



# CHM211 – Analytical Chemistry I Review

## Lesson III – Volumetric Analysis

# Volumetric Analysis

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Titrimetry includes a group of analytical methods that are based on determining the quantity of a reagent of known concentration that is required to react completely with the analyte.

**Standard solution:** is a reagent of exactly known concentration that is used in a titrimetric analysis.

**Titration:** is a process in which a standard reagent is added to a solution of an analyte until the reaction between the analyte and reagent is judged to be complete.

**Back-titration:** is a process in which the excess of a standard solution used to consume an analyte is determined by titration with a second standard solution. Back-titrations are often required when the rate of reaction between the analyte and reagent is slow or when the standard solution lacks stability.

**The equivalence point:** in a titration is a 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 point in a titration when a physical change occurs that is associated with the condition of chemical equivalence.

The difference in volume or mass between the equivalence point and the end point is the ***titration error***.

$$E_t = V_{ep} - V_{eq}$$

### **A primary standard:**

is an ultra pure compound that serves as the reference material for a titrimetric method of analysis.

### **Important requirement**

1. High purity. Established methods for confirming purity should be available.
2. Atmospheric stability.
3. Absence of hydrate water so that the composition of the solid does not change with variations in humidity.
4. Modest cost.
5. Reasonable solubility in the titration medium.
6. Reasonably large molar mass so that the relative error associated with weighing the standard is minimized.

## Examples of Primary Standards

- **Primary standards for standardization of NaOH**

**Potassium acid phthalate (KHP)**

- **Primary standards for standardization of HCl**

**Sodium carbonate (pure!)**

# Secondary Standards

- Few materials meet all of the primary standard requirements
- Instead a secondary standard that is standardized with a primary standard!

### **A secondary standard:**

- is a compound whose purity has been established by chemical analysis and that serves as the reference material for a titrimetric method of analysis.
- The ideal standard solution for a titrimetric method will
  1. be sufficiently stable so that it is necessary to determine its concentration only once;
  2. react rapidly with the analyte so that the time required between additions of reagent is minimized;
  3. react more or less completely with the analyte so that satisfactory end points are realized; and
  4. undergo a selective reaction with the analyte that can be described by a balanced equation.

# **Standardization**

**is a process in which the concentration of a secondary standard is determined to a high level of accuracy by titration with a primary standard.**

# Volumetric Calculations

All the Examples from 13-2 to 13-9 are required

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## EXAMPLE 13-2

A standard 0.0100 M solution of  $\text{Na}^+$  is required to calibrate a flame photometric method to determine the element. Describe how 500 mL of this solution can be prepared from primary standard  $\text{Na}_2\text{CO}_3$  (105.99 g/mol).

We wish to compute the mass of reagent required to give a species molarity of 0.0100. Here, we will use millimoles, since the volume is in milliliters.

$$\begin{aligned}\text{amount Na}_2\text{CO}_3 &= 500 \text{ mL} \times \frac{0.0100 \text{ mmol Na}^+}{\text{mL}} \times \frac{1 \text{ mmol Na}_2\text{CO}_3}{2 \text{ mmol Na}^+} \\ &= 2.50 \text{ mmol}\end{aligned}$$

From the definition of millimole, we write

$$\text{mass Na}_2\text{CO}_3 = 2.50 \text{ mmol Na}_2\text{CO}_3 \times 0.10599 \frac{\text{g Na}_2\text{CO}_3}{\text{mmol Na}_2\text{CO}_3} = 0.265 \text{ g}$$

The solution is therefore prepared by dissolving 0.265 g of  $\text{Na}_2\text{CO}_3$  in water and diluting to 500 mL.

## Example 7-13

A 0.8040-g sample of an iron ore is dissolved in acid. The iron is then reduced to  $\text{Fe}^{2+}$  and titrated with 47.22 mL of 0.02242 M  $\text{KMnO}_4$  solution. Calculate the results of this analysis in terms of (a) % Fe (55.847 g/mol) and (b) %  $\text{Fe}_3\text{O}_4$  (231.54 g/mol). The reaction of the analyte with the reagent is described by the equation



(a) stoichiometric ratio =  $\frac{5 \text{ mmol Fe}^{2+}}{1 \text{ mmol KMnO}_4}$

$$\text{amount KMnO}_4 = 47.22 \text{ mL KMnO}_4 \times \frac{0.02242 \text{ mmol KMnO}_4}{\text{mL KMnO}_4}$$

$$\text{amount Fe}^{2+} = (47.22 \times 0.02242) \text{ mmol KMnO}_4 \times \frac{5 \text{ mmol Fe}^{2+}}{1 \text{ mmol KMnO}_4}$$

The mass  $\text{Fe}^{2+}$  is then given by

$$\begin{aligned} \text{mass Fe}^{2+} &= (47.22 \times 0.02242 \times 5) \text{ mmol Fe}^{2+} \\ &\quad \times 0.055847 \frac{\text{g Fe}^{2+}}{\text{mmol Fe}^{2+}} \end{aligned}$$

The percent  $\text{Fe}^{2+}$  is

Fe (w/w)

$$= \frac{W_{\text{Fe}}}{W_{\text{sample}}} \times 100\%$$

**Moles = CV**

$$\frac{\text{Mole}_{\text{Fe}^{2+}}}{C_{\text{KMnO}_4} \times V_{\text{KMnO}_4}} = \frac{5}{1}$$

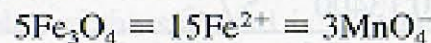
$$\% \text{Fe}^{2+} = \frac{(47.22 \times 0.02242 \times 5 \times 0.055847) \text{ g Fe}^{2+}}{0.8040 \text{ g sample}} \times 100\%$$

$$= 36.77\%$$

(b) In order to derive a stoichiometric ratio, we note that



Therefore,



and

$$\text{stoichiometric ratio} = \frac{5 \text{ mmol Fe}_3\text{O}_4}{3 \text{ mmol KMnO}_4}$$

As in part (a),

$$\text{amount KMnO}_4 = 47.22 \text{ mL KMnO}_4 \times 0.02242 \text{ mmol KMnO}_4/\text{mL KMnO}_4$$

$$\text{amount Fe}_3\text{O}_4 = (47.22 \times 0.02242) \text{ mmol KMnO}_4 \times \frac{5 \text{ mmol Fe}_3\text{O}_4}{3 \text{ mmol KMnO}_4}$$

$$\text{mass Fe}_3\text{O}_4 = (47.22 \times 0.02242 \times \frac{5}{3}) \text{ mmol Fe}_3\text{O}_4 \times 0.23154 \frac{\text{g Fe}_3\text{O}_4}{\text{mmol Fe}_3\text{O}_4}$$

$$\% \text{Fe}_3\text{O}_4 = \frac{(47.22 \times 0.02242 \times \frac{5}{3}) \times 0.23154 \text{ g Fe}_3\text{O}_4}{0.8040 \text{ g sample}} \times 100\%$$

$$= 50.81\%$$

Fe (w/w)

$$= \frac{W_{\text{Fe}}}{W_{\text{sample}}} \times 100\%$$

**Moles = CV**

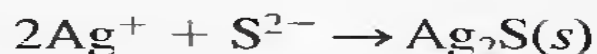
$$\frac{\text{Mole}_{\text{Fe}_3\text{O}_4}}{C_{\text{KMnO}_4} \times V_{\text{KMnO}_4}} = \frac{5}{3}$$

