇨ 30 - 300 cm<sup>2</sup> g<sup>-1</sup>

**Colloidal suspension: 10<sup>18</sup> particles of 10<sup>-6</sup> cm**  
 ⇨ 3 · 10<sup>6</sup> cm<sup>2</sup> g<sup>-1</sup>

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Coagulation

Process by which a colloidal suspension becomes a filterable solid.



**Primary layer**  
**Secondary layer**

AgCl

Na<sup>+</sup>, Cl<sup>-</sup>, H<sup>+</sup>

Coagulation

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Process by which a colloidal suspension becomes a filterable solid.

The diagram shows a central yellow circle labeled 'AgCl'. It is surrounded by a 'Primary layer' of smaller green circles labeled 'Cl<sup>-</sup>'. This primary layer is further surrounded by a 'Secondary layer' of blue circles labeled 'Na<sup>+</sup>'. Other ions like 'H<sup>+</sup>' and 'Ag<sup>+</sup>' are also shown in the surrounding solution.

Coagulation

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Process by which a colloidal suspension becomes a filterable solid.

The diagram shows a larger yellow circle labeled 'AgCl' compared to the previous slide. It has a primary layer of green 'Cl<sup>-</sup>' ions and a secondary layer of blue 'Na<sup>+</sup>' ions. The surrounding solution contains various ions including 'H<sup>+</sup>', 'Na<sup>+</sup>', and 'Ag<sup>+</sup>'.

Coagulation

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Process by which a colloidal suspension becomes a filterable solid.

The diagram shows a large yellow circle labeled 'AgCl'. Three blue circles labeled 'H<sup>+</sup>' are positioned around it, representing the effect of an electrolyte.

This phenomenon is favoured by:

- Temperature,
- Stirring, and
- Presence of electrolyte

Coagulation

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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.

The diagram shows a beaker containing a solution. At the bottom, there are several grey particles of varying sizes. A chemical reaction scheme is shown above the particles:  $AgCl + AgCl \rightleftharpoons Ag^+ + Cl^-$  and  $Ag^+ + NO_3^- \rightleftharpoons AgNO_3$ . The text 'Ostwald ripening' is written below the beaker.

©Gary Christian, Analytical Chemistry, 6th Ed. (Wiley)

Coagulation

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Cl<sup>-</sup> adsorbs on the particles when in excess (primary layer). A counter layer of cations forms. The neutral double layer causes the colloidal particles to coagulate. Washing with water will dilute the counter layer and the primary layer charge causes the particles to revert to the colloidal state (peptization). So we wash with an electrolyte that can be volatilized on heating (HNO<sub>3</sub>).

The diagram shows a central yellow circle labeled 'Colloidal AgCl'. It is surrounded by a 'Primary adsorptive layer' of blue circles labeled 'Cl<sup>-</sup>'. This is followed by a 'Counter layer' of blue circles labeled 'Na<sup>+</sup>'. Other ions like 'H<sup>+</sup>', 'K<sup>+</sup>', and 'NO<sub>3</sub><sup>-</sup>' are also shown.

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Representation of silver chloride colloidal particle and adsorptive layers when Cl<sup>-</sup> is in excess.

Coprecipitation

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

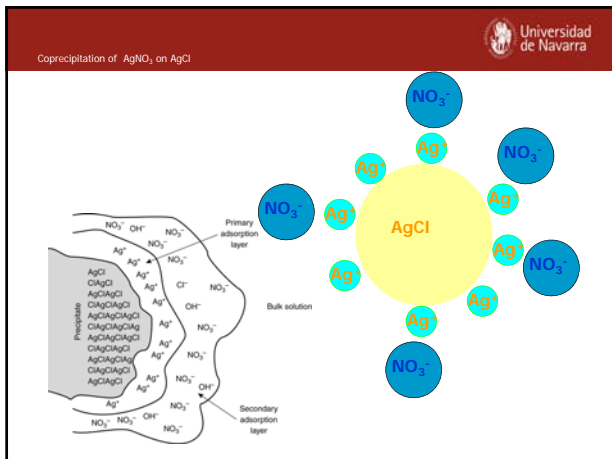
**Four main types of coprecipitation:**

- Surface adsorption (especially in colloids)
- Mixed-crystal formation
- Occlusion
- Mechanical entrapment

Equilibrium processes

Arise from kinetics of crystal growth





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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

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Minimizing Adsorbed Impurities on Colloids

•**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.

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Minimizing Adsorbed Impurities on Colloids

•**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.

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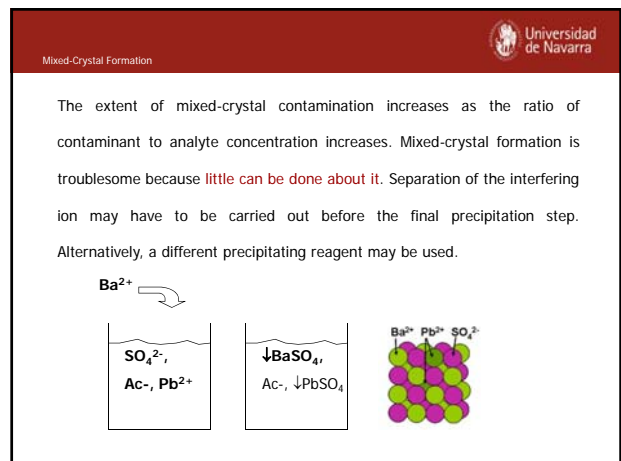
Mixed-Crystal Formation

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,  $\text{MgKPO}_4$ , in  $\text{MgNH}_4\text{PO}_4$ ,  $\text{SrSO}_4$  in  $\text{BaSO}_4$ , and  $\text{MnS}$  in  $\text{CdS}$ .

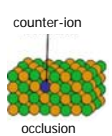


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Occlusion and Mechanical Entrapment

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.

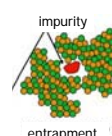
counter-ion



occlusion

**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.

impurity



entrapment

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Precipitation from Homogeneous Solution

A precipitating agent is generated in a solution of the analyte by a **slow chemical reaction**.

$$\text{CO}(\text{NH}_2)_2 + 3\text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + 2\text{NH}_4^+ + 2\text{OH}^-$$

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.

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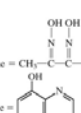
Precipitation from Homogeneous Solution


**TABLE 12-1**  
Methods for Homogeneous Generation of Precipitating Agents

Precipitating Agent	Reagent	Generation Reaction	Elements Precipitated
$\text{OH}^-$	Urea	$(\text{NH}_2)_2\text{CO} + 3\text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{NH}_4^+ + 2\text{OH}^-$	Al, Ga, Th, Bi, Fe, Sn
$\text{PO}_4^{3-}$	Trimethyl phosphate	$(\text{CH}_3)_3\text{PO} + 3\text{H}_2\text{O} \rightarrow 3\text{CH}_3\text{OH} + \text{H}_3\text{PO}_4$	Zr, Hf
$\text{C}_2\text{O}_4^{2-}$	Ethyl oxalate	$(\text{C}_2\text{H}_5)_2\text{C}_2\text{O}_4 + 2\text{H}_2\text{O} \rightarrow 2\text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{C}_2\text{O}_4$	Mg, Zn, Ca
$\text{SO}_4^{2-}$	Dimethyl sulfate	$(\text{CH}_3)_2\text{SO}_4 + 4\text{H}_2\text{O} \rightarrow 2\text{CH}_3\text{OH} + \text{SO}_4^{2-} + 2\text{H}_3\text{O}^+$	Ba, Ca, Sr, Pb
$\text{CO}_3^{2-}$	Trichloroacetic acid	$\text{Cl}_3\text{CCOOH} + 2\text{OH}^- \rightarrow \text{CHCl}_3 + \text{CO}_3^{2-} + \text{H}_2\text{O}$	La, Ba, Ra
H <sub>2</sub> S	Thioacetamide <sup>a</sup>	$\text{CH}_3\text{CSNH}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CONH}_2 + \text{H}_2\text{S}$	Sr, Mn, Cu, Cd
DMG <sup>b</sup>	Biacetyl + hydroxylamine	$\text{CH}_3\text{COCCH}_3 + 2\text{H}_2\text{NOH} \rightarrow \text{DMG} + 2\text{H}_2\text{O}$	Ni
HOQ <sup>c</sup>	8-Acetoxyquinoline <sup>d</sup>	$\text{CH}_3\text{COOQ} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + \text{HOQ}$	Al, U, Mg, Zn

<sup>a</sup> $\text{CH}_3\text{C}(=\text{S})\text{NH}_2$

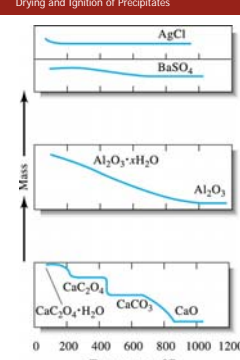
<sup>b</sup>DMG = Dimethylglyoxime =  $\text{CH}_3\text{C}(\text{OH})=\text{N}-\text{C}(\text{OH})=\text{N}-\text{CH}_3$

<sup>c</sup>HOQ = 8-Hydroxyquinoline = 

<sup>d</sup>

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Drying and Ignition of Precipitates



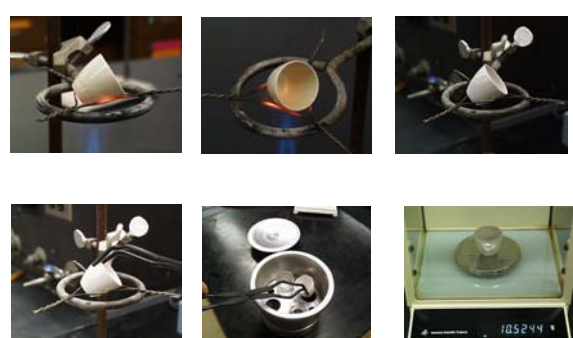
After filtration, a gravimetric precipitate is heated until its **mass becomes constant**.

**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.

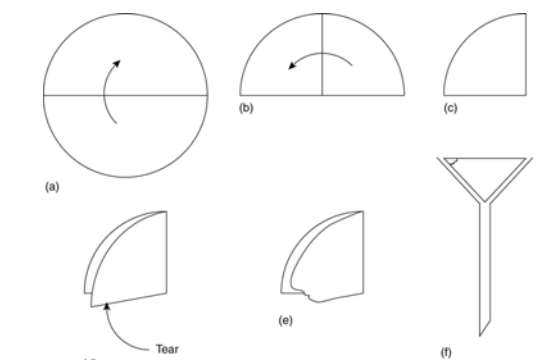
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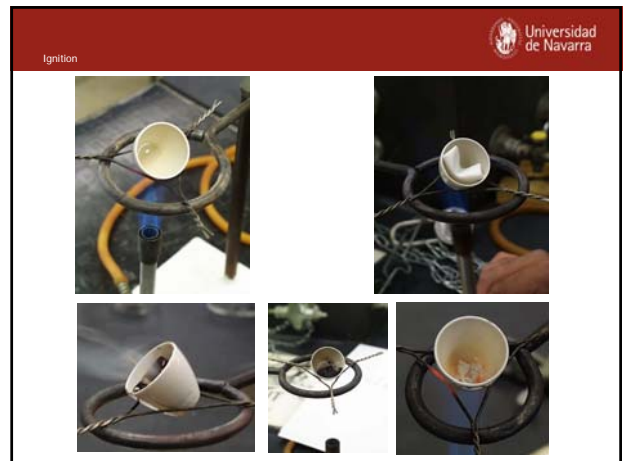
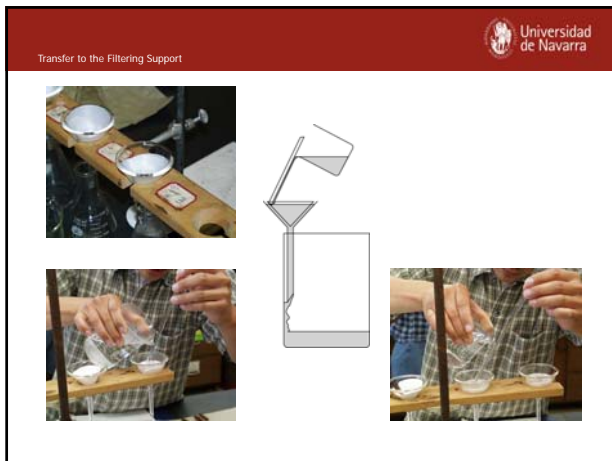
Tare of the Crucible



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Disposition of the Filter Paper in the Funnel





Common Sources of Errors

- ⇒ Incomplete elimination of either H<sub>2</sub>O or volatile electrolytes.
- ⇒ Reduction of the precipitate by the C from the filter paper.
  - Dry in the air.
- ⇒ Overignition: decomposition and obtaining of unknown products.
- ⇒ Readsorption of H<sub>2</sub>O or CO<sub>2</sub>
  - Cap and use desiccator.

Precipitating Reagents

**Precipitating Agents**

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

Inorganic Precipitating Agents

Precipitating agent	Precipitated element
NH <sub>3</sub> (aq)	Be (BeO), Al (Al <sub>2</sub> O <sub>3</sub> ), Fe (Fe <sub>2</sub> O <sub>3</sub> )
H <sub>2</sub> S	Zn (ZnO, ZnSO <sub>4</sub> ), As (As <sub>2</sub> O <sub>3</sub> , As <sub>2</sub> O <sub>5</sub> ), Sb (Sb <sub>2</sub> O <sub>3</sub> , Sb <sub>2</sub> O <sub>5</sub> )
(NH <sub>4</sub> ) <sub>2</sub> S	Hg (HgS)
(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>	Mg (Mg <sub>3</sub> P <sub>2</sub> O <sub>7</sub> )
H <sub>2</sub> SO <sub>4</sub>	Sr, Ca, Pb, Ba (XSO <sub>4</sub> )
(NH <sub>4</sub> ) <sub>2</sub> MoO <sub>4</sub>	Pb (PbMoO <sub>4</sub> )
AgNO <sub>3</sub>	Cl (AgCl), Br (AgBr), I (AgI)
(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub>	Bi (Bi <sub>2</sub> O <sub>3</sub> )
BaCl <sub>2</sub>	SO <sub>4</sub> <sup>2-</sup> (BaSO <sub>4</sub> )
MgCl <sub>2</sub> , NH <sub>4</sub> Cl	PO <sub>4</sub> <sup>3-</sup> (Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub> )

Organic Precipitating Agents

Reagent	Structure	Metals Precipitated
Dimethylglyoxime	CH <sub>3</sub> -C(=NOH) CH <sub>3</sub> -C(=NOH)	Ni(II) in NH <sub>3</sub> or buffered HOAc; Pd(II) in HCl (M <sup>2+</sup> + 2HR → MR <sub>2</sub> + 2H <sup>+</sup> )
α-Benzoinzime (cupron)		Cu(II) in NH <sub>3</sub> and tartrate; Mo(VI) and W(VI) in H <sup>+</sup> (M <sup>2+</sup> + H <sub>2</sub> R → MR <sub>2</sub> + 2H <sup>+</sup> ; M <sup>2+</sup> = Cu <sup>2+</sup> , MoO <sub>4</sub> <sup>2-</sup> , WO <sub>4</sub> <sup>2-</sup> ) Metal oxide weighed
Ammonium nitrosophenylhydroxylamine (cupferon)		Fe(III), V(V), Ti(IV), Zr(IV), Sn(IV), U(IV) (M <sup>2+</sup> + nNH <sub>2</sub> R → MR <sub>n</sub> + nNH <sub>4</sub> <sup>+</sup> ) Metal oxide weighed
8-Hydroxyquinoline (oxine)		Many metals. Useful for Al(III) and Mg(II) (M <sup>2+</sup> + nHR → MR <sub>n</sub> + nH <sup>+</sup> )
Sodium diethylthiocarbamate		Many metals from acid solution (M <sup>2+</sup> + nNaR → MR <sub>n</sub> + nNa <sup>+</sup> )
Sodium tetraphenylboron	NaB(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub>	K <sup>+</sup> , Rb <sup>+</sup> , Cs <sup>+</sup> , Tl <sup>+</sup> , Ag <sup>+</sup> , Hg(I), Cu(I), NH <sub>4</sub> <sup>+</sup> , RNH <sub>3</sub> <sup>+</sup> , R <sub>2</sub> NH <sub>2</sub> <sup>+</sup> , R <sub>3</sub> NH <sup>+</sup> , R <sub>4</sub> N <sup>+</sup> . Acidic solution (M <sup>+</sup> + NaR → MR + Na <sup>+</sup> )
Tetraphenylarsonium chloride	(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> AsCl	CrO <sub>4</sub> <sup>2-</sup> , MoO <sub>4</sub> <sup>2-</sup> , ReO <sub>4</sub> <sup>-</sup> , MoO <sub>4</sub> <sup>2-</sup> , WO <sub>4</sub> <sup>2-</sup> , ClO <sub>4</sub> <sup>-</sup> , I <sub>3</sub> <sup>-</sup> . Acidic solution (A <sup>+</sup> + nRCl → R <sub>n</sub> A + nCl <sup>-</sup> )

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Organic Functional Groups that may be determined Gravimetrically

**TABLE 12-4**  
Gravimetric Methods for Organic Functional Groups

Functional Group	Basis for Method	Reaction and Product Weighed*
Carbonyl	Mass of precipitate with 2,4-dinitrophenylhydrazine	$RCHO + H_2NNHC_6H_4(NO_2)_2 \rightarrow R-CH=N-NHC_6H_4(NO_2)_2 + H_2O$ (RCOR' reacts similarly)
Aromatic carbonyl	Mass of $CO_2$ formed at 230°C in quinoline; $CO_2$ distilled, absorbed, and weighed	$ArCHO \xrightarrow[CaCO_3]{230^\circ C} Ar + CO_2(g)$
Methoxyl and ethoxyl	Mass of AgI formed after distillation and decomposition of $CH_3I$ or $C_2H_5I$	$ROCH_3 + HI \rightarrow ROH + CH_3I$ $ROCH_2CH_3 + HI \rightarrow ROH + C_2H_5I$ $CH_3I + Ag^+ + H_2O \rightarrow AgI(s) + CH_3OH$
Aromatic nitro	Mass loss of Sn	$RNO_2 + \frac{1}{2}Sn(s) + 6H^+ \rightarrow RNH_2 + \frac{1}{2}Sn^{4+} + 2H_2O$
Azo	Mass loss of Cu	$RN=N R' + 2Cu(s) + 4H^+ \rightarrow RNH_2 + R'NH_2 + 2Cu^{2+}$
Phosphate	Mass of Ba salt	$RO(POH)_2 + Ba^{2+} \rightarrow ROPO_3Ba(s) + 2H^+$
Sulfamic acid	Mass of $BaSO_4$ after oxidation with $HNO_3$	$RNHSO_2H + HNO_3 + Ba^{2+} \rightarrow ROH + BaSO_4(s) + N_2 + 2H^+$
Sulfimic acid	Mass of $Fe_2O_3$ after ignition of Fe(III) sulfinate	$3ROS(OH) + Fe^{3+} \rightarrow (ROS(O))_2Fe(s) + 3H^+$ $(ROS(O))_2Fe \xrightarrow{\Delta} CO_2 + H_2O + SO_2 + Fe_2O_3(s)$

\*The substance weighed is underlined.  
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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.

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Volatilization Gravimetry

**Volatilization**  
**H<sub>2</sub>O and CO<sub>2</sub>**

- **Direct:** Water vapor is collected on a solid desiccant, and its mass is determined from the mass gain of the desiccant.
- **Indirect:** Loss of mass of the sample during heating (assuming that water is the only component that is volatilized).

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Volatilization Gravimetry: CO<sub>2</sub>

**Example: Determination of NaHCO<sub>3</sub> content of antacid tablets.**

$$HCO_3^- + H^+ \rightleftharpoons H_2CO_3 \rightarrow \uparrow CO_2 + H_2O$$

The pure stream of CO<sub>2</sub> in N<sub>2</sub> passes through a weighed absorption tube containing the absorbent Ascarite (NaOH absorbed on a nonfibrous silicate), that also contains a desiccant such as CaSO<sub>4</sub> to prevent loss of the water produced in this latter reaction:

$$2 NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$$

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Volatilization Gravimetry

**S<sup>2-</sup> and SO<sub>3</sub><sup>2-</sup>:**

H<sub>2</sub>S and SO<sub>2</sub> evolved from the sample after treatment with acid is collected in a suitable absorbent.

**C, H in organic compounds:**

The combustion products, CO<sub>2</sub> and H<sub>2</sub>O, are collected selectively on weighed absorbents. The increase in mass serves as the analytical variable.

Lesson 3. Fundamentals of Volumetric Analysis

1. Thermodynamic and Kinetic Characteristics of Reactions Useful in Volumetric Analysis.

2. Titration Curves.

3. End Point Indication Systems.

4. Volumetric Calculations.

5. Volumetric Error.

End Point Indication

**Indicating systems**

**1. Chemical or visual indicators**

- Colored indicators
  - Auto indicators
  - Strict sense indicators
- Fluorescent
- Turbidimetric
- Adsorption

**2. Physico-chemical indicators**

- Photometric
- Electrochemical
  - Potentiometric
  - Amperometric


General Principles of Volumetric Analysis

**Titration** are based on a **reaction** between the **analyte** and a standard reagent known as **titrant**.

A volumetric titration demands:

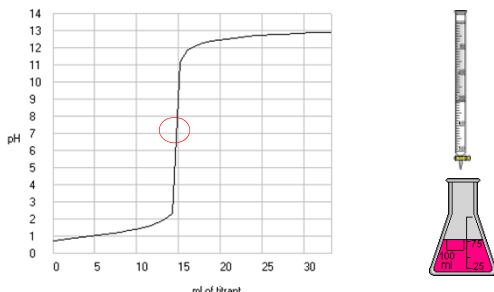
- adding an **accurately measured volume**
- of a solution of **known concentration**,
- to produce a **chemical change** in the test solution
- exactly fitting to a **stoichiometric** equation.

$$a A + t T \rightleftharpoons p P$$



Titration Curve

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**.



Characteristics of the Chemical Reaction Involved in a Volumetric Analysis

- Must be stoichiometric
- High equilibrium constant
- Fast kinetics
- End of the reaction detectable in a simple way

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**.

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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.

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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, **AgNO<sub>3</sub>**, which is used for the determination of the halogens, the halogen-like anions. Titrations with silver nitrate are sometimes called **argentometric titrations**.

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Argentometric Titrations: Drawbacks

**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.

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Argentometric Calculations

50.00 mL of NaCl 0.10 M titrated with AgNO<sub>3</sub> 0.10 M.  $P_s \text{ AgCl} = 1.0 \cdot 10^{-10}$

1. Start.  $[\text{Cl}^-] = 10^{-1} \text{ M} \Rightarrow \text{pCl} = -\log(0.1) = 1.00$
2. Pre-equivalence. + 10 mL de AgNO<sub>3</sub>  

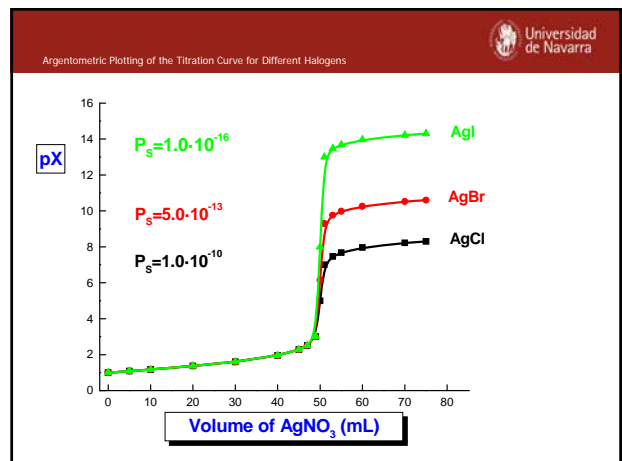
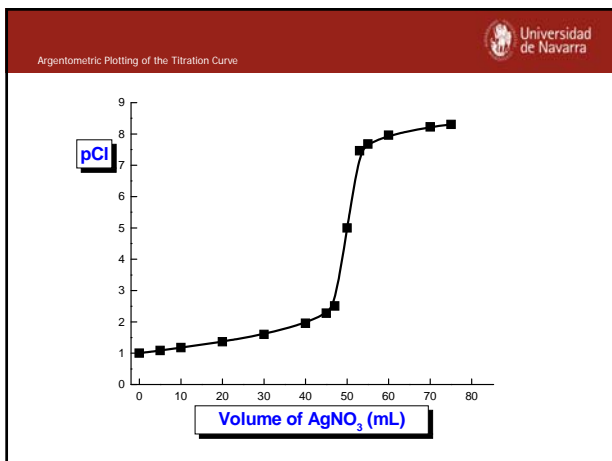
$$[\text{Cl}^-] = \frac{50.0\text{mL} \cdot 0.1\text{M} - 10.0\text{mL} \cdot 0.1\text{M}}{(50+10)\text{mL}} = 0.067\text{M} \quad \text{pCl} = 1.17$$
3. Equivalence Point. + 50 mL of AgNO<sub>3</sub>  

$$\text{AgCl} \rightleftharpoons \text{Ag}^+ + \text{Cl}^-; \quad P_s = [\text{Ag}^+][\text{Cl}^-] = [\text{Cl}^-]^2 = 1.0 \cdot 10^{-10}$$

$$[\text{Cl}^-] = 1.0 \cdot 10^{-5} \text{ M} \Rightarrow \text{pCl} = 5.00$$
4. Post-equivalence. + 60 mL of AgNO<sub>3</sub>  

$$[\text{Ag}^+] = \frac{60.0\text{mL} \cdot 0.1\text{M} - 50.0\text{mL} \cdot 0.1\text{M}}{(60+50)\text{mL}} = 9.1 \cdot 10^{-3} \text{ M} \quad \text{pAg} = 2.04$$

$$\text{pAg} + \text{pCl} = \text{p}P_s = 10.0 \Rightarrow \text{pCl} = 10.0 - 2.04 = 7.96$$



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Argentometric Titration: variables involved

**Value of K**

$$\text{Ag}^+ + \text{X}^- \rightleftharpoons \text{AgX}\downarrow; \quad K = \frac{1}{[\text{Ag}^+][\text{X}^-]} = \frac{1}{P_s}$$

The greater the insolubility of the precipitate, the higher K and, accordingly, the better the quantitiveness.

**Effect of the concentration**

$\Delta pX$  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  $\Delta pX$  at the end-point.
- The lower [Ag<sup>+</sup>], the lower pX in the post-equivalence ( $pAg + pX = pP_s$ ) and smaller  $\Delta pX$  at the end-point.

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Argentometric Titration: variables involved

**Increment of the measure around the equivalence: feasibility and appreciation of the end-point**

$\Delta pX = 2$  units around the equivalence point

$$\text{Ag}^+ + \text{X}^- \rightleftharpoons \text{AgX}\downarrow; \quad K = \frac{1}{[\text{Ag}^+][\text{X}^-]} = \frac{1}{P_s}$$

When you've added 49.95 mL of Ag<sup>+</sup>:

$$[\text{X}^-] = \frac{50\text{mL} \cdot 0.1\text{M} - 49.95\text{mL} \cdot 0.1\text{M}}{(50 + 49.95)\text{mL}} = 5 \cdot 10^{-6}\text{M} \quad pX = -\log(5 \cdot 10^{-6}) = 4.3$$




If  $\Delta pX = 2$  after having added 0.1 mL more:  $pX = 4.3 + 2 = 6.3$

$$\left. \begin{aligned} pX = 6.3 \Rightarrow [\text{X}^-] = 5 \cdot 10^{-7}\text{M} \\ [\text{Ag}^+] = \frac{0.05\text{mL} \cdot 0.1\text{M}}{(50 + 50.05)\text{mL}} = 5 \cdot 10^{-6}\text{M} \end{aligned} \right\} K = \frac{1}{[\text{Ag}^+][\text{X}^-]} = \frac{1}{(5 \cdot 10^{-6}) \cdot (5 \cdot 10^{-7})} = 4 \cdot 10^{10}$$

$$P_s = \frac{1}{K} = 2.5 \cdot 10^{-11}$$

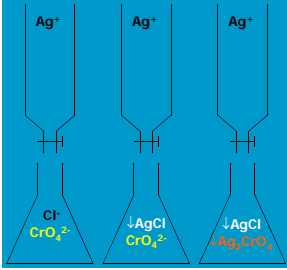
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Argentometric Titration: Indicators and Methods

- MOHR:**  
 $\text{CrO}_4^{2-}$   
  $\text{Ag}_2\text{CrO}_4$  brick-red
- VOLHARD:**  
 $\text{Fe}^{3+}$   
  $\text{Fe}(\text{SCN})^{2+}$  red
- FAJANS:**  
Adsorption indicators  


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Argentometric Titration: The Mohr Method



$\text{Na}_2\text{CrO}_4$  can serve as an indicator for the argentometric determination of Cl<sup>-</sup>, Br<sup>-</sup>, and CN<sup>-</sup> 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<sup>-</sup> and Br<sup>-</sup> (X<sup>-</sup>) are:

**Titration reaction:**  
 $\text{Ag}^+ + \text{X}^- \rightleftharpoons \text{AgX}_{(s)} \text{ [white]}$

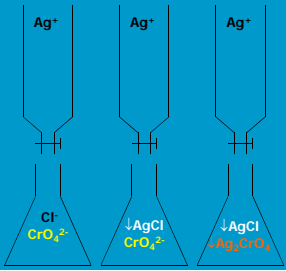
**Indicator reaction:**  
 $2\text{Ag}^+ + \text{CrO}_4^{2-} \rightleftharpoons \text{Ag}_2\text{CrO}_{4(s)} \text{ [red]}$

$P_{s, \text{Ag}_2\text{CrO}_4} = 2 \cdot 10^{-12}$ ;  $S_{\text{Ag}_2\text{CrO}_4} = 7.9 \cdot 10^{-5}\text{M}$   
 $P_{s, \text{AgCl}} = 1 \cdot 10^{-10}$ ;  $S_{\text{AgCl}} = 1.0 \cdot 10^{-5}\text{M}$

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

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Argentometric Titration: The Mohr Method



**INDICATOR:**  
Between 0.005 M and 0.01 M

**pH:**  
from 6 to 10

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

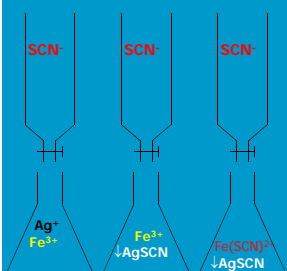
$$2\text{CrO}_4^{2-} + 2\text{H}^+ \rightleftharpoons \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$$

$P_{s, \text{Ag}_2\text{CrO}_4} = 2 \cdot 10^{-12}$ ;  $S_{\text{Ag}_2\text{CrO}_4} = 7.9 \cdot 10^{-5}\text{M}$   
 $P_{s, \text{AgCl}} = 1 \cdot 10^{-10}$ ;  $S_{\text{AgCl}} = 1.0 \cdot 10^{-5}\text{M}$

The theoretical concentration of indicator would be:  $[\text{CrO}_4^{2-}] = \frac{P_s}{[\text{Ag}^+]^2} = \frac{2 \cdot 10^{-12}}{(1 \cdot 10^{-5})^2} = 0.02\text{M}$

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Argentometric Titration: The Volhard Method



**INDICATOR:**  
not critical:  $\approx 0.01\text{M}$

**pH:**  
acid

Determination of Ag<sup>+</sup> and, indirectly, X<sup>-</sup>, in industrial samples

**Titration reaction:**  $\text{Ag}^+ + \text{SCN}^- \rightleftharpoons \downarrow \text{AgSCN}$

**Indicator reaction:**  $\text{Fe}^{3+} + \text{SCN}^- \rightleftharpoons \text{Fe}(\text{SCN})^{2+}$

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Argentometric Titration: The Volhard Method

**Direct determination: Ag<sup>+</sup> with SCN<sup>-</sup>**

⊗ Risk: The precipitate that is being formed ↓AgSCN adsorbs Ag<sup>+</sup> ions on its fresh surface and anticipates the final point.

⊕ Remedy ⇔ Vigorously shake the Erlenmeyer flask.

**Indirect determination: Cl<sup>-</sup>**

Add a well known excess of AgNO<sub>3</sub>

$\Leftrightarrow P_S AgSCN > P_S AgX$

Otherwise, you have to filter ↓AgX before the titration step with SCN<sup>-</sup>

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Argentometric Titration: The Fajans Method. Adsorption Indicators

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Argentometric Titration: The Fajans Method. Adsorption Indicators

<p><b>Fluorescein</b></p>	<p>For chlorides, bromides, and iodides and thiocyanate</p> <p>This is a very weak acid.</p> <p>The optimum pH range is between 7 and 10.</p>
<p><b>Dichlorofluorescein</b></p>	<p>For chlorides, bromides, and iodides and thiocyanate</p> <p>Stronger acid and may be used in slightly acid solution of pH greater than 4.4.</p>
<p><b>Eosin</b></p>	<p>Bromides, and iodides and thiocyanate (<b>NOT for Cl<sup>-</sup></b>)</p> <p>Stronger acid and can be used down to a pH of 1.2. The color change is sharpest in an acetic acid.</p>

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Determination of Cl<sup>-</sup> with Ag<sup>+</sup> according to Fajans using dichlorofluorescein as indicator

Start                      Pre-equivalence                      Adsorbed Indicator

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Most Frequent Argentometric Determinations

Analyte	Titrant reagent <sup>a</sup>	Indicator <sup>b</sup>
AsO <sub>4</sub> <sup>3-</sup>	AgNO <sub>3</sub> , KSCN	Volhard
Br <sup>-</sup>	AgNO <sub>3</sub> AgNO <sub>3</sub> , KSCN	Mohr or Fajans Volhard
Cl <sup>-</sup>	AgNO <sub>3</sub> AgNO <sub>3</sub> , KSCN	Mohr or Fajans Volhard*
CO <sub>3</sub> <sup>2-</sup>	AgNO <sub>3</sub> , KSCN	Volhard*
C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	AgNO <sub>3</sub> , KSCN	Volhard*
CrO <sub>4</sub> <sup>2-</sup>	AgNO <sub>3</sub> , KSCN	Volhard*
I <sup>-</sup>	AgNO <sub>3</sub> AgNO <sub>3</sub> , KSCN	Mohr or Fajans Volhard
PO <sub>4</sub> <sup>3-</sup>	AgNO <sub>3</sub> , KSCN	Volhard*
S <sup>2-</sup>	AgNO <sub>3</sub> , KSCN	Volhard*
SCN <sup>-</sup>	AgNO <sub>3</sub> , KSCN	Volhard

<sup>a</sup> When two reactants are given, the analysis is a back titration. The first reagent is added in excess and the second is used to back titrate the excess.

<sup>b</sup> In Volhard methods identified with an asterisk (\*), you must remove the silver precipitate before performing the back titration.

Data from "Modern Analytical Chemistry" by David Harvey.



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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.
5. Determination of Nitrogen Compounds: Kjeldahl Method.

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Titration Curves: Typical Steps

1) Start      2) Pre-equivalence      3) Equivalence      4) Post-equivalence

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Titration Curves: (pH vs. Volume of titrant reagent)

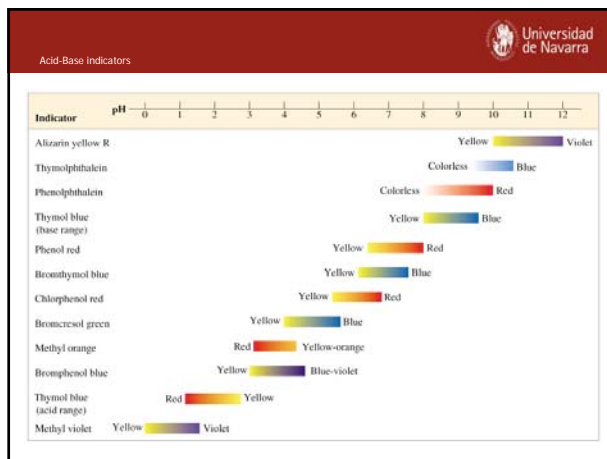
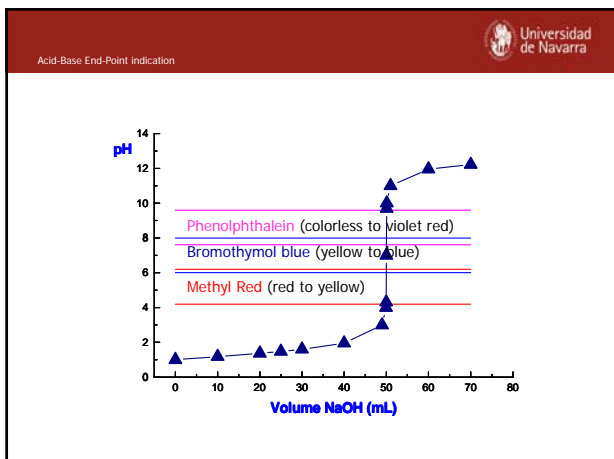
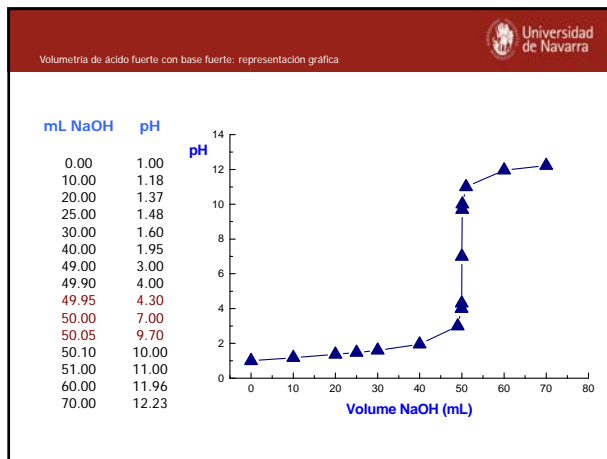
**Titration of 50 mL of HCl 0.100 M with NaOH 0.100 M**

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

2) Pre-equivalence       $V_{\text{NaOH}} = 10 \text{ mL}$   
 $[\text{H}^+] = \frac{50 \text{ mL} \cdot 0.100 \text{ mmol/mL} - 10 \text{ mL} \cdot 0.100 \text{ mmol/mL}}{(50 + 10) \text{ mL}} = 6.67 \cdot 10^{-2} \text{ M}$        $\text{pH} = 1.18$

3) Equivalence       $V_{\text{NaOH}} = 50 \text{ mL}$        $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$        $\text{pH} = 7$

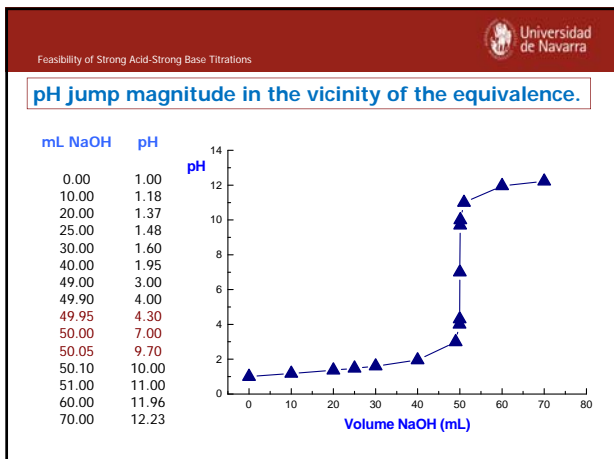
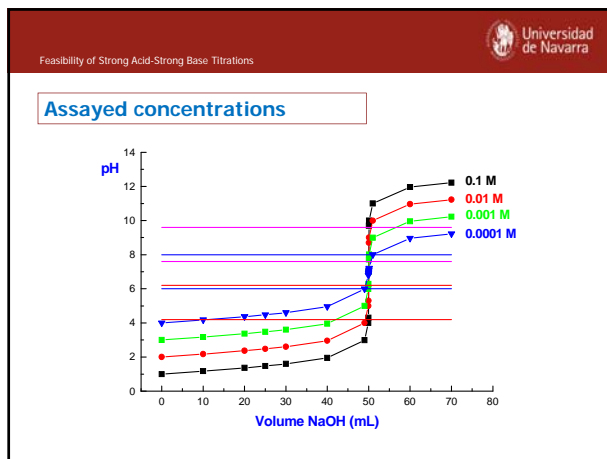
4) Post-equivalence       $V_{\text{NaOH}} = 60 \text{ mL}$        $\text{NaOH} \rightarrow \text{Na}^+ + \text{OH}^-$   
 $[\text{OH}^-] = \frac{60 \text{ mL} \cdot 0.100 \text{ mmol/mL} - 50 \text{ mL} \cdot 0.100 \text{ mmol/mL}}{(60 + 50) \text{ mL}} = 9.1 \cdot 10^{-3} \text{ M}$        $\text{pOH} = 2.04 \Rightarrow \text{pH} = 11.96$



Feasibility of Strong Acid-Strong Base Titrations

Reaction completeness  
Analyte and titrant reagent concentrations  
pH jump magnitude in the vicinity of the equivalence.

**The effect of reaction completeness, K value:**

$$\text{H}^+ + \text{OH}^- \rightleftharpoons \text{H}_2\text{O} \quad K = \frac{1}{K_w} = 10^{14}$$


Titration of a Weak Acid with a Strong Base

- 1) pH at the start: weak acid,  $\text{pH} = f(C_a, K_a)$
- 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 HAc 0.10 M with NaOH 0.10 M**

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

$$\text{HAc} \rightleftharpoons \text{H}^+ + \text{Ac}^- \quad K_a = 1.75 \cdot 10^{-5} \quad [\text{H}^+] = \frac{C_a \cdot K_a}{K_a + [\text{H}^+] + \frac{K_w}{[\text{H}^+]}}$$

Since  $[\text{H}^+] \gg K_a$ :  $[\text{H}^+]^2 = C_a \cdot K_a \quad [\text{H}^+] = 1.32 \cdot 10^{-3} \text{ M} \Rightarrow \text{pH} = 2.88$

Titration of a Weak Acid with a Strong Base

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

$$[\text{HAc}] = \frac{50 \text{ mL} \cdot \frac{0.10 \text{ mmol}}{\text{mL}} - 10 \text{ mL} \cdot \frac{0.10 \text{ mmol}}{\text{mL}}}{60 \text{ mL}} = \frac{4}{60} \text{ M}; \quad [\text{NaAc}] = \frac{10 \text{ mL} \cdot \frac{0.10 \text{ mmol}}{\text{mL}}}{60 \text{ mL}} = \frac{1}{60} \text{ M}$$

$$K_a = 1.75 \cdot 10^{-5} = \frac{[\text{H}^+] \cdot [\text{Ac}^-]}{[\text{HAc}]} = \frac{[\text{H}^+] \cdot \left(\frac{1}{60}\right)}{\left(\frac{4}{60}\right)} \Rightarrow [\text{H}^+] = 7.00 \cdot 10^{-6} \text{ M} \Rightarrow \text{pH} = 4.16$$

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

$$\text{NaAc} + \text{H}_2\text{O} \rightleftharpoons \text{HAc} + \text{NaOH}$$

$$\text{Ac}^- + \text{H}_2\text{O} \rightleftharpoons \text{HAc} + \text{OH}^- \quad [\text{NaAc}] = \frac{50 \text{ mL} \cdot \frac{0.1 \text{ mmol}}{\text{mL}}}{100 \text{ mL}} = 0.05 \text{ M}$$

If  $[\text{HAc}] \cong [\text{OH}^-]$ :

$$K_h = \frac{[\text{HAc}] \cdot [\text{OH}^-]}{[\text{Ac}^-]} = \frac{K_w}{K_a} = K_b = \frac{1.00 \cdot 10^{-14}}{1.75 \cdot 10^{-5}} = 5.71 \cdot 10^{-10} = \frac{[\text{OH}^-]^2}{0.05 \text{ M}} \Rightarrow \text{pH} = 8.73$$

Titration of a Weak Acid with a Strong Base

The approximation is good because the same result can be reached using Noyes:  $[\text{H}^+] = \sqrt{\frac{1 + \frac{[\text{salt}]}{K_a} \cdot K_a}{1 + \frac{[\text{salt}]}{K_a}}} \rightarrow \infty \Rightarrow \text{pH} = 8.724$