Fe (w/w)

$$= \frac{W_{\text{Fe}_3\text{O}_4}}{W_{\text{sample}}} \times 100\%$$

### EXAMPLE 13-7

A 100.0-mL sample of brackish water was made ammoniacal, and the sulfide it contained was titrated with 16.47 mL of 0.02310 M  $\text{AgNO}_3$ . The analytical reaction is



Calculate the concentration of  $\text{H}_2\text{S}$  in the water in parts per million.  
At the end point

$$\text{stoichiometric ratio} = \frac{1 \text{ mmol H}_2\text{S}}{2 \text{ mmol AgNO}_3}$$

$$\text{amount AgNO}_3 = 16.47 \text{ mL } \cancel{\text{AgNO}_3} \times 0.02310 \frac{\text{mmol AgNO}_3}{\cancel{\text{mL AgNO}_3}}$$

$$\text{amount H}_2\text{S} = (16.47 \times 0.02310) \cancel{\text{mmol AgNO}_3} \times \frac{1 \text{ mmol H}_2\text{S}}{2 \cancel{\text{mmol AgNO}_3}}$$

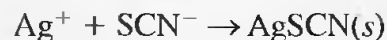
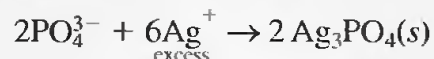
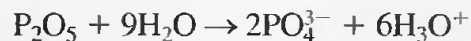
$$\begin{aligned} \text{mass H}_2\text{S} &= \left( 16.47 \times 0.02310 \times \frac{1}{2} \right) \cancel{\text{mmol H}_2\text{S}} \times 0.034802 \frac{\text{g H}_2\text{S}}{\cancel{\text{mmol H}_2\text{S}}} \\ &= 6.620 \times 10^{-3} \text{ g H}_2\text{S} \end{aligned}$$

$$\begin{aligned} \text{concd H}_2\text{S} &= \frac{6.620 \times 10^{-3} \text{ g H}_2\text{S}}{100.0 \cancel{\text{ mL sample}} \times 1.000 \text{ g sample}/\cancel{\text{ mL sample}}} \times 10^6 \text{ ppm} \\ &= 6.62 \text{ ppm H}_2\text{S} \end{aligned}$$

### EXAMPLE 13-8

The phosphorus in a 4.258-g sample of a plant food was converted to  $\text{PO}_4^{3-}$  and precipitated as  $\text{Ag}_3\text{PO}_4$  through the addition of 50.00 mL of 0.0820 M  $\text{AgNO}_3$ . The excess  $\text{AgNO}_3$  was back-titrated with 4.86 mL of 0.0625 M KSCN. Express the results of this analysis in terms of %  $\text{P}_2\text{O}_5$ .

The chemical reactions are



Thus, the stoichiometric ratios are

$$\frac{1 \text{ mmol P}_2\text{O}_5}{6 \text{ mmol AgNO}_3} \quad \text{and} \quad \frac{1 \text{ mmol KSCN}}{1 \text{ mmol AgNO}_3}$$

$$\text{total amount AgNO}_3 = 50.00 \text{ mL} \times 0.0820 \frac{\text{mmol AgNO}_3}{\text{mL}} = 4.100$$

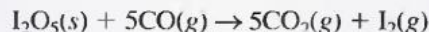
$$\begin{aligned} \text{amount AgNO}_3 \text{ consumed by KSCN} &= 4.06 \text{ mL} \times 0.0625 \frac{\text{mmol KSCN}}{\text{mL}} \\ &\quad \times \frac{1 \text{ mmol AgNO}_3}{1 \text{ mmol KSCN}} \\ &= 0.2538 \text{ mmol} \end{aligned}$$

$$\begin{aligned} \text{amount P}_2\text{O}_5 &= (4.100 - 0.254) \text{ mmol AgNO}_3 \times \frac{1 \text{ mmol P}_2\text{O}_5}{6 \text{ mmol AgNO}_3} \\ &= 0.6410 \text{ mmol P}_2\text{O}_5 \end{aligned}$$

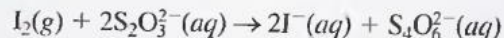
$$\% \text{ P}_2\text{O}_5 = \frac{0.6410 \text{ mmol} \times \frac{0.1419 \text{ g P}_2\text{O}_5}{\text{mmol}}}{4.258 \text{ g sample}} \times 100\% = 2.14\%$$

**EXAMPLE 13-9**

The CO in a 20.3-L sample of gas was converted to CO<sub>2</sub> by passing the gas over iodine pentoxide heated to 150°C:



The iodine was distilled at this temperature and was collected in an absorber containing 8.25 mL of 0.01101 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.



The excess Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> was back-titrated with 2.16 mL of 0.00947 M I<sub>2</sub> solution. Calculate the concentration in milligrams of CO (28.01 g/mol) per liter of sample.

Based on the two reactions, the stoichiometric ratios are

$$\frac{5 \text{ mmol CO}}{1 \text{ mmol I}_2} \quad \text{and} \quad \frac{2 \text{ mmol Na}_2\text{S}_2\text{O}_3}{1 \text{ mmol I}_2}$$

We divide the first ratio by the second to get a third useful ratio:

$$\frac{5 \text{ mmol CO}}{2 \text{ mmol Na}_2\text{S}_2\text{O}_3}$$

This relationship reveals that 5 mmol of CO are responsible for the consumption of 2 mmol of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. The total amount of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> is

$$\begin{aligned} \text{amount Na}_2\text{S}_2\text{O}_3 &= 8.25 \text{ mL Na}_2\text{S}_2\text{O}_3 \times 0.01101 \frac{\text{mmol Na}_2\text{S}_2\text{O}_3}{\text{mL Na}_2\text{S}_2\text{O}_3} \\ &= 0.09083 \text{ mmol Na}_2\text{S}_2\text{O}_3 \end{aligned}$$

The amount of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> consumed in the back-titration is

$$\begin{aligned} \text{amount Na}_2\text{S}_2\text{O}_3 &= 2.16 \text{ mL I}_2 \times 0.00947 \frac{\text{mmol I}_2}{\text{mL I}_2} \times \frac{2 \text{ mmol Na}_2\text{S}_2\text{O}_3}{1 \text{ mmol I}_2} \\ &= 0.04091 \text{ mmol Na}_2\text{S}_2\text{O}_3 \end{aligned}$$

The number of millimoles of CO can then be obtained by using the third stoichiometric ratio:

$$\begin{aligned} \text{amount CO} &= (0.09083 - 0.04091) \text{ mmol Na}_2\text{S}_2\text{O}_3 \times \frac{5 \text{ mmol CO}}{2 \text{ mmol Na}_2\text{S}_2\text{O}_3} \\ &= 0.1248 \text{ mmol CO} \end{aligned}$$

$$\text{mass CO} = 0.1248 \text{ mmol CO} \times \frac{28.01 \text{ mg CO}}{\text{mmol CO}} = 3.4956 \text{ mg}$$

$$\frac{\text{mass CO}}{\text{vol sample}} = \frac{3.4956 \text{ mg CO}}{20.3 \text{ L sample}} = 0.172 \frac{\text{mg CO}}{\text{L sample}}$$

# GRAVIMETRIC TITRIMETRY

## *Weight or gravimetric titrimetry*

Differs from the volumetric titrimetry in that the mass of titrant is measured rather than the volume. Thus, in a weight titration, a balance and a weighable solution dispenser are substituted for a buret and its markings. Weight titrimetry actually predates volumetric titrimetry by 50 years tedious and time consuming.