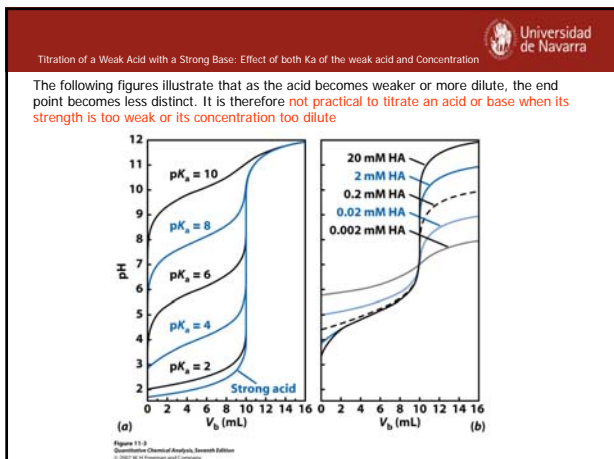
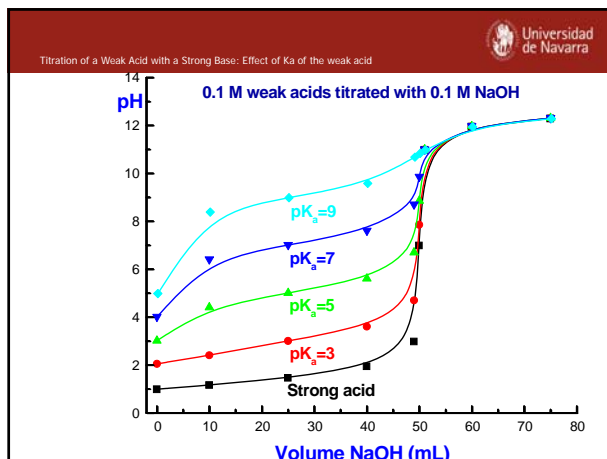
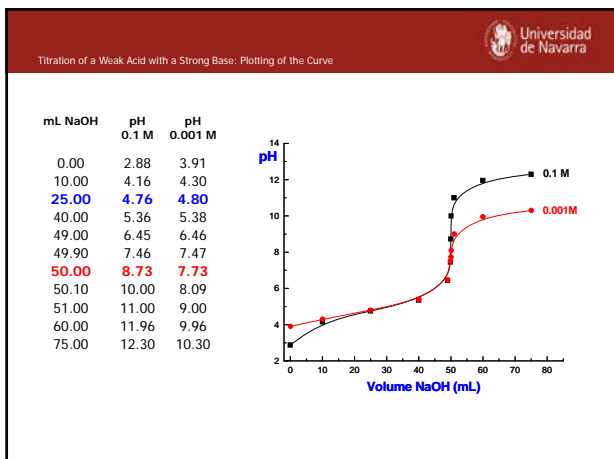
4) pH in the post-equivalence  $V_{\text{NaOH}} = 50.10 \text{ mL}$

Hydrolysis of the salt plus excess of strong base.

$$\text{Ac}^- + \text{H}_2\text{O} \rightleftharpoons \text{HAc} + \text{OH}^-; \quad \text{NaOH} \rightarrow \text{Na}^+ + \text{OH}^-$$

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

$$[\text{OH}^-] = \frac{50.10 \text{ mL} \cdot \frac{0.10 \text{ mmol}}{\text{mL}} - 50.00 \text{ mL} \cdot \frac{0.10 \text{ mmol}}{\text{mL}}}{100.1 \text{ mL}} = 1.00 \cdot 10^{-4} \text{ M} \Rightarrow \text{pH} = 10.00$$



Titration Errors with Acid-Base Indicators

**We find two types of titration errors in acid-base titrations**

- The pH at which the indicator changes color differs from the pH at the equivalence point.
  - Determinate error**
  - ⇒ Minimized by making a blank correction.
- Originates from the limited ability of the human eye to distinguish reproducibly the intermediate color of the indicator.
  - Indeterminate error**

Titration Errors with Acid-Base Indicators

**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**.

$$[\text{OH}^-] = 10^{-4} \text{ M} = \frac{10^{-2} \text{ mmol}}{(200+x) \text{ mL}} \Rightarrow x = 2.02 \text{ mL. Error} = \frac{2.02 \text{ mL}}{100 \text{ mL}} = 2.02\% \text{ in excess.}$$

If pH=5, we are in the **pre-equivalence**: there remains **HCL untitrated**.

$$[\text{H}^+] = 10^{-5} \text{ M} = \frac{100 \text{ mL} \cdot 10^{-2} \text{ mmol}}{(100+x) \text{ mL}} \Rightarrow x = 99.80 \text{ mL added.}$$

Error:  $(99.80-100) \text{ mL} / 100 \text{ mL} = -0.2 \%$

Titration Errors with Acid-Base Indicators

**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.  $K_a = 1.8 \cdot 10^{-5}$

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

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

$$[\text{NaAc}] = \frac{100 \text{ mL} \cdot 0.5 \text{ M}}{200 \text{ mL}} = 0.25 \text{ M}$$

If  $[\text{HAc}] \approx [\text{OH}^-]$ :

$$K_b = \frac{[\text{HAc}][\text{OH}^-]}{[\text{Ac}^-]} = \frac{K_w}{K_a} = \frac{1.00 \cdot 10^{-14}}{1.8 \cdot 10^{-5}} = 5.56 \cdot 10^{-10} = \frac{[\text{OH}^-]^2}{0.25 \text{ M}} \Rightarrow \text{pH} = 9.07$$

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Titration Errors with Acid-Base Indicators

**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.  $K_a = 1.8 \cdot 10^{-5}$

**I) If pH=6,** we are in the **pre-equivalence: buffer HAc/NaAc.**

$$K_a = 1.8 \cdot 10^{-5} = \frac{[H^+][Ac^-]}{[HAc]} \Rightarrow [H^+] = K_a \frac{[HAc]}{[Ac^-]}$$

$$[H^+] = 10^{-6} \text{ M} = 1.8 \cdot 10^{-5} \frac{100 \text{ mL} \cdot 0.5 \text{ M} - x \text{ mL} \cdot 0.5 \text{ M}}{x \text{ mL} \cdot 0.5 \text{ M}} \Rightarrow x = 94.73 \text{ mL added.}$$

Error:  $(94.73 - 100) \text{ mL} = -5.27 \text{ mL}$

**II) If pH=9.5,** we are in the **post-equivalence: excess of OH.**

$$[OH^-] = 10^{-4.5} \text{ M} = \frac{x \text{ mL} \cdot 0.5 \text{ M}}{(200 + x) \text{ mL}} \Rightarrow x = 0.013 \text{ mL in excess: scarcely an error.}$$

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Titration Curves for Polyfunctional Acids

$$H_2A + H_2O \rightleftharpoons HA^- + H_3O^+ \quad K_{a_1} = \frac{[HA^-][H^+]}{[H_2A]}$$

$$HA^- + H_2O \rightleftharpoons A^{2-} + H_3O^+ \quad K_{a_2} = \frac{[A^{2-}][H^+]}{[HA^-]}$$

$$A^{2-} + H_2O \rightleftharpoons HA^- + OH^- \quad K_{b_1} = \frac{K_w}{K_{a_2}} = \frac{[HA^-][OH^-]}{[A^{2-}]}$$

$$HA^- + H_2O \rightleftharpoons H_2A + OH^- \quad K_{b_2} = \frac{K_w}{K_{a_1}} = \frac{[H_2A][OH^-]}{[HA^-]}$$

$K_{a_1} \cdot K_{b_1} = K_w$ ;  $K_{a_2} \cdot K_{b_2} = K_w$

**When  $K_{a_1} \geq 10^4 K_{a_2}$ ,** equilibria can be addressed **independently**

Before the 1<sup>st</sup> equivalence:  $K_{a_1} = \frac{[HA^-][H^+]}{[H_2A]} \Rightarrow \text{pH} = \text{p}K_{a_1} + \log \frac{[HA^-]}{[H_2A]}$

Between the 1<sup>st</sup> and the 2<sup>nd</sup> equivalence:  $K_{a_2} = \frac{[A^{2-}][H^+]}{[HA^-]} \Rightarrow \text{pH} = \text{p}K_{a_2} + \log \frac{[A^{2-}]}{[HA^-]}$

In the 1<sup>st</sup> equivalence:  $HA^-$ , acid and base:  $[H^+] = \sqrt{K_{a_1} \cdot K_{a_2}} \Rightarrow \text{pH} = \frac{1}{2}(\text{p}K_{a_1} + \text{p}K_{a_2})$

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Calculation in the Titration Curves for a Diprotic Acid

50 mL of 0.10M H<sub>2</sub>A titrated with 0.10M NaOH.  $K_{a_1} = 1.00 \cdot 10^{-3}$ ;  $K_{a_2} = 1.00 \cdot 10^{-7}$

**1) pH at the start**  $V_{NaOH} = 0 \text{ mL}$  Weak acid partially dissociated

$$H_2A \rightleftharpoons H^+ + HA^- \quad K_{a_1} = 1 \cdot 10^{-3} \quad [H^+] = \frac{C_a \cdot K_{a_1}}{K_{a_1} + [H^+]} + \frac{K_w}{[H^+]}$$

Since  $[H^+] \gg K_{a_1}$ :  $[H^+]^2 = C_a \cdot K_{a_1}$   $[H^+] = 1.00 \cdot 10^{-2} \text{ M} \Rightarrow \text{pH} = 2.00$

**2) pH in 1<sup>st</sup> pre-equivalence**  $V_{NaOH} = 10 \text{ mL}$  H<sub>2</sub>A/NaHA

$$[H_2A] = \frac{50 \text{ mL} \cdot 0.10 \text{ mmol/mL} - 10 \text{ mL} \cdot 0.10 \text{ mmol/mL}}{60 \text{ mL}} = \frac{4}{60} \text{ M}; [NaHA] = \frac{10 \text{ mL} \cdot 0.10 \text{ mmol/mL}}{60 \text{ mL}} = \frac{1}{60} \text{ M}$$

$$\text{pH} = \text{p}K_{a_1} + \log \frac{[HA^-]}{[H_2A]} = 3.00 + \log \frac{\frac{1}{60} \text{ M}}{\frac{4}{60} \text{ M}} = 2.40$$

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Calculation in the Titration Curves for a Diprotic Acid

50 mL of 0.10M H<sub>2</sub>A titrated with 0.10M NaOH.  $K_{a_1} = 1.00 \cdot 10^{-3}$ ;  $K_{a_2} = 1.00 \cdot 10^{-7}$

**3) pH in 1<sup>st</sup> equivalence point**  $V_{NaOH} = 50 \text{ mL}$

$$\text{pH} = \frac{1}{2}(\text{p}K_{a_1} + \text{p}K_{a_2}) = \frac{1}{2}(3.00 + 7.00) = 5.00$$

**4) pH in between the two equivalence points**  $V_{NaOH} = 60 \text{ mL}$

The proton from HA<sup>-</sup> is being neutralized:  $HA^- + OH^- \rightleftharpoons A^{2-} + H_2O$

$$[HA^-] = \frac{50 \text{ mL} \cdot 0.10 \text{ mmol/mL} - 10 \text{ mL} \cdot 0.10 \text{ mmol/mL}}{110 \text{ mL}} = \frac{4}{110} \text{ M}; [A^{2-}] = \frac{10 \text{ mL} \cdot 0.10 \text{ mmol/mL}}{110 \text{ mL}} = \frac{1}{110} \text{ M}$$

$$\text{pH} = \text{p}K_{a_2} + \log \frac{[A^{2-}]}{[HA^-]} = 7.00 + \log \frac{\frac{1}{110} \text{ M}}{\frac{4}{110} \text{ M}} = 6.40$$

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Calculation in the Titration Curves for a Diprotic Acid

50 mL of 0.10M H<sub>2</sub>A titrated with 0.10M NaOH.  $K_{a_1} = 1.00 \cdot 10^{-3}$ ;  $K_{a_2} = 1.00 \cdot 10^{-7}$

**5) pH in the 2<sup>nd</sup> equivalence point**  $V_{NaOH} = 100 \text{ mL}$  Hydrolysis of salt

$$A^{2-} + H_2O \rightleftharpoons HA^- + OH^- \quad K_b = \frac{[HA^-][OH^-]}{[A^{2-}]} = \frac{K_w}{K_{a_2}} = K_{b_1}$$

$$[A^{2-}] = \frac{50 \text{ mL} \cdot 0.1 \text{ M}}{150 \text{ mL}} = 0.033 \text{ M} \quad \text{If } [HA^-] \cong [OH^-]:$$

$$\frac{[OH^-]^2}{0.033} = \frac{1.0 \cdot 10^{-14}}{1.0 \cdot 10^{-7}} \Rightarrow [OH^-] = 5.8 \cdot 10^{-5} \text{ M} \Rightarrow \text{pOH} = 4.24 \Rightarrow \text{pH} = 9.76$$

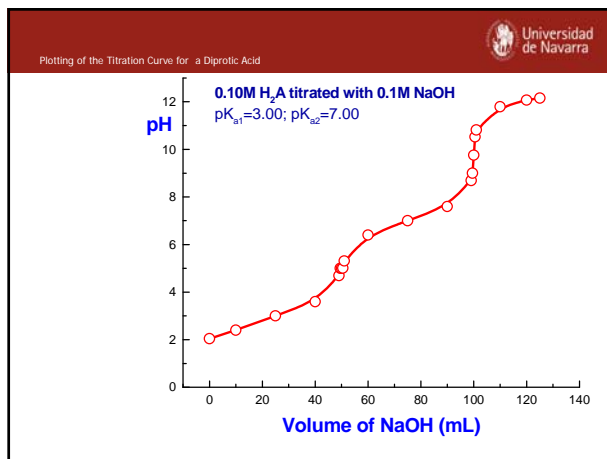
**6) pH in post-2<sup>nd</sup> equivalence**  $V_{NaOH} = 110 \text{ mL}$  Hydrolysis of salt plus base excess

$$A^{2-} + H_2O \rightleftharpoons HA^- + OH^- \quad NaOH \rightarrow Na^+ + OH^-$$

Hydrolysis contribution is negligible compared to the contribution of the base.

$$[OH^-] = \frac{110 \text{ mL} \cdot 0.10 \text{ mmol/mL} - 50.00 \text{ mL} \cdot 0.10 \text{ mmol/mL}}{160 \text{ mL}} = \frac{2 \text{ mmol OH}^-}{160 \text{ mL}} = 6.25 \cdot 10^{-3} \text{ M} \Rightarrow \text{pH} = 11.80$$

Also:  $[OH^-] = \frac{10 \text{ mL} \cdot 0.1 \text{ mmol/mL}}{160 \text{ mL}} = 6.25 \cdot 10^{-3} \text{ M}$



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Carbonation: source of errors

**The sodium, potassium and barium hydroxides avidly react with atmospheric CO<sub>2</sub>:**  $\text{CO}_2 + 2 \text{OH}^- \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O}$

**Do we always lose alkali ability to neutralize the acid?**

- Use of an indicator that changes color in the **acidic** zone:  
 $\text{CO}_3^{2-} + 2 \text{H}^+ \rightarrow \text{H}_2\text{CO}_3$  **No error is committed**
- Use of an indicator that changes color in the **basic** zone:  
 $\text{CO}_3^{2-} + \text{H}^+ \rightarrow \text{HCO}_3^-$  **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.

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Analysis of Basic Mixtures: CO<sub>3</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>, OH<sup>-</sup>

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**:

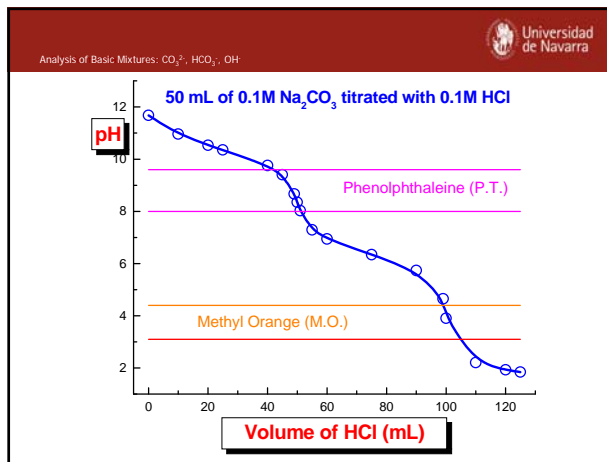
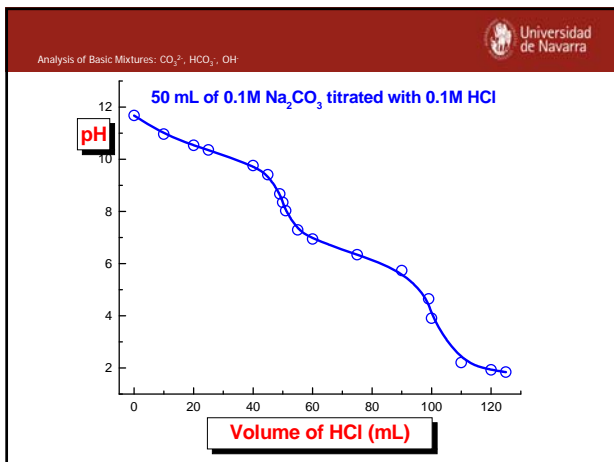
- One using an indicator that changes color in the basic zone (P.T.)
- Another using an indicator that changes color in the acidic zone (M.O.)

$$\text{H}_2\text{CO}_3 \rightleftharpoons \text{HCO}_3^- + \text{H}^+ \quad K_{a_1} = 10^{-6.34}$$

$$\text{HCO}_3^- \rightleftharpoons \text{CO}_3^{2-} + \text{H}^+ \quad K_{a_2} = 10^{-10.36}$$

$\text{CO}_3^{2-} + \text{H}^+ \rightleftharpoons \text{HCO}_3^-$       **Reactions in which the titrimetric analysis relies**

$\text{HCO}_3^- + \text{H}^+ \rightleftharpoons \text{H}_2\text{CO}_3$



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Analysis of Basic Mixtures: CO<sub>3</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>, OH<sup>-</sup>: Warder Method 1

**Titration of two identical aliquots, each one using a different indicator**

Component(s)	NaOH	Na <sub>2</sub> CO <sub>3</sub>	NaHCO <sub>3</sub>	NaOH + Na <sub>2</sub> CO <sub>3</sub>	Na <sub>2</sub> CO <sub>3</sub> + NaHCO <sub>3</sub>
Relationship between V <sub>FT</sub> and V <sub>NM</sub> for aliquots with the same volume	V <sub>FT</sub> = V <sub>NM</sub>	V <sub>FT</sub> = 1/2 V <sub>NM</sub>	V <sub>FT</sub> = 0; V <sub>NM</sub> > 0	V <sub>FT</sub> > 1/2 V <sub>NM</sub>	V <sub>FT</sub> < 1/2 V <sub>NM</sub>

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Analysis of Basic Mixtures: CO<sub>3</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>, OH<sup>-</sup>: Warder Method 2

**Titration of just the one aliquot by using consecutively two indicators**

Component(s)	Relationship between V <sub>1</sub> and V <sub>2</sub> for just the one aliquot
NaOH	V <sub>2</sub> = 0
Na <sub>2</sub> CO <sub>3</sub>	V <sub>1</sub> = V <sub>2</sub>
NaHCO <sub>3</sub>	V <sub>1</sub> = 0
NaOH + Na <sub>2</sub> CO <sub>3</sub>	V <sub>1</sub> > V <sub>2</sub>
Na <sub>2</sub> CO <sub>3</sub> + NaHCO <sub>3</sub>	V <sub>1</sub> < V <sub>2</sub>

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Analysis of a Mixture of Na<sub>2</sub>CO<sub>3</sub> and NaOH: Winkler Methodology

A) In one portion, the TOTAL alkalinity (CO<sub>3</sub><sup>2-</sup> + OH<sup>-</sup>) is determined by titration up to color change of M.O.

B) In a second portion the CO<sub>3</sub><sup>2-</sup> is precipitated as BaCO<sub>3</sub>, by adding an excess of BaCl<sub>2</sub>. Then, the remaining OH<sup>-</sup> is titrated with HCl using P.T. as indicator.

$$V_A - V_B \propto [\text{CO}_3^{2-}]$$

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Analysis of a Mixture of Na<sub>2</sub>CO<sub>3</sub> and NaHCO<sub>3</sub>: Winkler Methodology

A) In one portion, the TOTAL alkalinity (CO<sub>3</sub><sup>2-</sup> + HCO<sub>3</sub><sup>-</sup>) is determined by titration up to color change of M.O.

B) Another portion of the sample is treated with a known excess of standardized NaOH. Then, all CO<sub>3</sub><sup>2-</sup> (the original plus the generated upon reaction of NaOH with the HCO<sub>3</sub><sup>-</sup>) is precipitated by adding an excess of BaCl<sub>2</sub>. Finally, the excess of unreacted NaOH is titrated with HCl using P.T. as indicator.

$$V_A - (V_B - V_C) \propto [\text{CO}_3^{2-}]$$

$$V_B - V_C \propto [\text{HCO}_3^-]$$

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Determination of organic N: Kjeldahl Method

Professor Johan Gustav Christoffer Thorsager Kjeldahl, 1849-1900  
Former head of the chemical section at Carlsberg Lab

Since 1883, the Kjeldahl method has been the official worldwide standard for the determination of nitrogen in all kinds of food and beverage samples. The Kjeldahl digestion converts nitrogen compounds (proteins, amines, organic compounds) into ammonia compounds. Free ammonia is released by the addition of caustics, which are then expelled by distillation and subsequently titrated. The Kjeldahl method is also employed in environmental analysis and the agricultural industry for the determination of nitrates and ammonium. The method has been approved by various scientific associations including AOAC International, AACC International, AOCS, DIN, EPA, ISO, JAS, and USDA.

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Determination of organic N: Kjeldahl Method

1. Transformation of sample bound N into ammonium cation, NH<sub>4</sub><sup>+</sup>, by attack with hot and concentrated H<sub>2</sub>SO<sub>4</sub>.

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

$$\text{NH}_4^+ + \text{OH}^- \rightleftharpoons \text{NH}_3(\text{aq}) + \text{H}_2\text{O} \quad // \quad \text{NH}_3(\text{aq}) \rightleftharpoons \text{NH}_3(\text{g})$$

3. The gas is distilled and collected in an acidic solution, and an acid-base titration is used to do the final quantitation.

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Determination of organic N: Kjeldahl Method

1. Transformation of sample bound N into ammonium cation, NH<sub>4</sub><sup>+</sup>, by attack with hot and concentrated H<sub>2</sub>SO<sub>4</sub>.

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3. The gas is distilled and collected in an acidic solution, and an acid-base titration is used to do the final quantitation.

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Determination of organic N: Kjeldahl Method

3. A) The distillate is collected in an accurately measured volume of acid of known concentration. Upon completion of the distillation, the excess acid is titrated with a standard solution of base.


(Requires the use of 2 standard solutions)

3. B) Collect the NH<sub>3</sub> in an unmeasured excess of boric acid (H<sub>3</sub>BO<sub>3</sub>) which retains the NH<sub>3</sub>:

$$\text{H}_3\text{BO}_3 + \text{NH}_3 \rightarrow \text{NH}_4^+ + \text{H}_2\text{BO}_3^-$$

Dihydrogen borate is a strong enough base as to be titrated with standard acid solution.


(Requires the use of a single standard solution)



Determination of organic N. Kjeldhal Method


**CRITICAL step:**


**Decomposition of the sample by heating with  $H_2SO_4$ .**

- C y H  $\rightarrow$   $CO_2$  y  $H_2O$ , respectively.
- N amidico and aminic  $\rightarrow$   $NH_4^+$ , cuantitatively   $RNH_2$
- N in groups nitro, azo and azoxy  $\rightarrow$  N,  $\uparrow NO_x$  (losses)

$—NO_2, —N=N—, —\overset{+}{N}(=O)—$

This loss can be avoided by trying first the sample with a reducing agent such as  $Na_2S_2O_3$  or salicylic acid, which makes the N behave as amine or amide N.


  
salicylic acid




Determination of organic N. Kjeldhal Method

**CRITICAL step:**

**It takes a long time to completely diggest the sample (up to 1 h).**

- $\Rightarrow$  Adding a neutral salt,  $K_2SO_4$ , causes a **rise of the boiling point of  $H_2SO_4$** , thus allowing to use higher temperatures in the attack.
- $\Rightarrow$  Use of **catalysts** (pellets of  $Hg^0$ ,  $Cu^0$  y  $Se^0$ ), which catalyze decomposition of the sample by the  $H_2SO_4$ .




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  $NH_4^+$  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:

$$SO_{2(g)} + H_2O_2 \rightarrow H_2SO_4$$


  
SO<sub>2</sub> Determination in Beer by Distillation

The  $H_2SO_4$  is then titrated with standard base.

Lesson 6. Complexation Titrations

- Unidentate and multidentate ligands.
- Titration with inorganic complexes agents: determination of cyanides.
- Metal-chelate complexes: EDTA as complexometric agent. Titration curves.
- Metalochromic indicators.
- 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**.

Triethylenetetramine, "trien"

$K_1 = 2,5 \cdot 10^{20}$

$$\text{Cu}^{2+} + \text{NH}_3 \rightleftharpoons \text{Cu}(\text{NH}_3)^{2+}; K_1 = 1,9 \cdot 10^4$$

$$\text{Cu}(\text{NH}_3)^{2+} + \text{NH}_3 \rightleftharpoons \text{Cu}(\text{NH}_3)_2^{2+}; K_2 = 3,6 \cdot 10^3$$

$$\text{Cu}(\text{NH}_3)_2^{2+} + \text{NH}_3 \rightleftharpoons \text{Cu}(\text{NH}_3)_3^{2+}; K_3 = 7,9 \cdot 10^2$$

$$\text{Cu}(\text{NH}_3)_3^{2+} + \text{NH}_3 \rightleftharpoons \text{Cu}(\text{NH}_3)_4^{2+}; K_4 = 1,5 \cdot 10^2$$

$$\beta_4 = K_1 \cdot K_2 \cdot K_3 \cdot K_4 = 8,1 \cdot 10^{12}$$

Multidentate vs. Unidentate ligands

Titration curves for complexometric titrations. Titration of 60.0 mL of a solution that is 0.020 M in metal M with:

- (A) a 0.020 M solution of the tetridentate ligand D to give MD as the product
- (B) a 0.040 M solution of the bidentate ligand B to give MB<sub>2</sub>, and
- (C) a 0.080 M solution of the unidentate ligand A to give MA<sub>4</sub>.

The overall formation constant for each product is 10<sup>20</sup>.

Unidentate ligands

Typical Inorganic Complex-Forming Titrations		
Titrant	Analyte	Remarks
Hg(NO <sub>3</sub> ) <sub>2</sub>	Br <sup>-</sup> , Cl <sup>-</sup> , SCN <sup>-</sup> , CN <sup>-</sup> , thiourea	Products are neutral Hg(II) complexes; various indicators used
AgNO <sub>3</sub>	CN <sup>-</sup>	Product is Ag(CN) <sub>2</sub> <sup>-</sup> ; indicator is I <sup>-</sup> ;
NiSO <sub>4</sub>	CN <sup>-</sup>	Product is Ni(CN) <sub>4</sub> <sup>2-</sup> ; indicator is AgI;
KCN	Cu <sup>2+</sup> , Hg <sup>2+</sup> , Ni <sup>2+</sup>	titrate to first turbidity of AgI Products are Cu(CN) <sub>4</sub> <sup>2-</sup> , Hg(CN) <sub>2</sub> , and Ni(CN) <sub>4</sub> <sup>2-</sup> ; various indicators used

Complexometry with Unidentate ligand

**Liebig: Determination of CN<sup>-</sup> with Ag<sup>+</sup>**

$$2\text{CN}^- + \text{Ag}^+ \rightleftharpoons \text{Ag}(\text{CN})_2^-$$

Analytical reaction: formation of soluble complex

$$\text{Ag}(\text{CN})_2^- + \text{Ag}^+ \rightleftharpoons \downarrow \text{Ag}[\text{Ag}(\text{CN})_2]$$

End-point indication reaction

Risk of redissolution of the precipitate and thus of inaccuracy in end-point detection.

**Deniges: Determination in ammoniacal medium with KI as indicator**

El NH<sub>3</sub> prevents the anticipated precipitation of AgCN, and the first real excess of Ag<sup>+</sup> causes the appearance of a yellowish white turbidity due to the formation of ↓AgI

EDTA as an ideal Multidentate Ligand

**Acid-Base Forms**

- EDTA exists in up to **7** different acid-base forms depending on the solution pH.
- The most basic form (Y<sup>4-</sup>) is the one which primarily reacts with metal ions.



Formación constants for metal-EDTA complexes

CATION	$K_{MY}$	CATION	$K_{MY}$	pH	$\alpha_{Y^{4-}}$
Ag <sup>+</sup>	2.1·10 <sup>7</sup>	Cu <sup>2+</sup>	6.3·10 <sup>18</sup>	2.0	2.70·10 <sup>13</sup>
Mg <sup>2+</sup>	4.9·10 <sup>8</sup>	Zn <sup>2+</sup>	3.2·10 <sup>16</sup>	2.5	7.14·10 <sup>11</sup>
Ca <sup>2+</sup>	5.0·10 <sup>10</sup>	Cd <sup>2+</sup>	2.9·10 <sup>16</sup>	3.0	4.00·10 <sup>10</sup>
Sr <sup>2+</sup>	4.3·10 <sup>8</sup>	Hg <sup>2+</sup>	6.3·10 <sup>21</sup>	4.0	2.78·10 <sup>8</sup>
Ba <sup>2+</sup>	5.8·10 <sup>7</sup>	Pb <sup>2+</sup>	1.1·10 <sup>18</sup>	5.0	2.86·10 <sup>6</sup>
Mn <sup>2+</sup>	6.2·10 <sup>13</sup>	Al <sup>3+</sup>	1.3·10 <sup>16</sup>	6.0	4.55·10 <sup>4</sup>
Fe <sup>2+</sup>	2.1·10 <sup>14</sup>	Fe <sup>3+</sup>	1.3·10 <sup>25</sup>	7.0	2.08·10 <sup>3</sup>
Co <sup>2+</sup>	2.0·10 <sup>16</sup>	V <sup>3+</sup>	7.9·10 <sup>25</sup>	8.0	1.85·10 <sup>2</sup>
Ni <sup>2+</sup>	4.2·10 <sup>18</sup>	Th <sup>4+</sup>	1.6·10 <sup>23</sup>	9.0	19.23
				10.0	2.86
				11.0	1.17
				12.0	1.02

Calculations for the Plotting of Complexometric Titration Curves (pM vs. volume of Y<sup>4-</sup>)

**Titration of 50.0 mL of 0.01 M Ca<sup>2+</sup> with 0.01 M EDTA at pH = 10**

$Ca^{2+} + Y^{4-} \rightleftharpoons CaY^{2-}$        $K = 5.0 \cdot 10^{10}$ ;  $\alpha_{Y^{4-}, pH=10} = 2.86 \Rightarrow K' = \frac{K}{\alpha} = 1.8 \cdot 10^{10}$

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

2) Pre-equivalence       $V_{EDTA} = 10 \text{ mL}$

$[Ca] = \frac{50.0 \text{ mL} \cdot 0.01 \text{ M} - 10.0 \text{ mL} \cdot 0.01 \text{ M}}{(50 + 10) \text{ mL}} = 0.067 \text{ M}$        $pCa = 2.17$

3) Equivalence       $V_{EDTA} = 50 \text{ mL}$        $Ca^{2+} + Y^{4-} \rightleftharpoons CaY^{2-}$

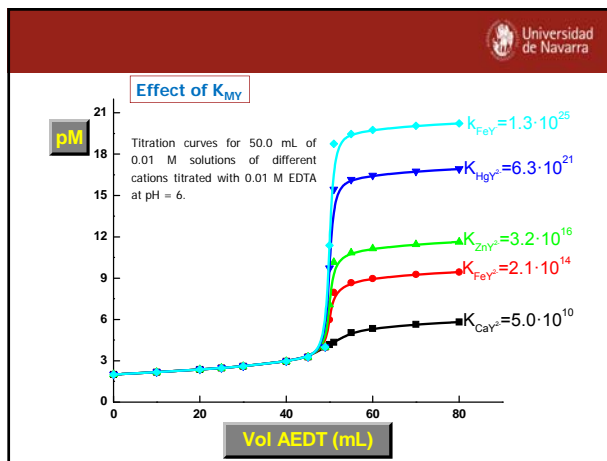
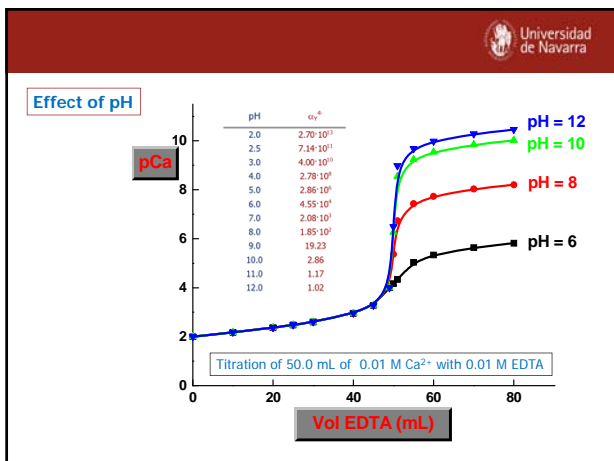
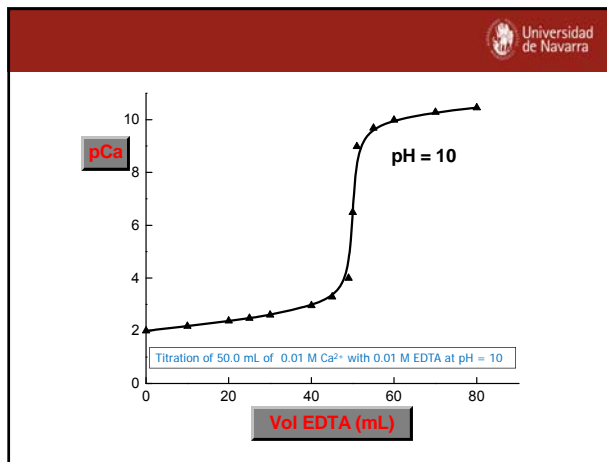
$[CaY^{2-}] = \frac{50.0 \text{ mL} \cdot 0.01 \text{ M}}{(50 + 50) \text{ mL}} = 5.0 \cdot 10^{-3} \text{ M}$

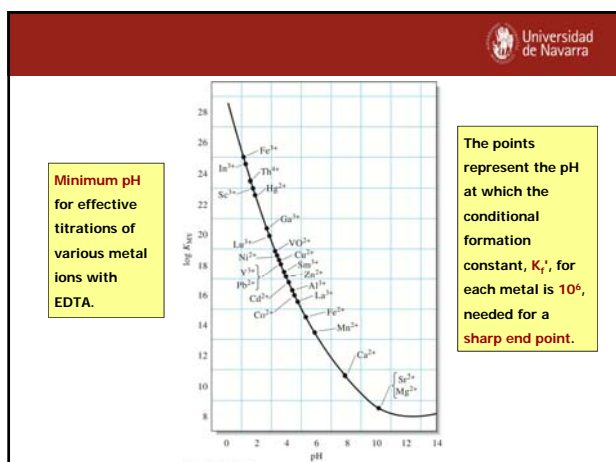
$K' = 1.8 \cdot 10^{10} = \frac{[CaY^{2-}]}{[Ca^{2+}][Y^{4-}]_T} = \frac{5.0 \cdot 10^{-3}}{[Ca^{2+}]^2} \Rightarrow [Ca^{2+}] = 5.2 \cdot 10^{-7} \text{ M}$        $pCa = 6.28$

4) Post-equivalence       $V_{EDTA} = 60 \text{ mL}$       Excess of reagent

$[CaY^{2-}] = \frac{50.0 \text{ mL} \cdot 0.01 \text{ M}}{(50 + 60) \text{ mL}} = 4.5 \cdot 10^{-3} \text{ M}$        $[Y^{4-}] = \frac{10 \text{ mL} \cdot 0.01 \text{ M}}{(50 + 60) \text{ mL}} = 9.1 \cdot 10^{-4} \text{ M}$

$K' = 1.8 \cdot 10^{10} = \frac{4.5 \cdot 10^{-3} \text{ M}}{[Ca^{2+}] \cdot (9.1 \cdot 10^{-4} \text{ M})} \Rightarrow [Ca^{2+}] = 2.8 \cdot 10^{-10} \text{ M}$        $pCa = 9.55$





Complexometry: Feasibility

•  $\Delta \text{pM} \geq 2$  around the equivalence ( $\pm 0.05 \text{ mL}$ )

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

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

If  $\Delta \text{pM} = 2$ , for  $V_{\text{EDTA}} = 50.05 \text{ mL}$  (just one drop after equivalence) :  $\text{pM} = 7.3$

$\text{pM} = 7.3 \Rightarrow [M] = 5 \cdot 10^{-8} \text{M}$

$$\left. \begin{aligned} [MY^{2-}] &= \frac{50\text{mL} \cdot 0.01\text{M}}{(50 + 50.05\text{mL})} = 5 \cdot 10^{-3} \text{M} \\ [Y^{4-}] &= \frac{0.05\text{mL} \cdot 0.01\text{M}}{(50 + 50.05\text{mL})} = 5 \cdot 10^{-6} \text{M} \end{aligned} \right\} K' = \frac{[MY^{2-}]}{[M^{2+}][Y^{4-}]} = \frac{5 \cdot 10^{-3}}{5 \cdot 10^{-8} \cdot 5 \cdot 10^{-6}} = 2 \cdot 10^{10}$$

Auxiliary complexing reagents

- 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 pM values the higher is the concentration of the ancillary ligand.
- Excess buffer solution may worsen unnecessarily the endpoint detection.

**CuSO<sub>4</sub>** With ammonia buffer, pH=10 Equivalence

Metalochromic Indicators

$\text{H}_2\text{O} + \text{H}_2\text{In}^{2-} \rightleftharpoons \text{HIn}^{2-} + \text{H}_3\text{O}^+$ ;  $\text{pK}_{a1} = 6.3$   
 red blue

$\text{H}_2\text{O} + \text{HIn}^{2-} \rightleftharpoons \text{In}^{3-} + \text{H}_3\text{O}^+$ ;  $\text{pK}_{a2} = 11.6$   
 blue orange

Eriochrome Black T (EBT)

Stable 1:1 Red Complexes ( $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ )

When  $\text{pH} > 7$ :

$$\text{MIn}^- + \text{HY}^{3-} \rightleftharpoons \text{HIn}^{2-} + \text{MY}^{2-}$$

red blue

EBT is blue in a buffered solution at pH 10. It turns red when  $\text{Ca}^{2+}$  ions are added.

This color change from wine red to violet to blue is due to the stable  $\text{Ca}^{2+}$ -NET complex formation. When the indicator is added to the hard water, the indicator EBT forms a complex with the  $\text{Ca}^{2+}$  ions that is red in color. As EDTA is added to the solution, the EDTA forms a more stable complex with the  $\text{Ca}^{2+}$  leaving the indicator EBT uncomplexed, which is blue in color.

EDTA ENDPOINT COLOR CHANGE

EBT or Eriochrome Black-T indicator is used in this titration. When it is chelated or acidifies, it produces a PINK RED solution. When it is not chelated and under basic conditions it is BLUE.

Titration of  $\text{Mg}^{2+}$  by EDT

Eriochrome Black T Indicator

Before Near Equivalence point After

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CC1=CC=C(N=N2C=C(O)C=C(O)S2)C=C1

**Calmagite**  
Stable in aqueous solution

$$\text{H}_2\text{O} + \text{H}_2\text{In}^+ \rightleftharpoons \text{HIn}^{2+} + \text{H}_3\text{O}^+; \quad pK_{a1} = 8.1$$

red                      blue

$$\text{H}_2\text{O} + \text{HIn}^{2+} \rightleftharpoons \text{In}^{3+} + \text{H}_3\text{O}^+; \quad pK_{a2} = 12.4$$

blue                      reddish orange

Indicator	pH	Cation
Calmagite	9-11	Ba, Ca, Mg, Zn
Eriochrome Black T (EBT)	7.5-10.5	Ba, Ca, Mg, Zn
Eriochrome Blue Black B	8-12	Ca, Mg, Zn, Cu
Murexide	6-13	Ca, Ni, Cu
Salicylic acid	2-3	Fe

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**End point** for the titration of hardness with EDTA using calmagite as an indicator; the indicator is:

- red prior to the end point due to the presence of the  $\text{Mg}^{2+}$ -indicator complex;
- purple at the titration's end point; and
- blue after the end point due to the presence of uncomplexed indicator.

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**Table 12-3 Common metal ion indicators**

Name	Structure	pK <sub>a</sub>	Color of free indicator	Color of metal ion complex
Calmagite	<chem>CC1=CC=C(N=N2C=C(O)C=C(O)S2)C=C1</chem>	pK <sub>1</sub> = 8.1 pK <sub>2</sub> = 12.4	H <sub>2</sub> In <sup>2+</sup> red HIn <sup>2+</sup> blue In <sup>3+</sup> orange	Wine red
Eriochrome black T	<chem>CC1=CC=C(N=N2C=C(O)C=C(O)S2)C=C1</chem>	pK <sub>1</sub> = 6.3 pK <sub>2</sub> = 11.6	H <sub>2</sub> In <sup>2+</sup> red HIn <sup>2+</sup> blue In <sup>3+</sup> orange	Wine red
Murexide	<chem>O=C1NC(=O)NC(=O)NC(=O)N1</chem>	pK <sub>1</sub> = 9.2 pK <sub>2</sub> = 10.9	H <sub>2</sub> In <sup>2+</sup> red-violet HIn <sup>2+</sup> blue	Yellow (with Ca <sup>2+</sup> , Ni <sup>2+</sup> ), red with Ca <sup>2+</sup>
Xylenol orange	<chem>CC1=CC=C(N=N2C=C(O)C=C(O)S2)C=C1</chem>	pK <sub>1</sub> = 2.32 pK <sub>2</sub> = 2.85 pK <sub>3</sub> = 6.70 pK <sub>4</sub> = 10.47 pK <sub>5</sub> = 12.23	H <sub>2</sub> In <sup>2+</sup> yellow H <sub>3</sub> In <sup>3+</sup> yellow H <sub>4</sub> In <sup>4+</sup> violet H <sub>5</sub> In <sup>5+</sup> violet In <sup>6+</sup> violet	Red
Pyrocatechol violet	<chem>CC1=CC=C(N=N2C=C(O)C=C(O)S2)C=C1</chem>	pK <sub>1</sub> = 0.2 pK <sub>2</sub> = 7.8 pK <sub>3</sub> = 9.8 pK <sub>4</sub> = 11.7	H <sub>2</sub> In <sup>2+</sup> red H <sub>3</sub> In <sup>3+</sup> yellow H <sub>4</sub> In <sup>4+</sup> violet In <sup>5+</sup> red purple	Blue

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Almost all elements can be determined by EDTA titration

Some Common Techniques used in these titrations include:

- Direct Titrations
- Back Titrations
- Displacement Titrations
- Indirect Titrations
- Masking Agents

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**a) Direct titrations** Ca, 40 cations may be titrated directly with EDTA.

- 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 metallochromic indicator, can be titrated directly.

$K_{\text{MgY}^{2-}} = 4.9 \cdot 10^8$

$K_{\text{CaY}^{2-}} = 5.0 \cdot 10^{10}$

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**b) Back titrations**

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

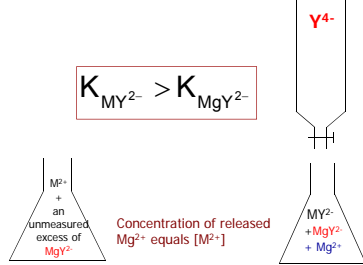
Y<sup>4-</sup>  
In a known excess

- Second metal ion must not displace analyte from EDTA

$K_{\text{MgY}^{2-}, \text{ZnY}^{2-}} < K_{\text{MY}^{2-}}$

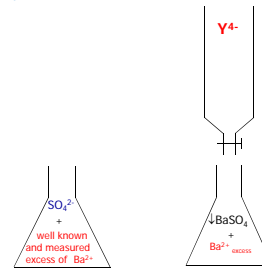
**c) Displacement titrations**

Particularly useful when an adequate indicator is not available.