# TITRATION CURVES IN TITRIMETRIC METHODS

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an end point is an observable physical change that occurs near the equivalence point of a titration. The two most widely used end

points involve

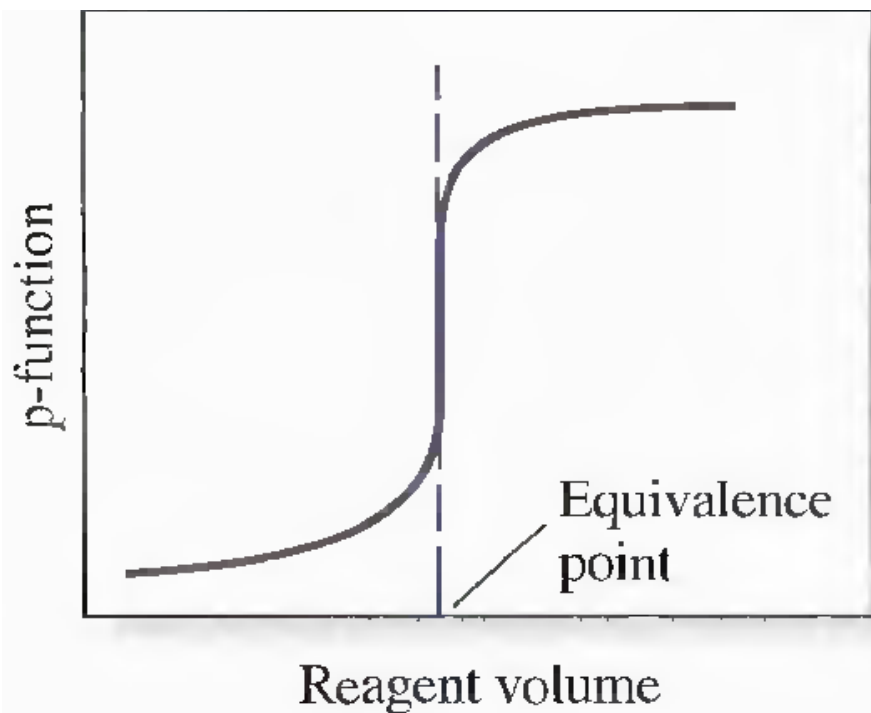
(1) changes in color due to the reagent, the analyte, or an indicator

(2) a change in potential of an electrode that responds to the concentration of the reagent or the analyte.

Titration curves are plots of a concentration-related variable as a function of reagent volume.

### Types of Titration Curves

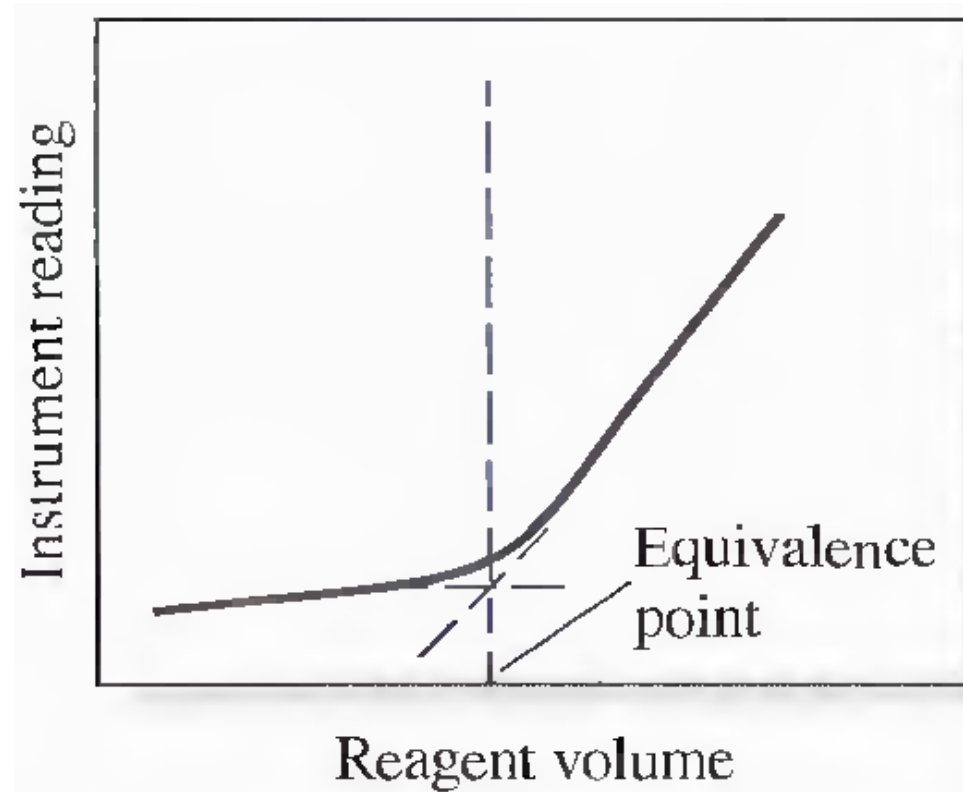
**A sigmoidal curve:** the p-function of analyte (or sometimes the reagent) is plotted as a function of reagent volume. observations are confined to a small region (typically 0.5 mL) surrounding the equivalence point.



(a) Sigmoidal curve

linear segment curve,

The vertical axis of a linear-segment titration curve is an instrument signal that is proportional to the concentration of the analyte or reagent.



(b) Linear-segment curve

# PRECIPITATION TITRIMETRY

- based on reactions that yield ionic compounds of limited solubility, is one of the oldest analytical techniques,
- There are only a few precipitating agents that can be used in titrimetry.
- most important precipitating reagent is silver nitrate, which is used for the determination of the halides, the halide-like anions ( $\text{SCN}^-$ ,  $\text{CN}^-$ ,  $\text{CNO}^-$ ) fatty acids, and several divalent and trivalent inorganic anions.
- Titrimetric methods based on silver nitrate are sometimes called argentometric methods.

## Precipitation Titration Curves Involving Silver Ion

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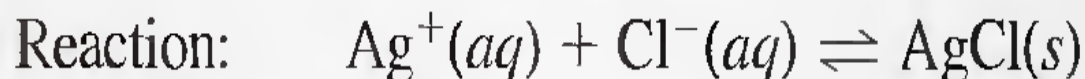
A titration curve for this method usually consists of a plot of  $pAg$  versus the volume of silver nitrate added.

To construct titration curves, three types of calculations are required:

- (1) preequivalence
- (2) equivalence.
- (3) postequivalence.

## EXAMPLE 13-10

Perform calculations needed to generate a titration curve for 50.00 mL of 0.0500 M NaCl with 0.1000 M AgNO<sub>3</sub> (for AgCl,  $K_{sp} = 1.82 \times 10^{-10}$ ).



### (1) Preequivalence-Point Data

Here the molar analytical concentration  $c_{\text{NaCl}}$  is readily computed. For example, when 10.00 mL of AgNO<sub>3</sub> has been added,

$$c_{\text{NaCl}} = \frac{\text{original number of mmol NaCl} - \text{no. mmol AgNO}_3 \text{ added}}{\text{total volume solution}}$$

$$\text{original number of mmol NaCl} = 50.00 \text{ mL} \times 0.0500 \frac{\text{mmol NaCl}}{\text{mL}} = 2.500$$

$$\text{number of mmol AgNO}_3 \text{ added} = 10.00 \text{ mL} \times 0.1000 \frac{\text{mmol AgNO}_3}{\text{mL}} = 1.000$$

$$\text{no. mmol NaCl remaining} = 1.500$$

$$c_{\text{NaCl}} = \frac{1.500 \text{ mmol NaCl}}{(50.00 + 10.00) \text{ mL}} = 0.02500 \frac{\text{mmol NaCl}}{\text{mL}} = 0.02500 \text{ M}$$

$$[\text{Cl}^-] = 0.02500 \text{ M}$$

$$[\text{Ag}^+] = K_{\text{sp}}/[\text{Cl}^-] = \frac{1.82 \times 10^{-10}}{0.02500} = 7.28 \times 10^{-9} \text{ M}$$

$$\text{pAg} = -\log (7.28 \times 10^{-9}) = 8.14$$

Additional points defining the curve in the preequivalence-point region are obtained in the same way. Results of calculations of this kind are shown in the second column of Table 13-2.