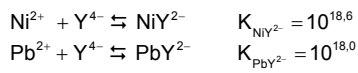


**d) Indirect titrations**

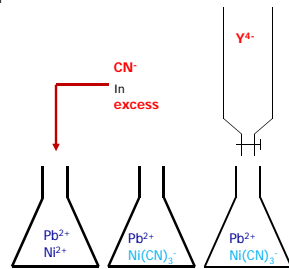
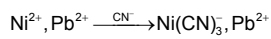
It is good to recourse to indirect methods in order to determine species that do not react with EDTA



**e) Masking agents**



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



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Lesson 7. Oxidation-Reduction Titrations

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

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### 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

$E_{\text{Ce(IV)/Ce(III)}}^0 = 1.44 \text{ V}; \quad E_{\text{Fe(III)/Fe(II)}}^0 = 0.68 \text{ V}$

$\text{Fe}^{2+} + \text{Ce}^{4+} \rightleftharpoons \text{Fe}^{3+} + \text{Ce}^{3+} \quad K \approx 10^{16}$

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- 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:

$$E = E_{\text{Ce(IV)/Ce(III)}} = E_{\text{Fe(III)/Fe(II)}}$$

$$E = E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 + \frac{0.059}{1} \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$$

$$E = E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^0 + \frac{0.059}{1} \log \frac{[\text{Ce}^{4+}]}{[\text{Ce}^{3+}]}$$

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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<sup>4+</sup> creates an equal number of moles of Ce<sup>3+</sup> and Fe<sup>3+</sup>
  - Excess unreacted Fe<sup>2+</sup> remains in solution
  - Amounts of Fe<sup>2+</sup> and Fe<sup>3+</sup> are known, and used to determine cell voltage.
  - Residual amount of Ce<sup>4+</sup> 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<sup>3+</sup> and Fe<sup>3+</sup>
  - Excess unreacted Ce<sup>4+</sup> remains in solution
  - Amounts of Ce<sup>3+</sup> and Ce<sup>4+</sup> are known, and can be used to determine cell voltage.
  - Residual amount of Fe<sup>2+</sup> is unknown

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- At the equivalence point.**
  - Enough Ce<sup>4+</sup> has been added to react with all Fe<sup>2+</sup>
    - Primarily only Ce<sup>4+</sup> and Fe<sup>3+</sup> present
    - Tiny amounts of Ce<sup>4+</sup> and Fe<sup>2+</sup> from equilibrium
  - Don't Know the Concentration of either Fe<sup>2+</sup> or Ce<sup>4+</sup>
  - Can't solve either equation independently to determine E.
  - Instead **add** both equations together

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**Potential at the equivalence; n<sub>1</sub> = n<sub>2</sub>**

$\text{Fe}^{2+} + \text{Ce}^{4+} \rightleftharpoons \text{Fe}^{3+} + \text{Ce}^{3+}$

$$E_{\text{e.p.}} = E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 + \frac{0.059}{1} \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}; \quad E_{\text{e.p.}} = E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^0 + \frac{0.059}{1} \log \frac{[\text{Ce}^{4+}]}{[\text{Ce}^{3+}]}$$

Adding both equations:

$$2E_{\text{p.e.}} = E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 + E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^0 + \frac{0.059}{1} \log \frac{[\text{Fe}^{3+}][\text{Ce}^{4+}]}{[\text{Fe}^{2+}][\text{Ce}^{3+}]}$$

According to the stoichiometry of the reaction:  $[\text{Fe}^{3+}] = [\text{Ce}^{3+}]; \quad [\text{Fe}^{2+}] = [\text{Ce}^{4+}]$

$$2E_{\text{e.p.}} = E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 + E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^0 + \frac{0.059}{1} \log \frac{[\text{Ce}^{3+}][\text{Ce}^{4+}]}{[\text{Ce}^{4+}][\text{Ce}^{3+}]}$$

$$E_{\text{e.p.}} = \frac{E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 + E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^0}{2} \quad \text{If } n_1 = n_2 \rightarrow \quad E_{\text{e.p.}} = \frac{E_1^0 + E_2^0}{2}$$

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**Potential at the equivalence;  $n_1 \neq n_2$**

$\text{Sn}^{4+} + 2e^- \rightleftharpoons \text{Sn}^{2+} \quad E^0 = 0.154 \text{ V}; \quad \text{Ce}^{4+} + e^- \rightleftharpoons \text{Ce}^{3+} \quad E^0 = 1.440 \text{ V}$

$$E_{e.p.} = E_{\text{Sn}^{4+}/\text{Sn}^{2+}}^0 + \frac{0.059}{2} \log \frac{[\text{Sn}^{4+}]}{[\text{Sn}^{2+}]}$$

$$E_{e.p.} = E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^0 + \frac{0.059}{1} \log \frac{[\text{Ce}^{4+}]}{[\text{Ce}^{3+}]}$$

Multiplying the first by 2 and adding the second :

$$3E_{e.p.} = 2E_{\text{Sn}^{4+}/\text{Sn}^{2+}}^0 + E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^0 + \frac{0.059}{1} \log \frac{[\text{Sn}^{4+}]^2 [\text{Ce}^{4+}]}{[\text{Sn}^{2+}]^2 [\text{Ce}^{3+}]}$$

According to the stoichiometry of the reaction:  $[\text{Ce}^{4+}] = 2[\text{Sn}^{2+}]; [\text{Ce}^{3+}] = 2[\text{Sn}^{4+}]$

$$3E_{e.p.} = 2E_{\text{Sn}^{4+}/\text{Sn}^{2+}}^0 + E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^0 + \frac{0.059}{1} \log \frac{[\text{Sn}^{4+}]^2 [2[\text{Sn}^{2+}]]}{[2[\text{Sn}^{4+}]]^2 [\text{Sn}^{2+}]}$$

$$E_{e.p.} = \frac{2E_{\text{Sn}^{4+}/\text{Sn}^{2+}}^0 + E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^0}{3}$$

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For the general case:

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

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

It holds that:

$$E_{e.p.} = \frac{a \cdot E_1^0 + b \cdot E_2^0}{a + b}$$

This general expression will be fulfilled for all cases where there is no exchange of either OH<sup>-</sup> or H<sup>+</sup>

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**Potential at the equivalence;  $n_1 \neq n_2, \text{H}^+$**

$5\text{Sn}^{2+} + 2\text{MnO}_4^- + 16\text{H}^+ \rightleftharpoons 5\text{Sn}^{4+} + 2\text{Mn}^{2+} + 8\text{H}_2\text{O}$

$\text{Sn}^{4+} + 2e^- \rightleftharpoons \text{Sn}^{2+}; E_{\text{Sn}^{4+}/\text{Sn}^{2+}}^0 = 0.154 \text{ V} \quad \text{MnO}_4^- + 8\text{H}^+ + 5e^- \rightleftharpoons \text{Mn}^{2+} + 4\text{H}_2\text{O}; E_{\text{MnO}_4^-/\text{Mn}^{2+}}^0 = 1.510 \text{ V}$

$$E_{e.p.} = E_{\text{Sn}^{4+}/\text{Sn}^{2+}}^0 + \frac{0.059}{2} \log \frac{[\text{Sn}^{4+}]}{[\text{Sn}^{2+}]}$$

$$E_{e.p.} = E_{\text{MnO}_4^-/\text{Mn}^{2+}}^0 + \frac{0.059}{5} \log \frac{[\text{MnO}_4^-][\text{H}^+]^8}{[\text{Mn}^{2+}]}$$

Multiplying the first by 2 and the second by 5, and adding :

$$7E_{e.p.} = 2E_{\text{Sn}^{4+}/\text{Sn}^{2+}}^0 + 5E_{\text{MnO}_4^-/\text{Mn}^{2+}}^0 + \frac{0.059}{1} \log \frac{[\text{Sn}^{4+}]^2 [\text{MnO}_4^-][\text{H}^+]^8}{[\text{Sn}^{2+}]^2 [\text{Mn}^{2+}]}$$

At the equivalence:  $[\text{Sn}^{2+}] = \frac{5}{2}[\text{MnO}_4^-]; [\text{Sn}^{4+}] = \frac{5}{2}[\text{Mn}^{2+}]$

$$7E_{e.p.} = 2E_{\text{Sn}^{4+}/\text{Sn}^{2+}}^0 + 5E_{\text{MnO}_4^-/\text{Mn}^{2+}}^0 + \frac{0.059}{1} \log [\text{H}^+]^8 \Rightarrow E_{e.p.} = \frac{2E_{\text{Sn}^{4+}/\text{Sn}^{2+}}^0 + 5E_{\text{MnO}_4^-/\text{Mn}^{2+}}^0}{7} - 0.068 \text{ pH}$$

**$E_{e.p.} = f(\text{pH})$**

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**Potential at the equivalence;  $n_1 \neq n_2, \text{H}^+ [\text{X}]$**

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

For this case we obtain:

$$7E_{e.p.} = E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 + 6E_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}}^0 + 0.059 \log \frac{[\text{Fe}^{3+}][\text{Cr}_2\text{O}_7^{2-}][\text{H}^+]^{14}}{[\text{Fe}^{2+}][\text{Cr}^{3+}]^2}$$

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

$$E_{e.p.} = \frac{E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 + 6E_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}}^0}{7} + \frac{0.059}{7} \log \frac{[\text{H}^+]^{14}}{2[\text{Cr}^{3+}]}$$

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**50.00 mL of 0.05 M Fe(II) with 0.1 M Ce(IV) in 1.0 M H<sub>2</sub>SO<sub>4</sub>**

$\text{Fe}^{2+} + \text{Ce}^{4+} \rightleftharpoons \text{Fe}^{3+} + \text{Ce}^{3+} \quad E_{\text{Ce(IV)/Ce(III)}}^0 = 1.44 \text{ V}; E_{\text{Fe(III)/Fe(II)}}^0 = 0.68 \text{ V}$

1) Start  $V_{\text{Ce}^{4+}} = 0 \text{ mL}$  Non-Nernstian condition

2) Pre-equivalence  $V_{\text{Ce}^{4+}} = 5 \text{ mL}$

$$[\text{Fe}^{3+}] = \frac{5.00 \text{ mL} \cdot 0.10 \text{ M}}{(50.00 + 5.00) \text{ mL}} = \frac{0.500}{55.00} \text{ M}$$

$$[\text{Fe}^{2+}] = \frac{50.00 \text{ mL} \cdot 0.05 \text{ M} - 5.00 \text{ mL} \cdot 0.10 \text{ M}}{(50.00 + 5.00) \text{ mL}} = \frac{2.00}{55.00} \text{ M}$$

$$E = 0.680 \text{ V} + \frac{0.059}{1} \log \frac{0.500}{2.00} = 0.640 \text{ V} \quad \log K = \frac{n}{0.059} (E_c^0 - E_d^0) \Rightarrow K = 7.6 \cdot 10^{12}$$

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

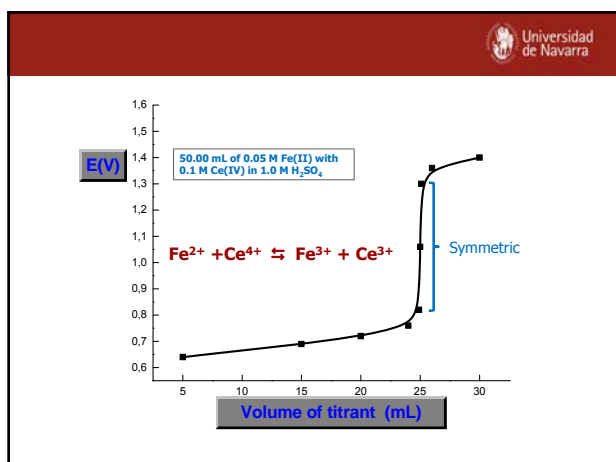
$$E_{e.p.} = \frac{E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 + E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^0}{2} = \frac{0.680 + 1.440}{2} = 1.060 \text{ V}$$

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

$$[\text{Ce}^{3+}] = \frac{25.00 \text{ mL} \cdot 0.10 \text{ M}}{75.10 \text{ mL}} = \frac{2.50}{75.10} \text{ M}$$

$$[\text{Ce}^{4+}] = \frac{25.10 \text{ mL} \cdot 0.10 \text{ M} - 50.00 \text{ mL} \cdot 0.05 \text{ M}}{75.10 \text{ mL}} = \frac{-0.01}{75.10} \text{ M}$$

$$E = 1.440 \text{ V} + \frac{0.059}{1} \log \frac{[\text{Ce}^{4+}]}{[\text{Ce}^{3+}]} = 1.440 \text{ V} + 0.059 \log \frac{0.01}{2.50} = 1.30 \text{ V}$$



50.00 mL of 0.05 M Fe(II) with 0.02 M MnO<sub>4</sub><sup>-</sup> in [H<sup>+</sup>] = 1.0 M

$5Fe^{2+} + MnO_4^- + 8H^+ \rightleftharpoons 5Fe^{3+} + Mn^{2+} + 4H_2O$

2) Pre-equivalence  $V_{MnO_4^-} = 5 \text{ mL}$

$$[Fe^{3+}] = \frac{5.00 \text{ mL} \cdot \frac{0.02 \text{ mmol MnO}_4^-}{\text{mL}} - 5 \text{ mmol Fe}^{2+}}{(50.00 + 5.00) \text{ mL}} = \frac{0.50 \text{ mmol Fe}^{3+}}{55.00 \text{ mL}}$$

$$[Fe^{2+}] = \frac{50.00 \text{ mL} \cdot \frac{0.05 \text{ mmol Fe}^{2+}}{\text{mL}} - 5.00 \text{ mL} \cdot \frac{0.02 \text{ mmol MnO}_4^-}{\text{mL}} - 5 \text{ mmol Fe}^{2+}}{(50.00 + 5.00) \text{ mL}} = \frac{2.00 \text{ mmol Fe}^{2+}}{55.00 \text{ mL}}$$

$$E = 0.680 \text{ V} + \frac{0.059}{1} \log \frac{0.500 \text{ M}}{\frac{2.00}{55.00} \text{ M}} = 0.640 \text{ V}$$

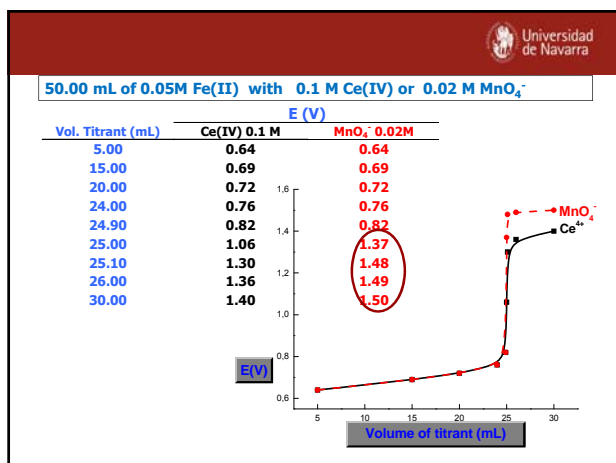
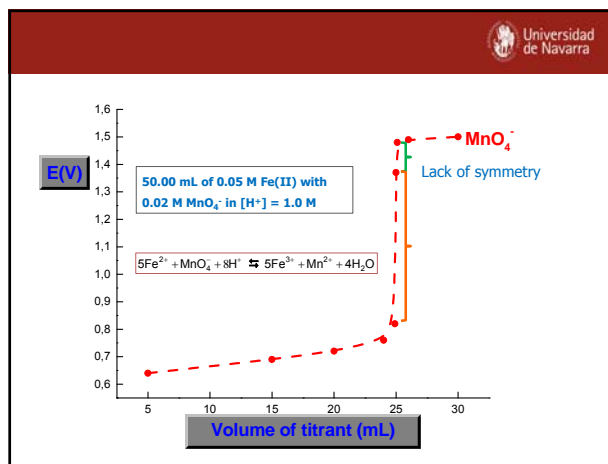
3) Equivalence  $V_{MnO_4^-} = 25 \text{ mL}$

$$E_{eq} = \frac{E_{Fe^{3+}/Fe^{2+}}^0 + 5E_{MnO_4^-/Mn^{2+}}^0}{6} + \frac{0.059}{6} \log [H^+]^8 = \frac{0.680 + 5 \cdot 1.510}{6} + \frac{0.059}{6} \cdot 8 \cdot \log(1.00) = 1.37 \text{ V}$$

4) Post-equivalence  $V_{MnO_4^-} = 25.10 \text{ mL}$

$$[Mn^{2+}] = \frac{50.00 \text{ mL} \cdot \frac{0.05 \text{ mmol Fe}^{2+}}{\text{mL}} - 1 \text{ mmol Mn}^{2+}}{(50.00 + 25.10) \text{ mL}} = \frac{0.50 \text{ mmol Mn}^{2+}}{75.10 \text{ mL}}$$

$$[MnO_4^-] = \frac{25.10 \text{ mL MnO}_4^- \cdot \frac{0.02 \text{ mmol MnO}_4^-}{\text{mL}} - 50.00 \text{ mL} \cdot \frac{0.05 \text{ mmol Fe}^{2+}}{\text{mL}} - 1 \text{ mmol MnO}_4^-}{(50.00 + 25.10) \text{ mL}} = \frac{0.002 \text{ mmol MnO}_4^-}{75.10 \text{ mL}}$$

$$E = 1.51 \text{ V} + \frac{0.059}{5} \log \frac{(1.00)^8 \cdot \frac{0.002}{75.10} \text{ M}}{\frac{0.50}{75.10} \text{ M}} = 1.63 \text{ V}$$


- ✓ 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 MnO<sub>4</sub><sup>-</sup> 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 ΔE in the equivalence for MnO<sub>4</sub><sup>-</sup> is a manifestation of the larger value of its K in the reaction with Fe(II).
-

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Feasibility

For a generic reaction:  $Ox_1 + Red_2 \rightleftharpoons Red_1 + Ox_2$

where the semi-systems involved are:

$$Ox_1 + a e^- \rightleftharpoons Red_1 \quad E_1^0$$

$$Ox_2 + b e^- \rightleftharpoons Red_2 \quad E_2^0$$

a) we will calculate the value of K so that around equivalence  $\Delta pRed_2 \geq 2$

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

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Titration of 50.00 mL of 0.1 M Red<sub>2</sub> with 0.1 M Ox<sub>1</sub>      Red<sub>2</sub> + Ox<sub>1</sub> ⇌ Ox<sub>2</sub> + Red<sub>1</sub>

a)  $[Red_2] = \frac{50.00 \text{ mL} \cdot 0.1 \text{ M} - 49.95 \text{ mL} \cdot 0.1 \text{ M}}{(50.00 + 49.95) \text{ mL}} = 5.0 \cdot 10^{-6} \text{ M}$        $pRed_2 = 4.30$

An increase of 2 units, means that for 50.05 mL added reagent, the pRed<sub>2</sub> should be 6.30.

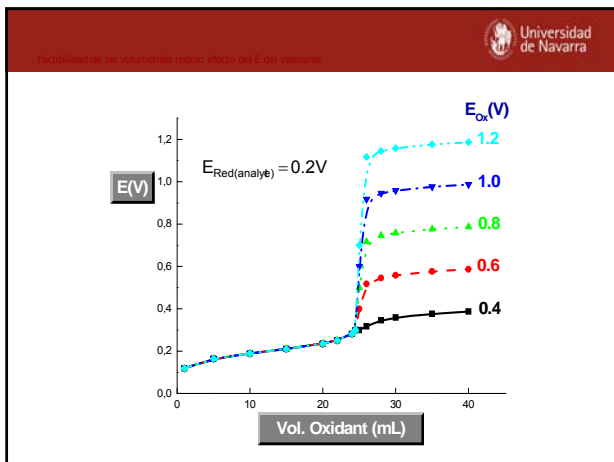
$pRed_2 = 6.30 \Rightarrow [Red_2] = 5.0 \cdot 10^{-7} \text{ M}$

$[Ox_1] = \frac{0.05 \text{ mL} \cdot 0.10 \text{ M}}{(50.00 + 50.05) \text{ mL}} = 5.0 \cdot 10^{-6} \text{ M}$        $[Red_1] = [Ox_2] = \frac{50.00 \text{ mL} \cdot 0.10 \text{ M}}{(50.00 + 50.05) \text{ mL}} = 5.0 \cdot 10^{-2} \text{ M}$

Accordingly:

$$K = \frac{[Red_1][Ox_2]}{[Ox_1][Red_2]} = \frac{(5.0 \cdot 10^{-2})^2}{(5.0 \cdot 10^{-6})(5.0 \cdot 10^{-7})} = 1.0 \cdot 10^6$$

b)

$$E_c^0 - E_a^0 = \frac{0.059}{n} \log K = 0.472 \text{ V}$$


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Redox Indicators

> GENERAL or "true" indicators

> SPECIFIC indicators

- ✓ General redox indicators are those substances that change color when oxidized or reduced.
- ✓ The change in color only depends on changes in the system's potential as titration goes.

$$In_{Ox} + n e^- \rightleftharpoons In_{Red} \quad E = E_{in}^0 + \frac{0.059}{n} \log \frac{[In_{Ox}]}{[In_{Red}]}$$

In general, a color change will be appreciated when :

$$\frac{[In_{Ox}]}{[In_{Red}]} \geq 10 \quad \text{to} \quad \frac{[In_{Ox}]}{[In_{Red}]} \leq 10 \quad E = E_{in}^0 \pm \frac{0.059}{n}$$

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$$\left[ \text{Fe(III)} \right]^{3+} + e^- \rightleftharpoons \left[ \text{Fe(II)} \right]^{2+} \quad E^0 = 1.06 \text{ V}$$

Oxidized ferroin (pale blue) In(oxidized)      Reduced ferroin (red) In(reduced)

- ✓ Reacts rapidly and reversibly
- ✓ Pronounced color change
- ✓ Solutions stable and easy to prepare
- ✓ Its oxidized form is inert to strong oxidizing agents

• Decomposes above 60 °C.

⇒ 5-nitro ( $E^0 = 1.25 \text{ V}$ ); 5-methyl ( $E^0 = 1.02 \text{ V}$ )

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Table 16-2 Redox indicators

Indicator	Color		$E^0$
	Oxidized	Reduced	
Phenosafranin	Red	Colorless	0.28
Indigo tetrasulfonate	Blue	Colorless	0.36
Methylene blue	Blue	Colorless	0.53
Diphenylamine	Violet	Colorless	0.75
4'-Ethoxy-2,4-diaminoazobenzene	Yellow	Red	0.76
Diphenylamine sulfonic acid	Red-violet	Colorless	0.85
Diphenylbenzidine sulfonic acid	Violet	Colorless	0.87
Tris(2,2'-bipyridine)iron	Pale blue	Red	1.120
Tris(1,10-phenanthroline)iron (ferroin)	Pale blue	Red	1.147
Tris(5-nitro-1,10-phenanthroline)iron	Pale blue	Red-violet	1.25
Tris(2,2'-bipyridine)ruthenium	Pale blue	Yellow	1.29

Table 16-2 Quantitative Chemical Analysis, Seventh Edition © 2007 W. H. Freeman and Company



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Diphenylamine and derivatives Knop, 1924: Fe(II) with  $K_2Cr_2O_7$

In the presence of a strong oxidizing agent:

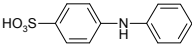
$$2 \text{C}_6\text{H}_5\text{NH}_2 \rightarrow \text{C}_6\text{H}_5\text{N}(\text{C}_6\text{H}_5)_2 + 2\text{H}^+ + 2\text{e}^-$$

Colorless Diphenylamine      Colorless Diphenylbenzidine

$$\text{C}_6\text{H}_5\text{N}(\text{C}_6\text{H}_5)_2 \rightarrow \text{C}_6\text{H}_5\text{N}(\text{C}_6\text{H}_4)_2 + 2\text{H}^+ + 2\text{e}^-$$

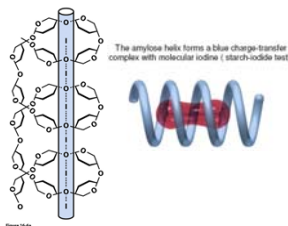

**Violet Diphenylbenzidine;  $E^0 \approx 0.76 \text{ V}$**

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



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A starch solution with a little  $\text{I}_3^-$  or  $\text{I}^-$  behaves like a **true redox indicator**, thanks to the **intense blue** complex that forms with the iodine ( $\text{I}_3^-$ ).