## (2) Equivalence Point pAg

Here,

$$[\text{Ag}^+] = [\text{Cl}^-] \quad \text{and} \quad [\text{Ag}^+][\text{Cl}^-] = 1.82 \times 10^{-10} = [\text{Ag}^+]^2$$

$$[\text{Ag}^+] = 1.349 \times 10^{-5} \text{ M} \quad \text{and} \quad \text{pAg} = -\log (1.349 \times 10^{-5}) = 4.87$$

## (3) Postequivalence-Point Data

At 26.00 mL AgNO<sub>3</sub> added, Ag<sup>+</sup> is in excess, so

$$[\text{Ag}^+] = c_{\text{AgNO}_3} = \frac{26.00 \times 0.1000 - 50.00 \times 0.0500}{50.00 - 26.00} = 1.316 \times 10^{-3} \text{ M}$$

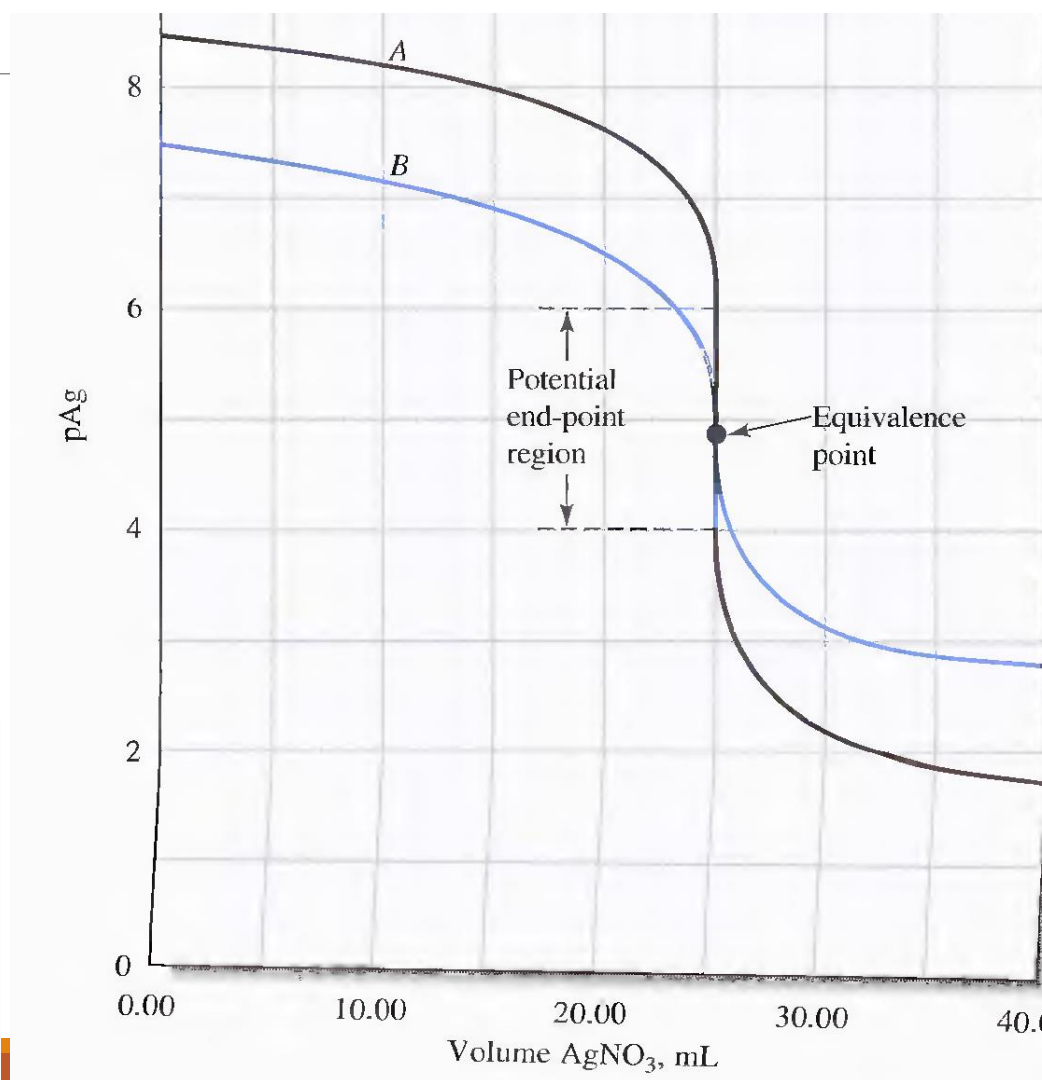
$$\text{pAg} = -\log (1.316 \times 10^{-3}) = 2.88$$

Additional postequivalence-point data are obtained in the same way and are shown in Table 13-2.

# The Effect of Concentration on Titration Curves

The higher the conc.  
of analyte and titrant the  
higher the  $pAg$  change  
at the equivalence  
point and the sharper  
the equivalence point

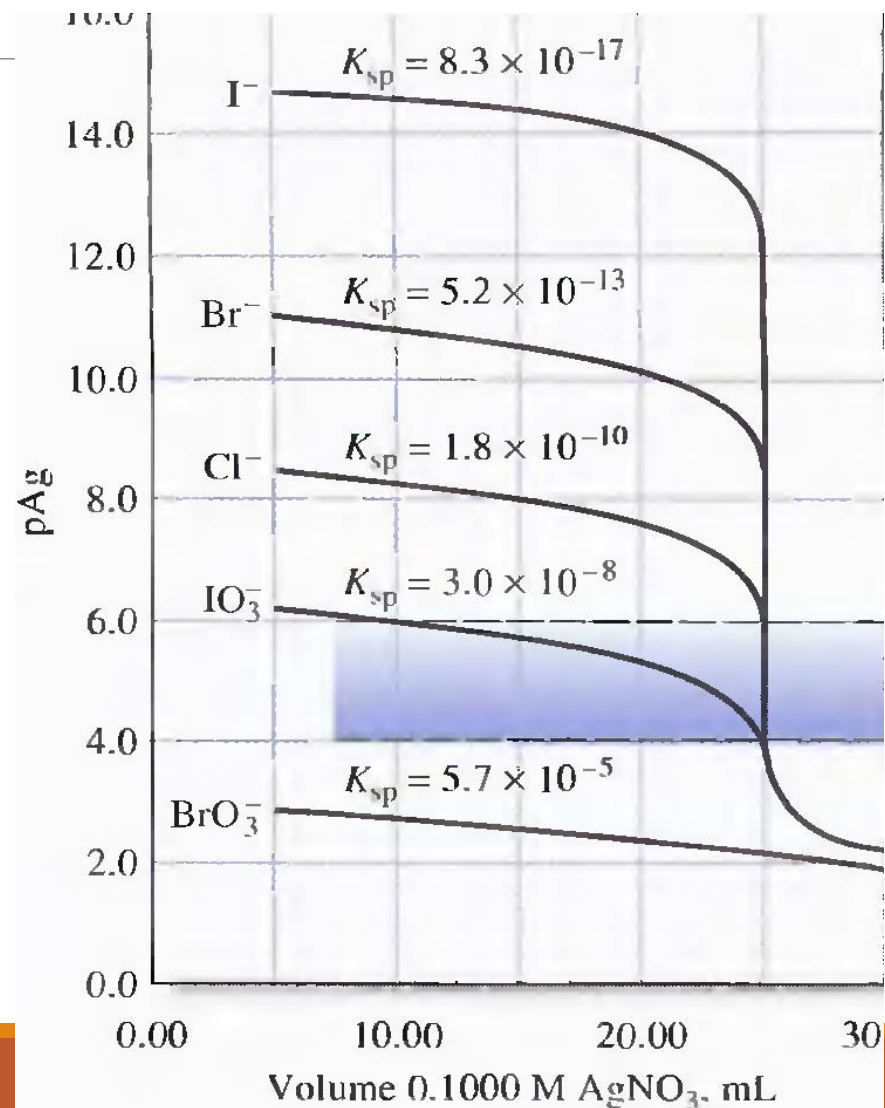
**Figure 13-4** Titration curve for A, 50.00 mL of 0.0500 M NaCl with 0.1000 M  $AgNO_3$ , and B, 50.00 mL of 0.00500 M NaCl with 0.0100 M  $AgNO_3$ .



# The Effect of Reaction Completeness on Titration Curves

The lower the solubility of the precipitate, the more the reaction completeness and thus higher the pAg change at the equivalence point and the sharper is the equivalence point

**Figure 13-5** Effect of reaction completeness on precipitation titration curves. For each curve, 50.00 mL of a 0.0500 M solution of the anion was titrated with 0.1000 M  $\text{AgNO}_3$ . Note that smaller values of  $K_{\text{sp}}$  give much sharper breaks at the end point.



# Titration Curves for Mixtures of Anions

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titration curves can be extended to mixtures that form precipitates of different solubilities.

consider the titration of 50.00 mL of a solution that is 0.0500 M in iodide ion and 0.0800 M in chloride ion with 0.1000 M silver nitrate. because silver chloride, with its much larger solubility product, does not begin to precipitate until well into the titration.

to determine how much iodide is precipitated before appreciable amounts of silver chloride form.

$$\frac{\cancel{[\text{Ag}^+]}[\text{I}^-]}{\cancel{[\text{Ag}^+]}[\text{Cl}^-]} = \frac{8.3 \times 10^{-17}}{1.82 \times 10^{-10}} = 4.56 \times 10^{-7}$$
$$[\text{I}^-] = (4.56 \times 10^{-7}) [\text{Cl}^-]$$

From this relation we see that the iodide concentration decreases to a tiny fraction of the chloride ion concentration before silver chloride begins to precipitate.

So silver chloride forms only after 25.00 mL of titrant have been added in this titration. At this point, the chloride ion concentration is approximately

$$c_{\text{Cl}} = [\text{Cl}^-] = \frac{50.00 \times 0.0800}{50.00 + 25.00} = 0.0533 \text{ M}$$

Substituting into the previous equation yields

$$[\text{I}^-] = 4.56 \times 10^{-7} \times 0.0533 = 2.43 \times 10^{-8} \text{ M}$$

The percentage of iodide unprecipitated at this point can be calculated as follows:

$$\text{no. mmol I}^- = (75.00 \text{ mL}) (2.43 \times 10^{-8} \text{ mmol I}^-/\text{mL}) = 1.82 \times 10^{-6}$$

$$\text{original no. mmol I}^- = (50.00 \text{ mL}) (0.0500 \text{ mmol/mL}) = 2.50$$

$$\text{I}^- \text{ unprecipitated} = \frac{1.82 \times 10^{-6}}{2.50} \times 100\% = 7.3 \times 10^{-5} \%$$

**As chloride ion begins to precipitate, the pAg is can be calculated from the solubility-product constant for silver chloride**

$$[\text{Ag}^+] = \frac{1.82 \times 10^{-10}}{0.0533} = 3.41 \times 10^{-9}$$

$$\text{pAg} = -\log (3.41 \times 10^{-9}) = 8.47$$

Further additions of silver nitrate decrease the chloride ion concentration, and the

curve then becomes that for the titration of chloride by itself.  
e.g. after 30.00 mL of titrant have been added,

$$c_{\text{Cl}} = [\text{Cl}^-] = \frac{50.00 \times 0.0800 + 50.00 \times 0.0500 - 30.00 \times 0.100}{50.00 + 30.00}$$

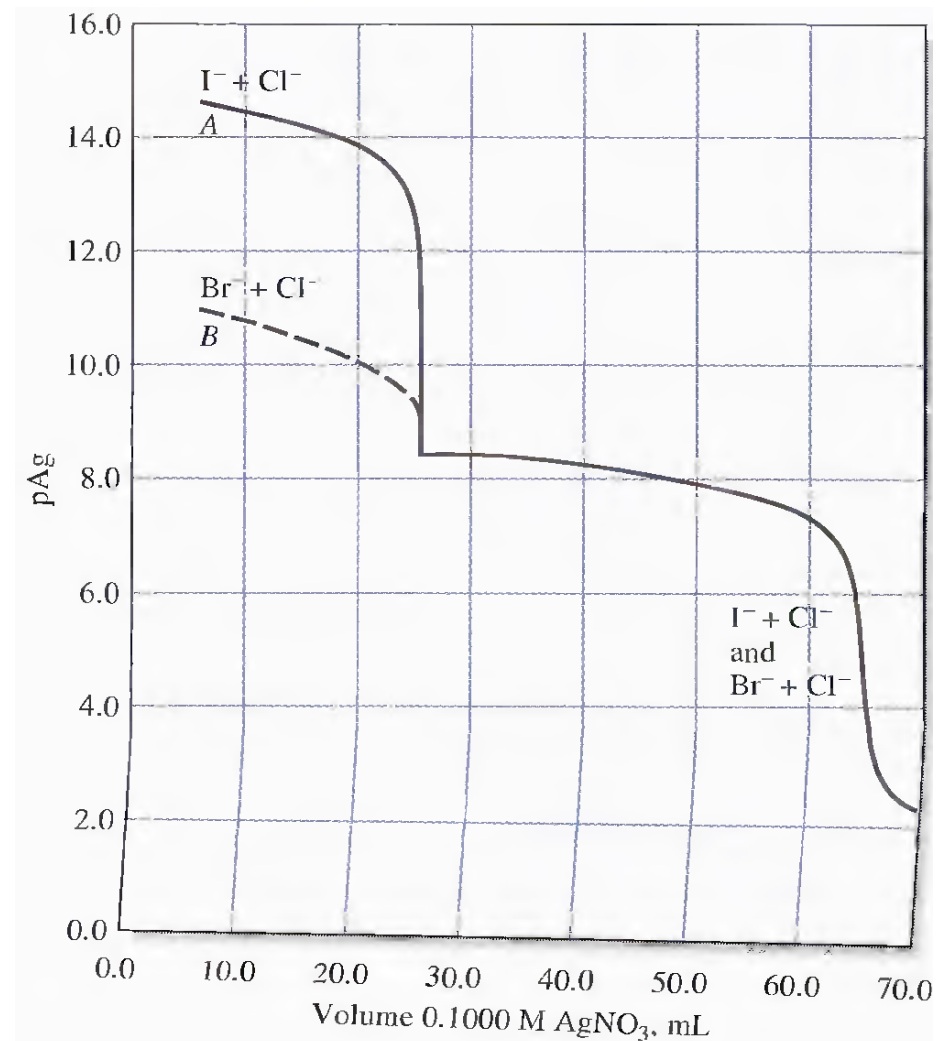
$$[\text{Cl}^-] = 0.0438 \text{ M}$$

$$[\text{Ag}^+] = \frac{1.82 \times 10^{-10}}{0.0438} = 4.16 \times 10^{-9}$$

$$\text{pAg} = 8.38$$

The remainder of the data points for this curve can be computed in the same way as for a curve of chloride by itself.