- ✓ In the presence of an excess of oxidizing agent, there is a high ratio  $\text{I}_3^- / \text{I}^-$  and the solution turns **blue**.
- ✓ If, on the contrary, there is an excess of reducing agent,  $\text{I}^-$  is the prevailing species and no color is observed.

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



- **SCN<sup>-</sup>**: useful in the determination of Fe (III). The disappearance of the red color of the complex  $\text{Fe}(\text{SCN})_2^{2+}$  provides an indication of the endpoint.
- **Starch**: valid for titrations involving iodine, with which it forms the dark blue complex.



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**Auxiliary Oxidizing and Reducing Reagents**

Attaining reliable quantitative results using a redox titration requires to be certain that the analyte be in a **single oxidation state at the outset**.

**To be useful as a preoxidant or a preductant, 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)

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**Common Auxiliary Pre-reducing Reagents**

Sticks, coils, grit or powder of metals can be immersed directly in the analyte solution:

**Zn, Al, Cd, Pb, Ni, Cu**

**Ag (in the presence of  $\text{Cl}^-$ )**

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.

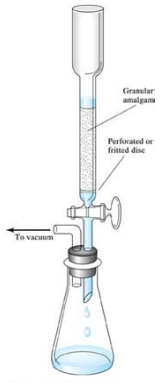
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**Jones «reductor»**

Column with amalgamated Zn packing.

$$2\text{Zn}_s + \text{Hg}^{2+} \rightarrow \text{Zn}^{2+} + \text{Zn}(\text{Hg})_s$$

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

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





**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\***

Walden	Jones
$Ag(s) + Cl^- \rightarrow AgCl(s) + e^-$	$Zn(Hg)(s) \rightarrow Zn^{2+} + Hg + 2e^-$
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$
$Cu^{2+} + e^- \rightarrow Cu^+$	$Cu^{2+} + 2e^- \rightleftharpoons Cu(s)$
$H_2MoO_4 + 2H^+ + e^- \rightarrow MoO_4^{2-} + 2H_2O$	$H_2MoO_4 + 6H^+ + 3e^- \rightleftharpoons Mo^{3+} + 3H_2O$
$UO_2^{2+} + 4H^+ + 2e^- \rightarrow U^{4+} + 2H_2O$	$UO_2^{2+} + 4H^+ + 2e^- \rightleftharpoons U^{4+} + 2H_2O$
$V(OH)_4^+ + 2H^+ + e^- \rightarrow VO^{2+} + 3H_2O$	$VO_2^+ + 4H^+ + 3e^- \rightleftharpoons V^{3+} + 2H_2O$
TiO <sup>2+</sup> not reduced	$Ti(OH)_4^+ + 4H^+ + 3e^- \rightleftharpoons Ti^{2+} + 4H_2O$
Cr <sup>3+</sup> not reduced	$TiO^{2+} + 2H^+ + e^- \rightleftharpoons Ti^{2+} + H_2O$
	$Cr^{3+} + e^- \rightleftharpoons Cr^{2+}$

\*From I. M. Kolthoff and R. Belcher, *Volumetric Analysis*, Vol 3, p. 12. New York: Interscience, 1957. This material is used by permission of John Wiley & Sons, Inc.  
 †A mixture of oxidation states is obtained. The Jones reductor may still be used for the determination of uranium, however, because any U<sup>2+</sup> formed can be converted to U<sup>4+</sup> by shaking the solution with air for a few minutes.

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**Common preoxidants**

- Sodium Bismuthate **NaBiO<sub>3</sub>**
- Ammonium Peroxydisulfate **(NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>**
- Hydrogen Peroxide **H<sub>2</sub>O<sub>2</sub>**


**NaBiO<sub>3</sub>**

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

- ✓ Available as a sparingly soluble solid; it is frequently used in a suspension under boiling for a brief time.
- ✓ Excess reagent is removed by filtration.

**Mn(II) → MnO<sub>4</sub><sup>-</sup>**  
**Cr(III) → Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>**  
**Ce(III) → Ce(IV)**

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**(NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>**


$$S_2O_8^{2-} + 2e^- \rightleftharpoons 2 SO_4^{2-}; E^0 = 2.01 V$$

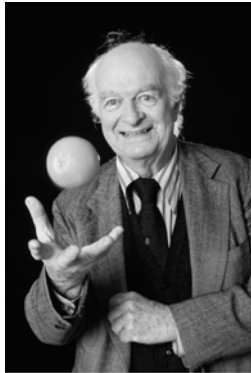
$$\begin{array}{c} OH & & OH \\ | & & | \\ O=S-O-O-S=O \\ | & & | \\ O & & O \end{array}$$

- ✓ The oxidations are catalyzed by trace amounts of Ag<sup>+</sup>.
- ✓ Excess reagent is readily decomposed by boiling:

$$2 S_2O_8^{2-} + 2 H_2O \rightarrow 4 SO_4^{2-} + O_2 + 4 H^+$$

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**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.**

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**H<sub>2</sub>O<sub>2</sub>**

$$H_2O_2 + 2 H^+ + 2 e^- \rightleftharpoons 2 H_2O; E^0 = 1.78 V$$

**In acidic medium: Fe(II) → Fe(III)**      **In alkaline medium: Cr(III) → CrO<sub>4</sub><sup>2-</sup>**  
**Mn(II) → MnO<sub>2</sub>**

- ✓ Excess reagent is eliminated by boiling:


$$2 H_2O_2 \rightleftharpoons 2 H_2O + O_2$$

Reminder:

Oxidant role:  $O_2^{2-} + 2e^- \rightarrow 2 O^{2-}$

Reductant role:  $O_2^{2-} - 2e^- \rightarrow O_2$

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**Some Common Oxidants Used as Standard Solutions**

Reagent and Formula	Reduction Product	Standard Potential, V	Standardized with	Indicator*	Stability†
Potassium permanganate, KMnO <sub>4</sub>	Mn <sup>2+</sup>	1.51 <sup>‡</sup>	Na <sub>2</sub> C <sub>2</sub> O <sub>4</sub> , Fe, As <sub>2</sub> O <sub>3</sub>	MnO <sub>4</sub> <sup>-</sup>	(b)
Potassium bromate, KBrO <sub>3</sub>	Br <sup>-</sup>	1.44 <sup>‡</sup>	KBrO <sub>3</sub>	(1)	(a)
Cerium(IV), Ce <sup>4+</sup>	Ce <sup>3+</sup>	1.44 <sup>‡</sup>	Na <sub>2</sub> C <sub>2</sub> O <sub>4</sub> , Fe, As <sub>2</sub> O <sub>3</sub>	(2)	(a)
Potassium dichromate, K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	Cr <sup>3+</sup>	1.33 <sup>‡</sup>	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> , Fe, As <sub>2</sub> O <sub>3</sub>	(3)	(a)
Iodine, I <sub>2</sub>	I <sup>-</sup>	0.536 <sup>‡</sup>	BaI <sub>2</sub> ·H <sub>2</sub> O, Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	starch	(c)

\* (1) α-Naphthoflavone; (2) 1,10-phenanthroline iron(II) complex (ferroin); (3) diphenylamine sulfonic acid.  
 † (a) Indefinitely stable; (b) moderately stable, requires periodic standardization; (c) somewhat unstable, requires frequent standardization.  
 ‡ E<sup>0</sup> in 1 M H<sub>2</sub>SO<sub>4</sub>.

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**Most frequent oxidants:  $\text{MnO}_4^-$  and  $\text{Ce(IV)}$**


Powerful oxidants with similar applicability.

$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightleftharpoons \text{Mn}^{2+} + 4\text{H}_2\text{O}; \quad E^\circ = 1,51\text{V}$   
 $\text{Ce}^{4+} + \text{e}^- \rightleftharpoons \text{Ce}^{3+}; \quad E^\circ = 1,44\text{V (H}_2\text{SO}_4\ 1\text{M)}$

This reaction for  $\text{MnO}_4^-$  only occurs in acidic medium 0.1 M or higher; otherwise the product may be Mn(III), Mn(IV) or Mn(VI)


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

- Solutions of **Ce (IV)** in sulfuric are **stable indefinitely**, while those of  $\text{MnO}_4^-$  decompose slowly and require periodic re-standardization.
- The **Ce (IV)** does not oxidize  $\text{Cl}^-$ , while  $\text{Cl}^-$  is slowly oxidized  $\text{MnO}_4^-$ .
- There is a salt, **cerium ammonium nitrate**, in sufficient purity for use as a **primary standard type**.




Despite the above mentioned drawbacks,  **$\text{MnO}_4^-$  is more widely used** because:


- $\text{MnO}_4^-$  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.



**Most frequent oxidants:  $\text{MnO}_4^-$  and  $\text{Ce(IV)}$ . Endpoint Indication**

- If a very dilute solution of  $\text{MnO}_4^-$  is used, ferroin and diphenylamine sulfonic acid can be used as indicators.
- 0.01 mL of a 0.02 M  $\text{MnO}_4^-$  solution gives a perceptible color to 100 mL of  $\text{H}_2\text{O}$ .
- The end point color is not permanent because:  
 $2\text{MnO}_4^- + 3\text{Mn}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons 5\text{MnO}_2 + 4\text{H}^+ \quad K \approx 10^{47}$   
 Due to the slow kinetics, color persists approximately 30 s
- The yellow-orange color of the **Ce (IV)** solutions is not strong enough to serve as self-indicator.
- Ferroin and its substituted derivatives are often used.





**The Preparation and Stability of Standard Solutions of  $\text{MnO}_4^-$**

$\text{MnO}_4^-$  tends to oxidize  $\text{H}_2\text{O}$ , albeit slowly:  $4\text{MnO}_4^- + 2\text{H}_2\text{O} \rightleftharpoons 4\text{MnO}_2 + 3\text{O}_2 + 4\text{OH}^-$


It is **catalyzed** by adverse factors:

- Light
- Heat
- Acids
- Bases
- Mn(II)
- $\text{MnO}_2$**

Removal of  $\text{MnO}_2$  by filtration before standardization markedly improves the stability of estándar  **$\text{MnO}_4^-$**  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  $\text{H}_2\text{O}$ .


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

- Brown deposits involve  $\text{MnO}_2$  formation**
- Periodic re-standardization**




**$\text{MnO}_4^-$  is standardized with:**


- Sodium oxalate**  
 $2\text{MnO}_4^- + 5\text{H}_2\text{C}_2\text{O}_4 + 6\text{H}^+ \rightleftharpoons 2\text{Mn}^{2+} + 10\text{CO}_2 + 8\text{H}_2\text{O}$



→ **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).  
 $5\text{Fe}^{2+} + \text{MnO}_4^- + 8\text{H}^+ \rightleftharpoons 5\text{Fe}^{3+} + \text{Mn}^{2+} + 4\text{H}_2\text{O}$
- Arsenous oxide**
  - ✓ Stable, non-hygroscopic, available in high purity.
  - ✓ Is dissolved in a basic medium and then in acid to titrate:  
 $5\text{HAsO}_2 + 2\text{MnO}_4^- + 6\text{H}^+ + 2\text{H}_2\text{O} \rightleftharpoons 2\text{Mn}^{2+} + 5\text{H}_3\text{AsO}_4$


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**The Preparation and Stability of Standard Solutions of Ce(IV)**

Reagents used:

- $\text{Ce}(\text{NO}_3)_4 \cdot 2\text{NH}_4\text{NO}_3$  Primary type standard
- $\text{Ce}(\text{SO}_4)_2 \cdot 2(\text{NH}_4)_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$
- $\text{Ce}(\text{OH})_4$
- $\text{Ce}(\text{HSO}_4)_4$


- ✓ **Ce(IV) solutions** are always prepared in **0.1 M  $\text{H}_2\text{SO}_4$**  to prevent precipitation of basic salts.
- ✓ Solutions are **stable** over several **months**.
- ✓ Solutions **can be boiled** without suffering alteration.

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**Oxidimetry: determination of Fe in minerals**


Most important iron ores :

- Hematites:  $\text{Fe}_2\text{O}_3$
- Magnetite:  $\text{Fe}_3\text{O}_4$
- Limonite:  $2 \text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$




Stages of the analysis:

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

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**1. Sample dissolving**

- Complete decomposition with hot concentrated HCl
- $\text{SnCl}_2$  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  $\text{Na}_2\text{CO}_3$  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

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**2. Reduction of iron to the divalent state**


- Normally, since we are in a hydrochloric acid medium, we use  $\text{SnCl}_2$ :

$$\text{Sn}^{2+} + 2\text{Fe}^{3+} \rightleftharpoons \text{Sn}^{4+} + 2\text{Fe}^{2+}$$

- The reduction is complete when the typical yellow color of Fe (III) hydrochloric solutions disappears
- The prereductant reagent excess is removed by adding  $\text{HgCl}_2$ :

$$\text{Sn}^{2+} + 2\text{HgCl}_2 \rightleftharpoons \text{Hg}_2\text{Cl}_2 + \text{Sn}^{4+} + 2\text{Cl}^-$$

- Generated  $\text{Hg}_2\text{Cl}_2$  does not reduce the oxidizing reagent [ $\text{MnO}_4^-$  or  $\text{Ce(IV)}$ ]
- Presence of  $\text{HgCl}_2$  excess is not able to re-oxidize Fe(II)

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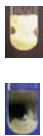
⊗ **Extreme care must be taken to avoid the reaction:**


$$\text{Sn}^{2+} + \text{Hg}_2\text{Cl}_2 \rightleftharpoons 2\text{Hg}^0 + 2\text{Cl}^- + \text{Sn}^{4+}$$

⊗ because  **$\text{Hg}^0$  reacts with the oxidizing agent  $\text{MnO}_4^-$** , thus consuming reagent.

⊗ **Certainty of the reaction completeness:**

- ✓ Appearance of silky white precipitate of  $\text{Hg}_2\text{Cl}_2$ .
- If not, it means that we have not added enough  $\text{Sn}^{2+}$ .
- ⊗ a black precipitate denotes formation of  $\text{Hg}^0$ : the sample must be **discarded!!!**



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**3. Titration of iron with oxidant ( $\text{MnO}_4^-$ )**

$$5\text{Fe}^{2+} + \text{MnO}_4^- + 8\text{H}^+ \rightleftharpoons 5\text{Fe}^{3+} + \text{Mn}^{2+} + 4\text{H}_2\text{O}$$

- **Fe(II) induces the oxidation of  $\text{Cl}^-$  to  $\text{Cl}_2$**  by  $\text{MnO}_4^-$
- (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  $\text{H}_2\text{SO}_4$
- **Chemically:** adding the **Zimmermann-Reinhardt** reagent that is composed of:

✓ **Mn (II) in a mixture of sulfuric and phosphoric acids**

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⇒ The presence of Mn(II) causes a decrease of the potential for semisystem Mn(III)/Mn(II)

$$E = E_{\text{Mn(III)/Mn(II)}}^0 + 0.059 \log \frac{[\text{Mn(III)}]}{[\text{Mn(II)}]}$$

⇒ PO<sub>4</sub><sup>3-</sup> forms stable complexes with Mn(III), what produces an identical effect

⇒ PO<sub>4</sub><sup>3-</sup> also complexes Fe(III), thus helping the reaction to reach completion more easily

⇒ PO<sub>4</sub><sup>3-</sup>/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

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

Titration curve for the titration of 50.0 mL of 0.100 M Fe<sup>2+</sup> with 0.100 M Ce<sup>4+</sup>. 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.

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### Oxidimetry: determination of Ca in limestone (CaCO<sub>3</sub>)

**Basis:** precipitation of Ca<sup>2+</sup> as oxalate, which is filtered, washed and dissolved in dilute acid, and then titrated with MnO<sub>4</sub><sup>-</sup>.

$$\text{Ca}^{2+} + \text{C}_2\text{O}_4^{2-} \rightleftharpoons \downarrow \text{CaC}_2\text{O}_4$$

$$\downarrow \text{CaC}_2\text{O}_4 + 2\text{H}^+ \rightleftharpoons \text{H}_2\text{C}_2\text{O}_4 + \text{Ca}^{2+}$$

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

⇒ Less time consuming than the gravimetric determination

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### 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 Fe<sup>2+</sup> and Sn<sup>2+</sup> using Ce<sup>4+</sup> 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.

Titration curve for the titration of 50.0 mL of 0.0125 M Sn<sup>2+</sup> and 0.0250 M Fe<sup>2+</sup> with 0.050 M Ce<sup>4+</sup>. Both the titrant and the titrand are 1M in HCl.

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### K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> as oxidant

$$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightleftharpoons 2\text{Cr}^{3+} + 7\text{H}_2\text{O}; \quad E^0 = 1.33 \text{ V}$$

green

- ✓ Titrations are usually carried out in 1 M H<sub>2</sub>SO<sub>4</sub> or HCl media (E<sup>0</sup> ≈ 1.0 – 1.1 V)
- ✓ Solutions are stable indefinitely, can be boiled and do not react with Cl<sup>-</sup>
- ✓ There exist a pure enough reagent as to be used as primary standard type

⊗ Unlike permanganate, dichromate titrations require an indicator.

- ✦ There are three indicators that may be used: diphenylamine, diphenylbenzidine and diphenylamine sulfonate. The color varies from green (Cr<sup>3+</sup>) to purple

⇒ Oxidation kinetics is sometimes slow.

⇒ Main disadvantage against MnO<sub>4</sub><sup>-</sup> or Ce(IV): its lower E<sup>0</sup>.

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### 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)**

$$\text{mmol Fe}^{2+} \text{ added} = \text{mmol Fe}^{2+} \text{ consumed} + \text{mmol Fe}^{2+} \text{ free in excess}$$

Ox: NO<sub>3</sub><sup>-</sup>, ClO<sub>3</sub><sup>-</sup>, MnO<sub>4</sub><sup>-</sup>...


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**I<sub>2</sub> as oxidant: Iodimetry**

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


$$I_3^- + 2 e^- \rightleftharpoons 3 I^- ; \quad E^0 = 0.536 V$$

- ✓ 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

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**The Preparation and Stability of Standard Solutions of I<sub>2</sub> (I<sub>3</sub><sup>-</sup>)**

- Low solubility in H<sub>2</sub>O (≈ 0.001 M). It is prepared by dissolving in KI :
 
$$I_2 + I^- \rightleftharpoons I_3^- \quad K = 7.1 \cdot 10^2$$
- Solutions unstable due to:
  - volatility of the solute, I<sub>2</sub>
  - most organic materials suffer a slow attack by I<sub>2</sub> .
    - Conservation in closed containers.
    - Avoid cork or rubber stoppers, as well as contact with fumes.
  - I<sup>-</sup> gets oxidized by air, thus increasing the concentration.
 
$$4 I^- + O_2 + 4 H^+ \rightleftharpoons 2 I_2 + 2 H_2O$$


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**I<sub>2</sub> as oxidant: Endpoint Indication**

- ✓ **Self-indicator:** [I<sub>3</sub><sup>-</sup>]=5.0·10<sup>-6</sup> 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 CCl<sub>4</sub> or HCCl<sub>3</sub>, 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<sub>3</sub><sup>-</sup> has come down from deep red to pale yellow.




I<sub>3</sub><sup>-</sup>    Close to equivalence    + Starch    Equivalence

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**I<sub>2</sub> as oxidant: Standardization**

It may be standardized with:


- ❖ **Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>**
  - ✓ very soluble in water and commercially available in primary type grade.
- ❖ **BaS<sub>2</sub>O<sub>3</sub>·H<sub>2</sub>O**
  - ✓ the salt is scarcely soluble in water, but the reaction proceeds even directly with the solid:
 
$$I_2 + 1BaS_2O_3 \cdot H_2O \rightleftharpoons S_4O_6^{2-} + Ba^{2+} + 2 I^-$$

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**I<sub>2</sub> 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:

$$I_2 + OH^- \rightleftharpoons IO^- + I^- + H^+; \quad 3 IO^- \rightleftharpoons IO_3^- + 2 I^-$$

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**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<sup>-</sup>.**

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**Fe as reductant**


- ❖ **Mohr's salt:**  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$
- ❖ **Oesper's salt:**  $\text{FeC}_2\text{H}_4(\text{NH}_3)_2(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$

⊗ **Fe(II)** easily oxidizable in air

- It is preserved in 0.5 M  $\text{H}_2\text{SO}_4$  acid medium

**Fe as reductant: practical applications**

- Determination of **Cr(VI)**, **Mo(VI)**,  **$\text{NO}_3^-$** ,  **$\text{ClO}_3^-$** ,  **$\text{ClO}_4^-$**


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**I<sup>-</sup> as reductant**  $2\text{I}^- \rightleftharpoons \text{I}_2 + 2\text{e}^-$

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

⇒ **Indirect determinations**

- **Iodometry:** an oxidizing analyte is added to excess iodide (KI) to produce iodine ( $\text{I}_2$ ), which is then titrated with standard thiosulfate solution ( $\text{Na}_2\text{S}_2\text{O}_3$ ) in neutral or slightly acidic medium.

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**Iodometry: the  $\text{I}_2 - \text{S}_2\text{O}_3^{2-}$  reaction**

$\text{I}_2 + 2\text{S}_2\text{O}_3^{2-} \rightleftharpoons 2\text{I}^- + \text{S}_4\text{O}_6^{2-}$


- Reaction is not longer quantitative at  $\text{pH} > 7$
- At  $\text{pH} > 7$  hypoiodite is generated, which is capable of oxidizing thiosulfate to sulfate:

$$\text{I}_2 + \text{OH}^- \rightleftharpoons \text{IO}^- + \text{I}^- + \text{H}^+$$

- When  $\text{I}_2$  0.05 M,  $\text{pH} \leq 6.5$
- When  $\text{I}_2$  0.005 M,  $\text{pH} \leq 5$
- The starch must be added at the end of the titration, to avoid its decomposition by prolonged contact with iodine.

$$2\text{S}_2\text{O}_3^{2-} \rightleftharpoons \text{S}_4\text{O}_6^{2-} + 2\text{e}^-$$

$$2 \begin{array}{c} \text{OH} \\ | \\ \text{O}=\text{S}-\text{SH} \\ | \\ \text{O} \end{array} \rightleftharpoons \begin{array}{c} \text{OH} \\ | \\ \text{O}=\text{S}-\text{S}-\text{S}=\text{O} \\ | \quad | \\ \text{O} \quad \text{O} \end{array} + 2\text{e}^-$$


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**$\text{S}_2\text{O}_3^{2-}$  solutions**

- ✓ Stable in air
- They show a tendency to **decomposition**:

$$\text{S}_2\text{O}_3^{2-} + \text{H}^+ \rightleftharpoons \text{HSO}_3^- + \text{S}_{(s)}$$

- The rate of this decomposition reaction depends on:
  - pH
  - **Presence of microorganisms** (metabolize the transformation of  $\text{S}_2\text{O}_3^{2-}$  to  $\text{SO}_3^{2-}$ ,  $\text{SO}_4^{2-}$  and  $\text{S}^0$ )
    - ⇒ Work in sterile conditions, and / or in the presence of bactericides.
  - Concentration of the solution
  - Presence of Cu(II)
  - Exposure to sunlight

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**$\text{S}_2\text{O}_3^{2-}$  solutions: standardization**

They are standardized against  $\text{KIO}_3$ , as a primary type standard.

The  $\text{KIO}_3$ , once weighed, is dissolved in water containing an excess of KI. Upon acidification, the formation of  $\text{I}_2$  takes place instantaneously:

$$\text{IO}_3^- + 5\text{I}^- + 6\text{H}^+ \rightleftharpoons 3\text{I}_2 + 2\text{H}_2\text{O}$$


The  $\text{S}_2\text{O}_3^{2-}$  is then titrated against this *in situ* liberated  $\text{I}_2$  :

$$\text{I}_2 + 2\text{S}_2\text{O}_3^{2-} \rightleftharpoons 2\text{I}^- + \text{S}_4\text{O}_6^{2-}$$

$$1 \text{ mol } \text{IO}_3^- \equiv 3 \text{ mol } \text{I}_2 \equiv 6 \text{ mol } \text{S}_2\text{O}_3^{2-}$$

$$\text{Cr}_2\text{O}_7^{2-} + 6\text{I}^- + 14\text{H}^+ \rightleftharpoons 2\text{Cr}^{3+} + 3\text{I}_2 + 7\text{H}_2\text{O}$$

$$\text{BrO}_3^- + 6\text{I}^- + 6\text{H}^+ \rightleftharpoons \text{Br}^- + 3\text{I}_2 + 3\text{H}_2\text{O}$$

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**Iodometric determination of Cu in minerals and alloys**

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

- Attack and dissolution with  $\text{HNO}_3$ :
  - metals with maximum oxidation state.

$$2\text{Cu}^{2+} + 4\text{I}^- \rightleftharpoons 2\text{CuI}(s) + \text{I}_2$$

⊗ **Interferences:** Fe, As, Sb

⇒ **Alternative:** you work in a  $\text{pH} 3.5$   $\text{HNH}_4\text{F}_2/\text{HF}$  buffered medium.

- $\text{FeF}_6^{3-}$  is formed: decrease of the Fe(III)/Fe(II) potential
- As and Sb are not able to oxidize  $\text{I}^-$ , contrary to what they do in strong acidic conditions.

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### Iodometric determination of O<sub>2</sub> dissolved in H<sub>2</sub>O: WINKLER

- 1) Precipitation of Mn(OH)<sub>2</sub> in basic medium
- 2) Oxidation to Mn(OH)<sub>3</sub> by the **dissolved O<sub>2</sub>**.
- 3) Mn(OH)<sub>3</sub> oxidizes I<sup>-</sup> to I<sub>2</sub> in acidic medium
- 4) The stoichiometrically generated I<sub>2</sub> is titrated with S<sub>2</sub>O<sub>3</sub><sup>2-</sup>.

Excess of Mn(II), NaI, OH<sup>-</sup>

$$2 \downarrow \text{Mn(OH)}_2 + \text{O}_2 + 2\text{H}_2\text{O} \rightleftharpoons 4 \downarrow \text{Mn(OH)}_3$$

O<sub>2</sub>

I<sup>-</sup>, Mn(OH)<sub>3</sub>

I<sup>-</sup>, Mn(OH)<sub>3</sub>

I<sub>2</sub>

I<sub>2</sub>

$$\text{I}_2 + 2\text{S}_2\text{O}_3^{2-} \rightleftharpoons 2\text{I}^- + \text{S}_4\text{O}_6^{2-}$$

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### 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 I<sub>3</sub><sup>-</sup>.
- (b) Titrating with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> converts I<sub>3</sub><sup>-</sup> to I<sup>-</sup> with the solution fading to a pale yellow color as we approach the end point.
- (c) Adding starch forms the deep purple starch-I<sub>3</sub><sup>-</sup> 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.

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### Special oxidants

- 1. KBrO<sub>3</sub>**  
Determination of olefinic groups and certain aromatic functional groups.
- 2. HIO<sub>4</sub>**  
Selective reaction with groups  $-\text{OH}, -\text{C}(=\text{O}), -\text{NH}_2$
- 3. Karl Fischer reagent**  
Determination of H<sub>2</sub>O

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### 1. KBrO<sub>3</sub>

$$\text{BrO}_3^- + 6\text{H}^+ + 6\text{e}^- \rightleftharpoons \text{Br}^- + 3\text{H}_2\text{O} \quad E^0 = 1.44 \text{ V}$$

- ✓ Primary type standard substance .
- ✓ Stable indefinitely.
- ✓ Precursor of Br<sub>2</sub>:

$$\text{BrO}_3^- + 5\text{Br}^- + 6\text{H}^+ \rightleftharpoons 3\text{Br}_2 + 3\text{H}_2\text{O}$$

standard      excess

- ⊗ Reactions with Br<sub>2</sub>: slow kinetics.
- ⊗ Few direct applications: As(III), Sb(III), Fe(II)
- ⇒ Indirect titrations are preferred instead.

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### 1. KBrO<sub>3</sub>: Indirect applications

Analyte, Red<sub>2</sub>

Br<sub>2</sub>, KBrO<sub>3</sub>

H<sup>+</sup>

I<sup>-</sup>, Br<sub>2</sub> exc.

S<sub>2</sub>O<sub>3</sub><sup>2-</sup>

I<sub>2</sub>

$$\text{Br}_2 + 2\text{I}^- \rightleftharpoons 2\text{Br}^- + \text{I}_2$$

$$\text{I}_2 + 2\text{S}_2\text{O}_3^{2-} \rightleftharpoons 2\text{I}^- + \text{S}_4\text{O}_6^{2-}$$

$$\text{BrO}_3^- + 5\text{Br}^- + 6\text{H}^+ \rightleftharpoons 3\text{Br}_2 + 3\text{H}_2\text{O}$$

standard      excess

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### 1. KBrO<sub>3</sub>: Substitution reactions

Indirect titration

Sufficiently rapid reaction:  
Direct titration

**Example: Determination of Al**

$$\text{Al}^{3+} + 3 \text{HOC}_9\text{H}_6\text{N} \xrightarrow{\text{pH}=4-9} \downarrow \text{Al}(\text{OC}_9\text{H}_6\text{N})_3 + 3 \text{H}^+$$

$$\downarrow \text{Al}(\text{OC}_9\text{H}_6\text{N})_3 \xrightarrow{\text{HCl } 4\text{M}, \Delta} 3 \text{HOC}_9\text{H}_6\text{N} + \text{Al}^{3+}$$

$$3 \text{HOC}_9\text{H}_6\text{N} + 6 \text{Br}_2 \rightarrow 3 \text{HOC}_9\text{H}_4\text{NBr}_2 + 6 \text{HBr}$$

**BrO<sub>3</sub><sup>-</sup> (standard) + Br<sup>-</sup>**

1 mol Al<sup>3+</sup> = 3 mol HQ = 6 mol Br<sub>2</sub>



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**1. KBrO<sub>3</sub>: Addition reactions**

$$\text{H}-\text{C}=\text{C}-\text{H} + \text{Br}_2 \rightarrow \text{H}-\text{C}(\text{Br})-\text{C}(\text{Br})-\text{H}$$

These reactions involve the opening of the olefinic double bond.

Basis of the estimation of unsaturated fats, oils and oil products.

**Example: Determination of ascorbic acid**

$$\text{C}_6\text{H}_7\text{O}_6 + \text{Br}_2 \rightarrow \text{C}_6\text{H}_5\text{O}_6 + 2\text{Br}^- + 2\text{H}^+$$

Analyte + KBr, H<sup>+</sup>      KBrO<sub>3</sub> + I<sup>-</sup>      Br<sub>2</sub> + 2 I<sup>-</sup> ⇌ 2 Br<sup>-</sup> + I<sub>2</sub>      S<sub>2</sub>O<sub>3</sub><sup>2-</sup>

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**2. HIO<sub>4</sub>**

In highly acidic media exists as paraperiodic acid:

$$\text{H}_5\text{IO}_6 (\text{I}_2\text{O}_7 + 5 \text{H}_2\text{O})$$

$$\text{H}_5\text{IO}_6 + \text{H}^+ + 2\text{e}^- \rightleftharpoons \text{IO}_3^- + 3\text{H}_2\text{O} \quad E^0 = 1.60 \text{ V}$$

Solutions may be prepared from :

- H<sub>5</sub>IO<sub>6</sub>, hygroscopic crystalline solid
- \* NaIO<sub>4</sub>, soluble in H<sub>2</sub>O (S = 0.06 M at 25°C)
- KIO<sub>4</sub>
- ✓ Variable stability. Best in sulfuric acid medium

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**2. HIO<sub>4</sub> Standardization**

It is carried out in a pH 8-9 CO<sub>3</sub><sup>2-</sup>/HCO<sub>3</sub><sup>-</sup> buffer by iodometry.

$$\text{H}_4\text{IO}_6^- + 2\text{I}^- \rightleftharpoons \text{IO}_3^- + \text{I}_2 + 2\text{OH}^- + \text{H}_2\text{O}$$

$$\text{IO}_4^- + 2\text{I}^- + \text{H}_2\text{O} \rightleftharpoons \text{IO}_3^- + \text{I}_2 + 2\text{OH}^-$$

**1 mol IO<sub>4</sub><sup>-</sup> = 1 mol I<sub>2</sub>**

$$\text{I}_2 + 2\text{S}_2\text{O}_3^{2-} \rightleftharpoons 2\text{I}^- + \text{S}_4\text{O}_6^{2-}$$

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**2. HIO<sub>4</sub> Selectivity of Malaprade reaction**

**C-C bond undergoes an oxidative cleavage** in the presence of HIO<sub>4</sub>, if both carbons have hydroxyl or carbonyl groups, or adjacent hydroxyl and carbonyl groups.

The oxidative power of HIO<sub>4</sub> causes a unit increase in the oxidation degree of every resulting fragment. In this way, after Malaprade reaction:

- > primary alcohols are oxidized to methanal
- > secondary alcohols are oxidized to aldehydes
- > tertiary alcohols are oxidized to ketones
- > aldehydes are oxidized to formic acid
- > ketones are oxidized to carboxylic acids
- > carboxylic acids are oxidized to CO<sub>2</sub>

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- **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

$$\text{HO}-\text{CH}_2-\text{CH}_2-\text{OH} + \text{H}_4\text{IO}_6^- \rightarrow 2 \text{H}_2\text{C}=\text{O} + \text{IO}_3^- + 3 \text{H}_2\text{O}$$

Ethylene glycol      Formaldehyde

**Positive assay:**  
 $\text{IO}_3^- + \text{Ag}^+ \rightleftharpoons \downarrow \text{AgIO}_3$   
 (white)

- **Non-adjacent groups are not oxidized**

$$\text{R}-\text{C}(\text{OH})-\text{C}(\text{H})-\text{C}(\text{H})-\text{C}(\text{OH})-\text{H} \rightarrow \text{no reaction}$$


non-adjacent hydroxyls

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

- ✓ Primary and secondary **α-hydroxyamines 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.


$$\begin{array}{c} \text{OHNH}_2 \\ | \\ \text{C}-\text{C}-\text{CO}_2\text{H} \\ | \quad | \\ \text{H}_2 \quad \text{H} \end{array} + \text{IO}_4^- \rightarrow \begin{array}{c} \text{O} \\ || \\ \text{CH}_2 \end{array} + \begin{array}{c} \text{O} \\ || \\ \text{C}-\text{CO}_2\text{H} \\ | \\ \text{H} \end{array} + \text{NH}_3 + \text{IO}_3^-$$

$$\begin{array}{c} \text{R} \\ | \\ \text{OHNH} \\ | \\ \text{C}-\text{C}-\text{H} \\ | \quad | \\ \text{H}_2 \quad \text{H} \end{array} + \text{IO}_4^- \rightarrow 2 \begin{array}{c} \text{O} \\ || \\ \text{CH}_2 \end{array} + \text{NH}_2\text{R} + \text{IO}_3^-$$


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Possible selective determination of the four  $\alpha$ -hydroxyamines present in proteins:

Serine	$\begin{array}{c} \text{OH} & \text{O} \\   &    \\ \text{C} - \text{C} - \text{C} - \text{OH} \\   &   \\ \text{H}_2 & \text{NH}_2 \end{array}$	
Treonine	$\begin{array}{c} \text{OHNH}_2 \\   \\ \text{H}_3\text{C} - \text{C} - \text{C} - \text{COOH} \\   &   \\ \text{H} & \text{H} \end{array}$	
$\beta$ -Hydroxyglutamic acid	$\begin{array}{c} \text{OHNH}_2 \\   \\ \text{HOOC} - \text{C} - \text{C} - \text{C} - \text{COOH} \\   &   &   \\ \text{H}_2 & \text{H} & \text{H} \end{array}$	
Hydroxylysine	$\begin{array}{c} \text{H} & \text{H} & \text{H} \\   &   &   \\ \text{H}_2\text{N} - \text{C} - \text{C} - \text{C} - \text{C} - \text{COOH} \\   &   &   &   \\ \text{H}_2 & \text{OH} & \text{H}_2 & \text{NH}_2 \end{array}$	


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**3. Karl-Fischer reagent** Mixture, dissolved in  $\text{CH}_3\text{OH}$ , of:

$$\begin{array}{ccc} \text{I}_2 & \text{C}_5\text{H}_5\text{N} & \text{SO}_2 \\ \mathbf{1} & \mathbf{: 10} & \mathbf{: 3} \end{array}$$

$$\text{C}_5\text{H}_5\text{NI}_2 + \text{C}_5\text{H}_5\text{N} \cdot \text{SO}_2 + \text{C}_5\text{H}_5\text{N} + \text{H}_2\text{O} \rightarrow 2\text{C}_5\text{H}_5\text{NH}^+ + \text{C}_5\text{H}_5\text{N} \cdot \text{SO}_3^-$$

It is carried out in a methylic medium:

$$\text{C}_5\text{H}_5\text{N}^+ \cdot \text{SO}_3^- + \text{CH}_3\text{OH} \rightarrow \text{C}_5\text{H}_5\text{NH}^+ \cdot \text{CH}_2\text{OSO}_3^-$$

In order to avoid:

$$\text{C}_5\text{H}_5\text{N} \cdot \text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{C}_5\text{H}_5\text{NHSO}_3\text{H}$$

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Lesson 8. Potentiometry, Electrogravimetry and Coulometry

- Indicator electrodes: classification.
- Glass membrane electrode: potentiometric measurement of pH.
- Coulometric titrations.
- Electrogravimetry.

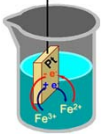
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**Indicator electrodes**

- > **Metallic**
  - ✓ Inert redox
  - ✓ First kind
  - ✓ Second kind
  - ✓ Third kind
- > **Membrane**
  - ✓ **Non-crystalline**
    - Glass
    - Liquid membrane
  - ✓ **Crystalline**
    - Monocrystal
    - Polycrystal


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**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.



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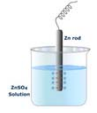
**First kind electrode**



**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.

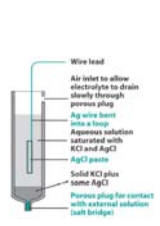
$$M^{n+} + ne^{-} \rightarrow M^0$$

$$E = E_{M^{n+}/M}^0 + \frac{0.059}{n} \log \frac{[M^{n+}]}{[M^0]} = E_{M^{n+}/M}^0 + \frac{0.059}{n} \log [M^{n+}]$$


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**Second kind electrode** **Ag/AgCl<sub>sat</sub>, KCl//**

**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).**



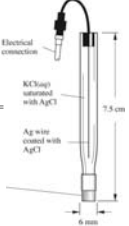
$$Ag^+ + e^{-} \rightleftharpoons Ag^0; E^0 = 0.792V$$

$$AgCl \rightleftharpoons Ag^+ + Cl^-; P_s = [Ag^+][Cl^-]$$

$$E = E_{Ag^+/Ag^0}^0 + \frac{0.059}{1} \log \frac{[Ag^+]}{[Ag^0]} = E_{Ag^+/Ag^0}^0 + 0.059 \log \frac{P_s}{[Cl^-]}$$

$$= E_{Ag^+/Ag^0}^0 + 0.059 \log P_s + 0.059 \log \frac{1}{[Cl^-]}$$

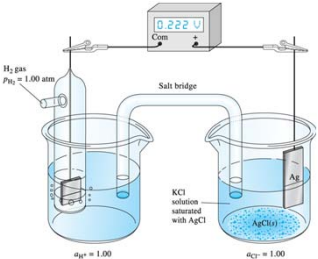
$$= E_{AgCl/Ag^0}^0 + 0.059 \log \frac{1}{[Cl^-]} = 0.222 + 0.059 \text{ pCl}$$

$$AgCl_{(s)} + e^{-} \rightleftharpoons Ag_{(s)} + Cl^-; E^0 = 0.222V$$


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

- > **Excellent reference electrodes !**



[KCl]	E/V
Sat'd	0.199
3.5 M	0.205
1.0 M	0.222

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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.

**Electrodes of the second kind have displaced the use of NHE as reference electrode.**

$+0.228 \text{ V (Ag/AgCl)}$   
 $+0.242 \text{ V (SCE)}$   
 $0 \text{ V (NHE)}$   
 $-0.532 \text{ V (vs. NHE)}$   
 $-0.774 \text{ V (vs. SCE)}$   
 $-0.760 \text{ V (vs. Ag/AgCl)}$

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### 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

Schematic representation of a liquid junction showing the source of the junction potential  $E_j$ . The length of the arrows corresponds to the relative mobility of the two ions.

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$E_j$  is minimized by a high concentration of a salt with nearly equal mobilities of cation and anion in the salt bridge, e.g., saturated KCl.

The flux of the migration of this electrolyte is much greater than more dilute ones, and largely determines  $E_j$ .

Ion	Mobility [ $\text{m}^2/\text{s} \cdot \text{V}$ ] <sup>a</sup>	Ion	Mobility [ $\text{m}^2/\text{s} \cdot \text{V}$ ] <sup>a</sup>
H <sup>+</sup>	$36.30 \times 10^{-8}$	OH <sup>-</sup>	$20.50 \times 10^{-8}$
K <sup>+</sup>	$7.62 \times 10^{-8}$	SO <sub>4</sub> <sup>2-</sup>	$8.27 \times 10^{-8}$
NH <sub>4</sub> <sup>+</sup>	$7.61 \times 10^{-8}$	Br <sup>-</sup>	$8.13 \times 10^{-8}$
La <sup>3+</sup>	$7.21 \times 10^{-8}$	I <sup>-</sup>	$7.96 \times 10^{-8}$
Ba <sup>2+</sup>	$6.59 \times 10^{-8}$	Cl <sup>-</sup>	$7.91 \times 10^{-8}$
Ag <sup>+</sup>	$6.42 \times 10^{-8}$	NO <sub>3</sub> <sup>-</sup>	$7.40 \times 10^{-8}$
Ca <sup>2+</sup>	$6.12 \times 10^{-8}$	ClO <sub>4</sub> <sup>-</sup>	$7.05 \times 10^{-8}$
Ca <sup>2+</sup>	$5.56 \times 10^{-8}$	F <sup>-</sup>	$5.70 \times 10^{-8}$
Na <sup>+</sup>	$5.19 \times 10^{-8}$	CH <sub>3</sub> CO <sub>2</sub> <sup>-</sup>	$4.24 \times 10^{-8}$
Li <sup>+</sup>	$4.01 \times 10^{-8}$		

Junction	Potential (mV)
0.1 M NaCl   0.1 M KCl	-6.4
0.1 M NaCl   3.5 M KCl	-0.2
1 M NaCl   3.5 M KCl	-1.9
0.1 M HCl   0.1 M KCl	+2.7
0.1 M HCl   3.5 M KCl	+3.1

NOTE: A positive sign means that the right side of the junction becomes positive with respect to the left side.

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### Electrodes with renewable liquid junctions

Orion double junction reference electrode

Single junction reference electrode

Thermo Orion double junction reference electrode

Thermo Orion single junction reference electrode

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- 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

$$\text{AgCl}_{\text{solid}} + \text{Cl}^- \rightleftharpoons \text{AgCl}_2^-$$

- 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 Ag<sub>2</sub>O which is a black/purple colored deposit.
- For this reason it is best to store the electrode in 3M KCl solution.
- The dilemma is that this solution is not suitable for storing the glass electrode.
- 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.