**Figure 13-6** Titration curves for 50.00 mL of a solution 0.0800 M in  $\text{Cl}^-$  and 0.0500 M in  $\text{I}^-$  or  $\text{Br}^-$ .



## Indicators for Argentometric Titrations

- (1) the color change should occur over a limited range in p-function of the reagent or the analyte and
- (2) the color change should take place within the steep portion of the titration curve for the analyte.

### The Mohr Method

Sodium chromate can serve as an indicator for the argentometric determination of chloride, bromide, and cyanide 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.

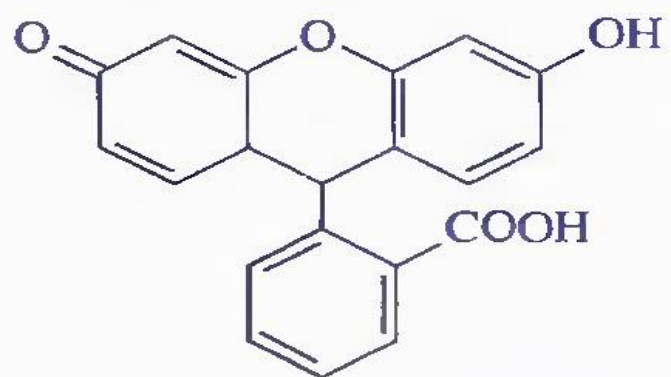
The Mohr titration must be carried out at a pH of 7 to 10 because chromate ion in more acidic solutions, is converted to chromic acid and the conc. of chromate ions will be too low to produce the precipitate near the equivalence point. Normally, a suitable pH is achieved by saturating the analyte  $\text{NaHCO}_3$

## Adsorption Indicators: The Fajans Method

An adsorption indicator is an organic compound that tends to be adsorbed on to the surface of the solid in a precipitation titration.

Ideally, the adsorption (or desorption) occurs near the equivalence point and results not only in a color change but also in a transfer of color from the solution to the solid (or the reverse).

Fluorescein is a typical adsorption indicator that is useful for the titration of chloride ion with silver nitrate. In aqueous solution, fluorescein partially dissociates into hydronium ions and negatively charged fluoresceinate ions that are yellow-green.



fluorescein



In the early stages of the titration of chloride ion with silver nitrate. the silver chloride particles are negatively charged because of adsorption of excess chloride ions . The dye anions are repelled from this surface and impart a yellow-green color to the solution.

Beyond the equivalence point. the silver chloride particles strongly adsorb silver ions and acquire a positive charge. Fluoresceinate anions are now attracted into the counter-ion layer that surrounds each colloidal silver chloride particle. The net result is the appearance of the red color of silver fluoresceinate change is an adsorption (not a precipitation) process,

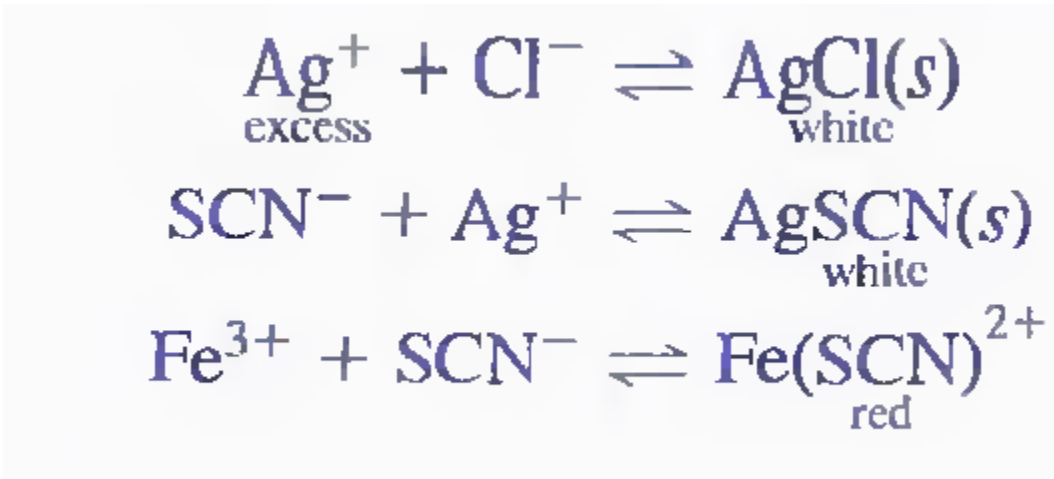
The adsorption is reversible, the dye being desorbed on back-titration with chloride ion.

Titration involving adsorption indicators are rapid, accurate, and reliable, but

**their application** is limited to the relatively few precipitation reactions in which a colloidal precipitate is formed rapidly.

# Iron(III) Ion; The Volhard Method

- A measured excess of standard silver nitrate solution is added to the sample, and the excess silver is determined by back-titration with a standard thiocyanate solution.
- Iron(III) serves as the indicator. The solution turns red with the first slight excess of thiocyanate ion:



The titration must be carried out in acidic solution to prevent precipitation of iron(III) as the hydrated oxide.

The strong acidic environment required for the Volhard procedure represents a distinct advantage over other titrimetric methods of halide analysis because such ions as carbonate, oxalate, and arsenate (which form slightly soluble silver salts in neutral media but not in acidic media) do not interfere.