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### Second kind electrode

**Hg/Hg<sub>2</sub>Cl<sub>2</sub>sat. KCl//**

$$\text{Hg}_2^{2+} + 2e^- \rightleftharpoons 2\text{Hg}$$

$$\text{Hg}_2\text{Cl}_2 \rightleftharpoons 2\text{Cl}^- + \text{Hg}_2^{2+}; P_s = [\text{Hg}_2^{2+}][\text{Cl}^-]^2$$

$$E = E^0 + \frac{0.059}{2} \log[\text{Hg}_2^{2+}] = E^0 + \frac{0.059}{2} \log \frac{P_s}{[\text{Cl}^-]^2}$$

$$E = f([\text{Cl}^-])$$

[KCl]	E/V
Sat'd	0.244
4.0 M	0.246
3.5 M	0.250
1.0 M	0.280
0.1 M	0.336

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TABLE 23-1 Potentials of Reference Electrodes in Aqueous Solutions

Temperature, °C	Electrode Potential vs. SHE, V				
	0.1 M <sup>a</sup> Calomel <sup>b</sup>	3.5 M <sup>a</sup> Calomel <sup>b</sup>	Saturated <sup>a</sup> Calomel <sup>b</sup>	3.5 M <sup>a,c</sup> Ag-AgCl	Saturated <sup>a,c</sup> Ag-AgCl
10	—	0.256	—	0.215	0.214
12	0.3362	—	0.2528	—	—
15	0.3362	0.254	0.2511	0.212	0.209
20	0.3359	0.252	0.2479	0.208	0.204
25	0.3356	0.250	0.2444	0.205	0.199
30	0.3351	0.248	0.2411	0.201	0.194
35	0.3344	0.246	0.2376	0.197	0.189
38	0.3338	—	0.2355	—	0.184
40	—	0.244	—	0.193	—

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**Second kind electrode** **Hg/HgY<sup>2-</sup>, Y<sup>4-</sup>//**

$\text{HgY}^{2-} + 2e^- \rightleftharpoons \text{Hg}_{(l)} + \text{Y}^{4-}; E^0 = 0,210\text{V}$

$E = 0,210 + \frac{0,059}{2} \log \frac{[\text{HgY}^{2-}]}{[\text{Y}^{4-}]}$

$K_{\text{HgY}^{2-}} = 6.3 \cdot 10^{21}; [\text{HgY}^{2-}] \cong \text{const.}$

$E = 0,21 + \frac{0,059}{2} \log [\text{HgY}^{2-}] + \frac{0,059}{2} \log \frac{1}{[\text{Y}^{4-}]}$

$E = K + \frac{0,059}{2} \text{pY}$  **E = f([Y<sup>4-</sup>])**

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**Third kind electrode** **Hg / HgY<sup>2-</sup> / CaY<sup>2-</sup> / Ca<sup>2+</sup> //**

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

$E = K - \frac{0,059}{2} \log [\text{Y}^{4-}]$

$\text{CaY}^{2-} \rightleftharpoons \text{Ca}^{2+} + \text{Y}^{4-}; K_1 = \frac{[\text{CaY}^{2-}]}{[\text{Ca}^{2+}][\text{Y}^{4-}]}$

$E = K - \frac{0,059}{2} \log \frac{[\text{CaY}^{2-}]}{K_1 [\text{Ca}^{2+}]}$

$E = K - \frac{0,059}{2} \log \frac{[\text{CaY}^{2-}]}{K_1} - \frac{0,059}{2} \log \frac{1}{[\text{Ca}^{2+}]} = K' - \frac{0,059}{2} \text{pCa}$

**E = f([Ca<sup>2+</sup>])**

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**Third kind electrode** **Hg<sub>0</sub> / Hg<sub>2</sub>C<sub>2</sub>O<sub>4</sub>(s) / CaC<sub>2</sub>O<sub>4</sub>(s) / Ca<sup>2+</sup> //**

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

$\text{Hg}_2^{2+} + 2e^- \rightleftharpoons 2\text{Hg}^0$

$\text{Hg}_2\text{C}_2\text{O}_4 \rightleftharpoons \text{Hg}_2^{2+} + \text{C}_2\text{O}_4^{2-}; P_{\text{Hg}_2\text{C}_2\text{O}_4} = [\text{Hg}_2^{2+}][\text{C}_2\text{O}_4^{2-}]$

$\text{CaC}_2\text{O}_4 + \text{Ca}^{2+} \rightleftharpoons \text{CaC}_2\text{O}_4; P_{\text{CaC}_2\text{O}_4} = [\text{Ca}^{2+}][\text{C}_2\text{O}_4^{2-}]$

**Global:**  $\text{Hg}_2\text{C}_2\text{O}_4 + \text{Ca}^{2+} + 2e^- \rightleftharpoons 2\text{Hg} + \text{CaC}_2\text{O}_4$

$E = E_{\text{Hg}_2^{2+}/\text{Hg}^0}^0 + \frac{0,059}{2} \log [\text{Hg}_2^{2+}] = E_{\text{Hg}_2^{2+}/\text{Hg}^0}^0 + \frac{0,059}{2} \log \frac{P_{\text{Hg}_2\text{C}_2\text{O}_4}}{[\text{C}_2\text{O}_4^{2-}]}$

$= E_{\text{Hg}_2^{2+}/\text{Hg}^0}^0 + \frac{0,059}{2} \log \frac{P_{\text{Hg}_2\text{C}_2\text{O}_4}}{P_{\text{CaC}_2\text{O}_4} [\text{Ca}^{2+}]}$

$= E_{\text{Hg}_2^{2+}/\text{Hg}^0}^0 + \frac{0,059}{2} \log P_{\text{Hg}_2\text{C}_2\text{O}_4} - \frac{0,059}{2} \log P_{\text{CaC}_2\text{O}_4} + \frac{0,059}{2} \log [\text{Ca}^{2+}]$

**E = K - \frac{0,059}{2} \text{pCa}**

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**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

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**Glass membrane**

Outer reference electrode | H<sup>+</sup> (aq, outside) | H<sup>+</sup> (aq, inside) | Inner reference electrode

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**Glass electrode**

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

External reference electrode:  $E_{ESC}$ ,  $E_j$

Internal reference electrode:  $E_{Ag/AgCl}$

Boundary potential:  $E_b = E_1 - E_2$

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Ion exchange equilibrium determine by  $[H^+]$  in solution

Corning 0015: 22%  $Na_2O$ ; 6%  $CaO$ ; 72%  $SiO_2$

Schematic diagram of the structure of glass, which consists of an irregular network of  $SiO_4$  tetrahedra connected through their oxygen atoms.  $\ominus = O$ ,  $\bullet = Si$ ,  $\circ =$  Cation. Cations such as  $Li^+$ ,  $Na^+$ ,  $K^+$ , and  $Ca^{2+}$  are coordinated to the oxygen atoms. The silicate network is not planar. This diagram is a projection of each tetrahedron onto the plane of the page. [Adapted from

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Hydroscopicity: 50 mg  $H_2O/cm^3$  glass

Internal solution ( $\mathcal{A}_{int} = 0.1$ )

External solution ( $\mathcal{A}_{ext}$  is variable)

Hydrated gel layer (Exchange sites occupied by  $H^+$  and  $Na^+$ )

Dry glass layer (All sites occupied by  $Na^+$ )

Hydrated gel layer (Exchange sites occupied by  $H^+$  and  $Na^+$ )

$Na^+$  provides conductivity

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**Hydration of the membrane**

$$H^+ + Na^+R^- \rightleftharpoons Na^+ + H^+R^-$$

Soln Glass Soln Glass

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

$$H^+ + R^- \rightleftharpoons H^+R^-$$

Soln1 Glass1 Glass1

$$H^+R^- \rightleftharpoons H^+ + R^-$$

Glass2 Soln2 Glass2

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The pH is determined by the **boundary potential** is developed on both sides of the glass membrane.

Variable  $[H^+]$  or  $a_{H^+}$  on exterior of pH electrode

Fixed  $[H^+]$  or  $a_{H^+}$  on interior of pH electrode

Glass Membrane

Glass Surface

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Reference electrode 1: SCE

External analyte solution:  $[H_3O^+] = a_1$

Glass membrane

Internal reference solution:  $[H_3O^+] = a_2$ ,  $[Cl^-] = 0.1 M$ ,  $AgCl (sat'd) | Ag$

Reference electrode 2

Reference electrodes potentials:  $E_{SCE} + E_{Ag/AgCl}$

Liquid junction potential:  $E_j$

Assymetry potential:  $E_{assy}$

Boundary potential:  $E_b = E_1 - E_2$

$$E_1 = j_1 + 0.059 \log \frac{a_1}{a_1}$$

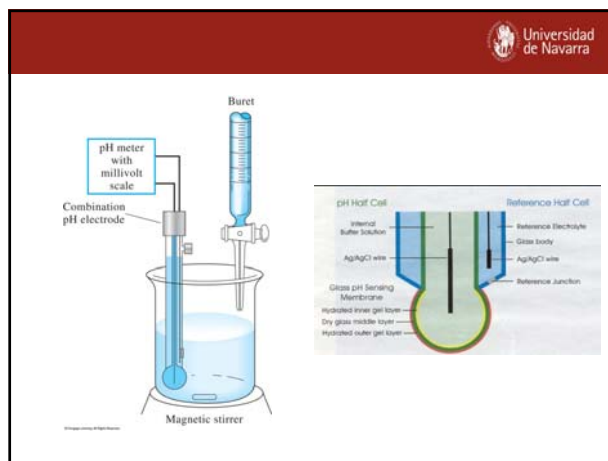
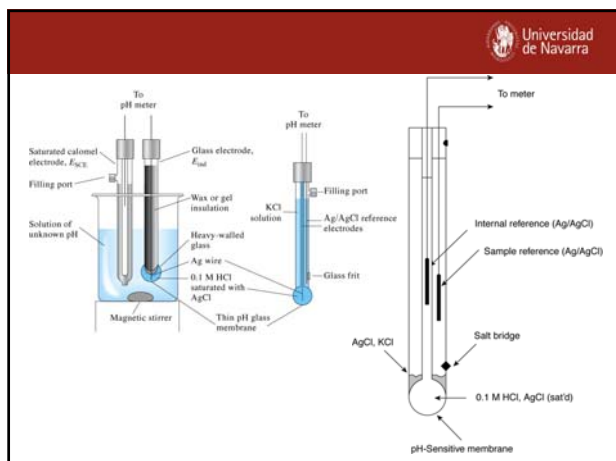
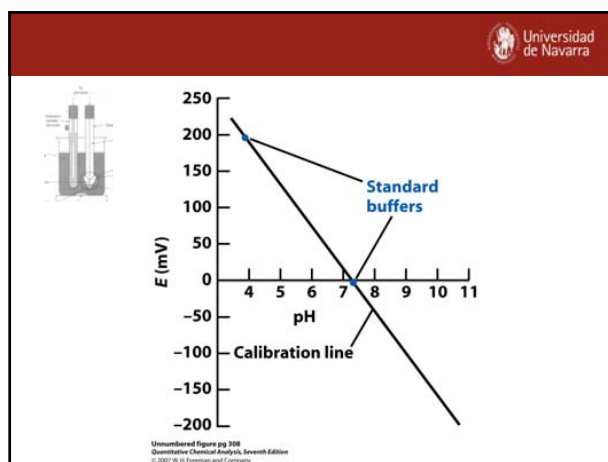
$$E_2 = j_2 + 0.059 \log \frac{a_2}{a_2}$$

$$E_b = 0.059 \log \frac{a_1}{a_2}$$

$E_b = 0.059 \log a_1 - 0.059 \log a_2 = 0.059 \log a_1 + L' = L' - 0.059 \text{ pH}$

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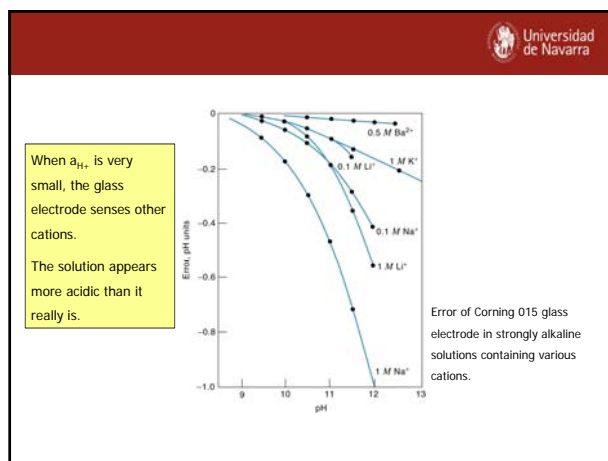
$E_{ind(glass\ electrode)} = E_{Ag/AgCl} + E_{assy} + E_b$   
 $E_{ind(glass\ electrode)} = E_{Ag/AgCl} + E_{asi} + L' + 0.059 \log a_1$   
 $E_{ind(glass\ electrode)} = L + 0.059 \log a_1$       $E_{ind} = L - 0.059\ pH$   
 $\Delta E_{cell} = E_{ind} - E_{SCE(Ext\ Ref)} = L - 0.059\ pH - M = N - 0.059\ pH$



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$H^+R + B^+ \rightleftharpoons B^+R + H^+$   
 Glass    Soln                      Glass    Soln

$$K = \frac{a_1' b_1}{a_1 b_1'}$$

$$\frac{b_1'}{a_1} = \frac{b_1}{a_1} K$$


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In very acid solutions, the activity of water is less than unity (it solvates the proton). The  $a_{H^+}$  is decreased, and the pH reading is increased.  
High concentrations of dissolved salts or adding a nonaqueous solvent does the same.

Error of glass electrode in hydrochloric acid solutions.

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❖ Glass electrode:  $E = L + 0.059 \log a_i$

❖ In general, for any ion selective electrode:  $E = \text{const.} + \frac{0.059}{z} \log a_i$

➤ In the presence of interfering ions :

$$E = \text{const.} + \frac{0.059}{z} \log(a_i + K_{ij} \cdot a_j^{z/a} + K_{ik} \cdot a_k^{z/b} + \dots)$$

$K_{ij}$  : selectivity coefficient for the detmn. of  $i$  in the presence of interfering  $j$

$z$ : charge of principal ion  $i$

$a, b, \dots$ : charges of interfering ions  $j, k, \dots$

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$K_{ij}$  can be determined by 2 methods:

- ❑ **Method A:** requires 2 potentiometric measurements
  1. Solution of known concentration of analyte
  2. Solution with known concentrations of both analyte and potential interfering
- ❑ **Method B:** method of constant interference
 

Measurements of several solutions of increasing concentrations of analyte and constant concentration of interfering ion.

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**Method A**

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

$$E = \text{const} + 0.059 \log a_{K^+}$$

$$0.528 \text{ V} = \text{const.} + 0.059 \log(1.05 \cdot 10^{-4} M)$$

$$\text{const.} = 0.528 - 0.059 \log(1.05 \cdot 10^{-4}) = 0.762 \text{ V}$$

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

$$0.602 \text{ V} = 0.762 \text{ V} + 0.059 \log(2.5 \cdot 10^{-4} + K_{K^+,Li^+} \cdot 1.70 \cdot 10^{-4}) \Rightarrow K_{K^+,Li^+} = 10$$

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**Method B: Fixed interference calibration curve**

$$K_{i,j} = \frac{a_i}{a_j^{z/a}}$$

$a_A = a_B K_{i,j}^{z/a}$

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.

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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:

$$Q = n F N$$

$n$  = # mol of electrons transferred per mol of analyte  
 $F$  = Faraday's constant = 96485 C mol<sup>-1</sup>  
 $N$  = number of mol of analyte  
 Coulomb = C = Ampere · second = A · s

For electrogravimetry, product of electrolysis is weighed as a deposit on one of the electrodes.



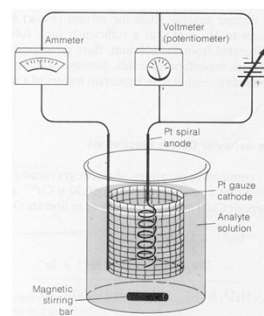
- > The current is kept constant until an **indicator signals completion** of the analytical reaction.
- > The quantity of electricity required to attain the end point is calculated from the magnitude of the current and the time of its passage.
- > Controlled-current coulometry, also known as **coulometric 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.

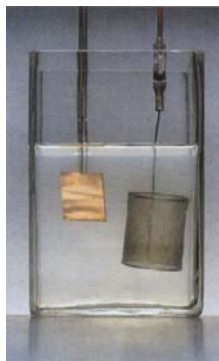
Other necessary instrumental components for controlled-current coulometry is an **accurate clock** (a digital clock provides accurate measurement of time, with errors of  $\pm 1$  ms) for measuring the electrolysis time,  $t_e$ , and a **switch** for starting and stopping the electrolysis.



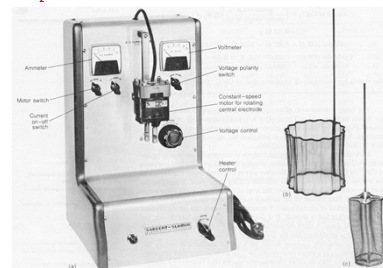
In an **electrogravimetric analysis**, the analyte is quantitatively deposited as a solid on the cathode or anode.

- ✓ 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.



- Cu:** is deposited from acidic solution using a Pt cathode
- Ni:** is deposited from a basic solution
- Zn:** is deposited from acidic citrate solution
- 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<sup>2+</sup>** as **PbO<sub>2</sub>** and **Mn<sup>2+</sup>** as **MnO<sub>2</sub>**



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Lesson 9. Photometric endpoint indication

1. Fundamentals of molecular absorption spectroscopy.
2. Deduction of Beer's Law.
3. Additivity of Beer's law: analysis of mixtures.
4. Titration with photometric indication.

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**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

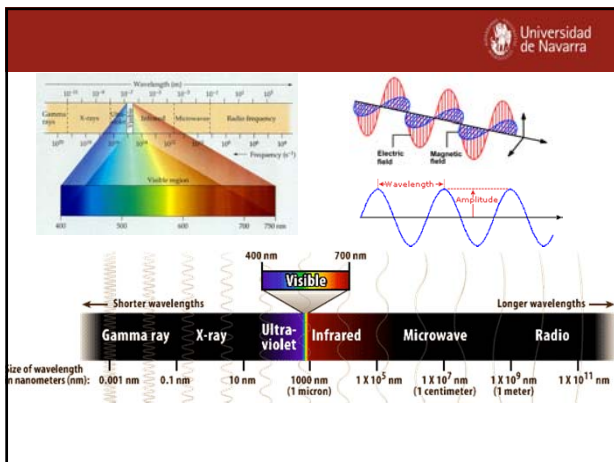
Type of experiment

Absorption

Emission

Fluorescence

Scattering

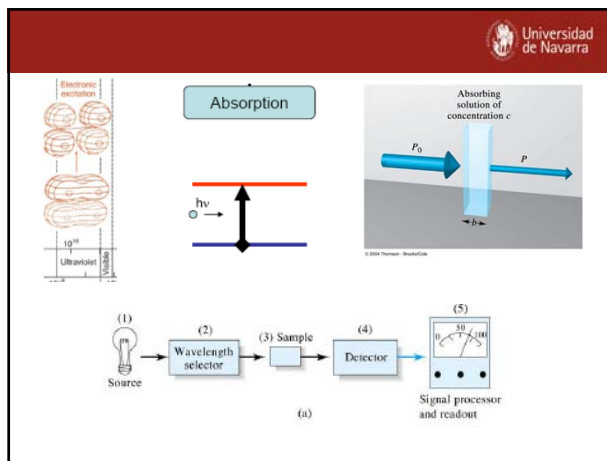
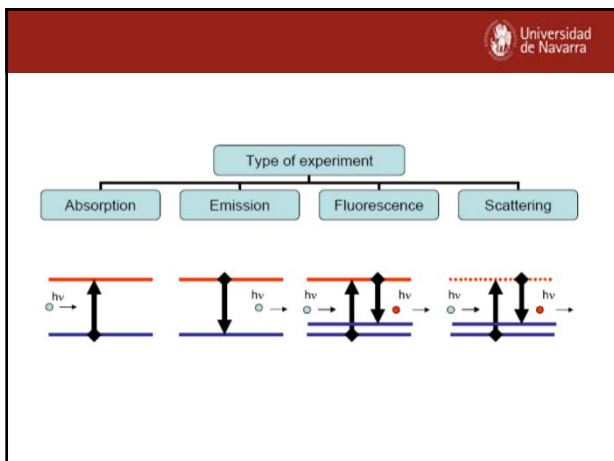


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**Spectroscopy:** studies the interaction of the electric field of electromagnetic radiation with matter by means of phenomena such as absorption, emission and light scattering.

Type of quantum change:	Change of spin	Change of orientation	Change of configuration or	Change of electron distribution	Change of nuclear configuration
	$10^{-3}$	1	100	$10^4$	$10^8$
	10 m	100 cm	1 cm	1000 nm	100 pm
	$3 \times 10^8$	$3 \times 10^6$	$3 \times 10^{16}$	$3 \times 10^{14}$	$3 \times 10^{18}$
	$10^{-19}$	$10^{-11}$	10	$10^4$	$10^8$
Type of spectroscopy:	NMR	ESR	Microwave	Infrared	Visible and ultraviolet
					X-ray
					g-ray

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$b = 10 \text{ mm}$

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$dP \propto N \cdot P$  (# of absorbing particles) · P (# of photons)

$dV = S \cdot db$ ;  $dV [=] \text{cm}^2 \cdot \text{cm} [=] \text{cm}^3$

$N = C \left( \frac{\text{mol}}{\text{L}} \right) \cdot 6,023 \cdot 10^{23} \frac{\text{atoms}}{\text{mol}} \cdot dV (\text{L}) \cdot 10^{-3} = \frac{6,023 \cdot 10^{20}}{C} \cdot S \cdot db \cdot C$

$dP = \text{const} \cdot N \cdot P = \underbrace{\text{const} \cdot K'}_K \cdot db \cdot C \cdot P = K \cdot db \cdot C \cdot P$

$dP = -K \cdot db \cdot C \cdot P$ ;  $\frac{dP}{P} = -K \cdot C \cdot db$

$\int_{P_0}^P \frac{dP}{P} = -K \cdot C \int_0^b db$ ;  $\ln \frac{P}{P_0} = -K \cdot C \cdot b$

$-\log \frac{P}{P_0} = \frac{K}{2,303} \cdot b \cdot C$      $-\log \frac{P}{P_0} = -\log T = \text{Abs}$

**Abs = a · b · C** Beer's law

$\left. \begin{matrix} b [=] \text{cm} \\ c [=] \text{mol/L} \end{matrix} \right\} a = \epsilon, \text{ molar absorptivity}; \epsilon [=] \text{L mol}^{-1} \text{cm}^{-1}$

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**Absorbancies are always additive**

Beer's law applies to a medium containing more than one kind of absorbing substance. Provided there is no interaction among the various species, the total absorbance for a multicomponent system is given by:

$$A_{\text{total}} = A_1 + A_2 + \dots + A_n$$

$$= \epsilon_1 b c_1 + \epsilon_2 b c_2 + \dots + \epsilon_n b c_n$$

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

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$\lambda'$ :  $A' = \epsilon_M' b[M] + \epsilon_N' b[N]$

$\lambda''$ :  $A'' = \epsilon_M'' b[M] + \epsilon_N'' b[N]$

FIGURE mixture. Absorption spectrum of a two-component

The two components behave **independently** of one another.

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

$\lambda$ (nm)	$\epsilon$ (L mol <sup>-1</sup> cm <sup>-1</sup> )	
	X	Y
272	16440	3870
327	3990	6420

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.**

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$$\text{Abs}^{745} = \epsilon_{\text{Cu}^{2+}}^{745} [\text{Cu}^{2+}] + \epsilon_{\text{Bi}^{3+}}^{745} [\text{Bi}^{3+}] + \epsilon_{\text{CuY}^{2-}}^{745} [\text{CuY}^{2-}] + \epsilon_{\text{BiY}^-}^{745} [\text{BiY}^-] + \epsilon_{\text{Y}^{4-}}^{745} [\text{Y}^{4-}]$$

Photometric titration curve of 100 mL of a solution that was  $2.0 \times 10^{-3} \text{ M}$  in  $\text{Bi}^{3+}$  and  $\text{Cu}^{2+}$ . Wavelength: 745 nm.