# Applications of Standard Silver Nitrate Solutions

**TABLE 13-3**

## Typical Argentometric Precipitation Methods

| Substance Being Determined                                                                                                                                        | End Point                                                                        | Remarks                                                                                                                                                                                                      |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| $\text{AsO}_4^{3-}$ , $\text{Br}^-$ , $\text{I}^-$ , $\text{CNO}^-$ , $\text{SCN}^-$                                                                              | Volhard                                                                          | Removal of silver salt not required                                                                                                                                                                          |
| $\text{CO}_3^{2-}$ , $\text{CrO}_4^{2-}$ , $\text{CN}^-$ , $\text{Cl}^-$ , $\text{C}_2\text{O}_4^{2-}$ , $\text{PO}_4^{3-}$ , $\text{S}^{2-}$ , $\text{NCN}^{2-}$ | Volhard                                                                          | Removal of silver salt required before back-titration of excess $\text{Ag}^+$                                                                                                                                |
| $\text{BH}_4^-$                                                                                                                                                   | Modified Volhard                                                                 | Titration of excess $\text{Ag}^+$ following<br>$\text{BH}_4^- + 8\text{Ag}^+ + 8\text{OH}^- \rightarrow 8\text{Ag}(s) + \text{H}_2\text{BO}_3^- + 5\text{H}_2\text{O}$                                       |
| Epoxide                                                                                                                                                           | Volhard                                                                          | Titration of excess $\text{Cl}^-$ following hydrohalogenation                                                                                                                                                |
| $\text{K}^+$                                                                                                                                                      | Modified Volhard                                                                 | Precipitation of $\text{K}^+$ with known excess of $\text{B}(\text{C}_6\text{H}_5)_4^-$ , addition of excess $\text{Ag}^+$ giving $\text{AgB}(\text{C}_6\text{H}_5)_4(s)$ , and back-titration of the excess |
| $\text{Br}^-$ , $\text{Cl}^-$                                                                                                                                     | $2\text{Ag}^+ + \text{CrO}_4^{2-} \rightarrow \text{Ag}_2\text{CrO}_4(s)$<br>red | In neutral solution                                                                                                                                                                                          |
| $\text{Br}^-$ , $\text{Cl}^-$ , $\text{I}^-$ , $\text{SeO}_3^{2-}$                                                                                                | Adsorption indicator                                                             |                                                                                                                                                                                                              |
| $\text{V}(\text{OH})_4^+$ , fatty acids, mercaptans                                                                                                               | Electroanalytical                                                                | Direct titration with $\text{Ag}^+$                                                                                                                                                                          |
| $\text{Zn}^{2+}$                                                                                                                                                  | Modified Volhard                                                                 | Precipitation as $\text{ZnHg}(\text{SCN})_4$ , filtration, dissolution in acid addition of excess $\text{Ag}^+$ , back-titration of excess $\text{Ag}^+$                                                     |
| $\text{F}^-$                                                                                                                                                      | Modified Volhard                                                                 | Precipitation as $\text{PbClF}$ , filtration, dissolution in acid, addition of excess $\text{Ag}^+$ , back-titration of excess $\text{Ag}^+$                                                                 |

# 1. Essence and classification of methods redox titration.

---

**Redox titration** – this is titration in which titrant is substance with oxidation-reduction properties

**oxidimetry** – is titration in which titrant is oxidizer

**Reducimetry** – is titration in which titrant is reducer

# Classification of methods precipitation titration (on nature of titrant):

---

Permanganatometry

Dichromatometry

iodometry

iodimetry

Iodatometry

Chloriodimetry

Bromatometry

Bromometry

Nitritometry

Cerimetry

Ascorbinometry

Titanometry

Chromometry

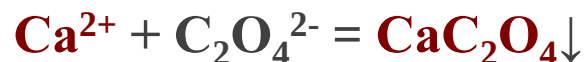
# Types of reactions which are accompanied by oxidation-reduction:

---

**Determinate substance** (for example, Fe (II) ions to Fe (III) ions):

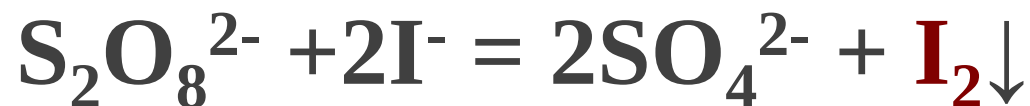


**Reagents**, which react with determinate substance stoichiometric (for example,  $\text{C}_2\text{O}_4^{2-}$  ions react with  $\text{Ca}^{2+}$  ions with formation of precipitate of  $\text{CaC}_2\text{O}_4$ ):



Substances which are formed in the process of interaction of acidic persulphate solutions with potassium iodide:

---



Ions which give certain value pH medium in which redox-reactions quantitatively pass:



**iodine** (which forms) is titated by **sodium thiosulphate**.

# Requirements to reactions in redoxometry:

the titration reaction must occur rapidly (on speed influences EMF,  $C_{\text{ox}}$ ,  $C_{\text{red}}$ , temperature, the nature of substances, catalyst, medium).

all reactions involving the titrant and analyte must be of known stoichiometry, quantitatively and to and.

Reaction must pass проходить irreversibly.

a suitable method must be available for determining the end point with an acceptable level of accuracy.

Titration should not **be** accompanied by collateral reactions which deform the results of the analysis.

# DIRECT REDOXOMETRY

---

## Application conditions:

Reactions should be specific

Reaction involving the titrant and analyte must be of known stoichiometry, quantitatively

The titration reaction must occur rapidly ( $EMF \geq 0,4 \text{ B}$ )

Equilibrium constant must be high enough

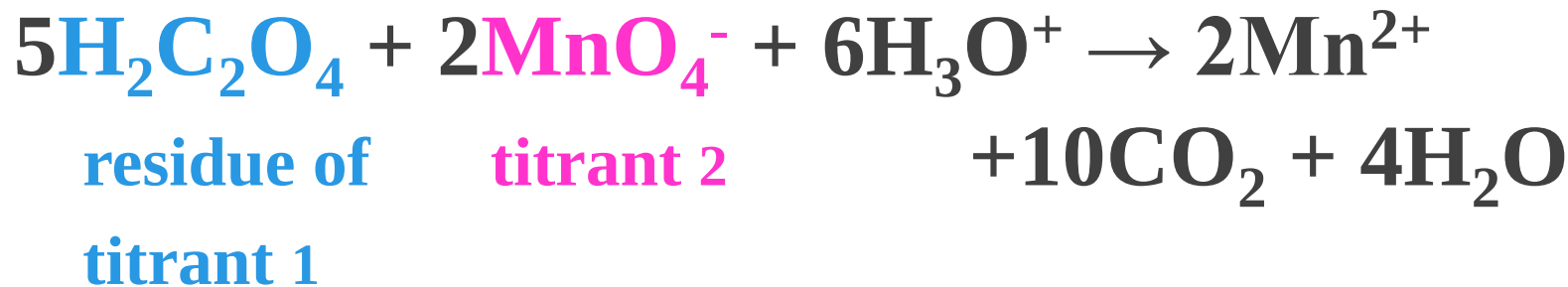
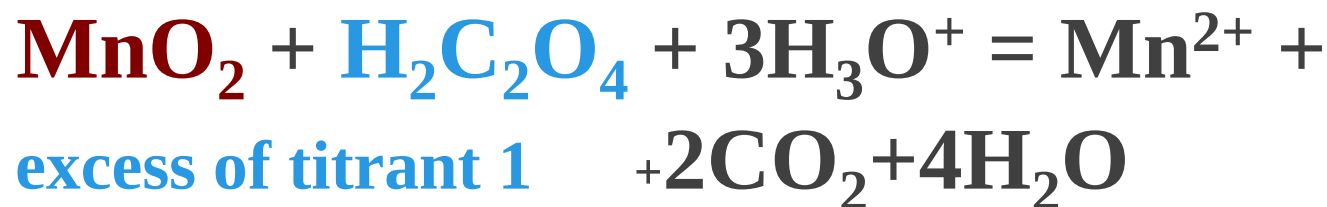
A suitable method must be available for determining the end point with an acceptable level of accuracy

# BACK REDOXOMETRY

---

Application conditions:

the titration reaction is too slow



# DISPLACEMENT REDOXOMETRY

---

## Application conditions:

Analyte doesn't react with titrant

reaction involving the titrant and analyte mustn't be of known stoichiometry, quantitatively



analyte

*substituent*

Iodine (**substituent**) is titrated by sodium thiosulphate solution:



*substituent*    titrant

## 2. Titration Curves in redoxometry.

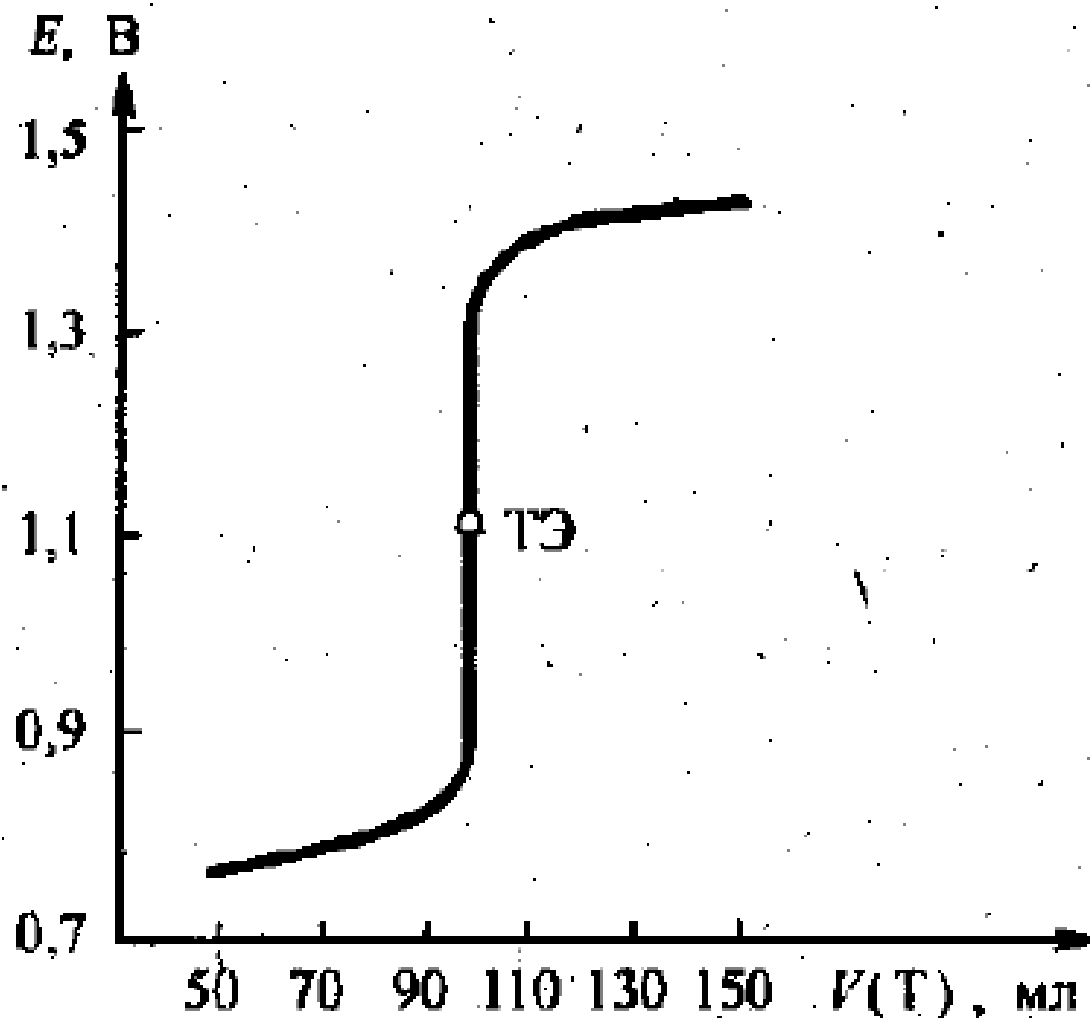
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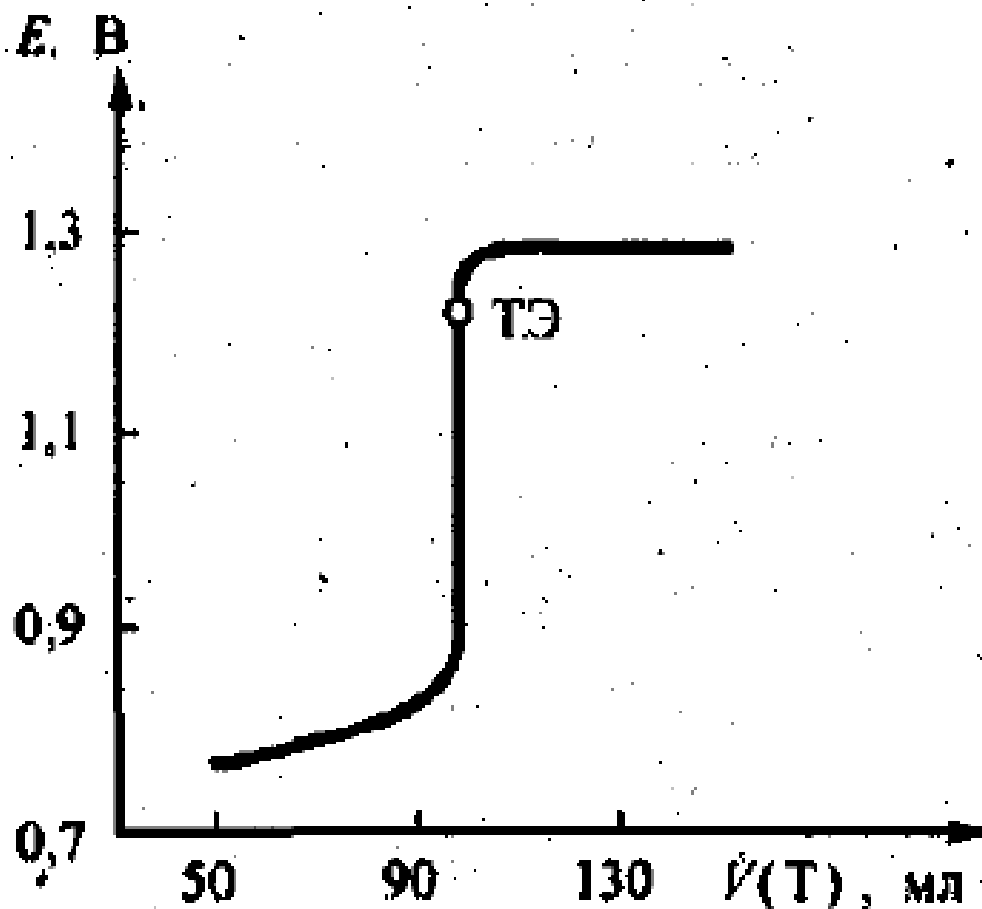
For each half-reaction are **Nernst equation** (at  $\mu=0$ ,  $f_{\pm}=1$ ):

$$E_1 = E_1^{\circ} + \frac{0,059}{n_1} \lg \frac{[\text{Ox}_1]}{[\text{Red}_1]},$$

Titration curves are plotted in **coordinates** – **electrode potential of system** (**E**, V) – **titrant volume** (**V**, mL) or **level of titration** (**f**).



Redox titration curve for 100.0 mL of  $\text{Fe}^{2+}$  with  $\text{Ce(IV)}$ .  $E$  — potential of solution,  $V(T)$  — volume of titrant;  $\text{TЭ}$  — equivalence point



Redox titration curve for 100.0 mL of  $\text{Fe}^{2+}$  with potassium dichromate.  $E$  – potential of solution,  $V(T)$  — volume of titrant;  $\text{TЭ}$  — equivalence point, Concentration of  $\text{H}^+$  ions equal 1 mol/L.

# The factors which define value of inflection points of titration on curves of redox titration

---

Nature of analyte and titrant (as more difference of their standard potentials, as more inflection point)

Value of pH medium (if  $H^+$  ions take part in oxidation-reduction reaction)

Inflection point presence on a titration curve can be used for exact fixing of equivalence point by means of indicators.

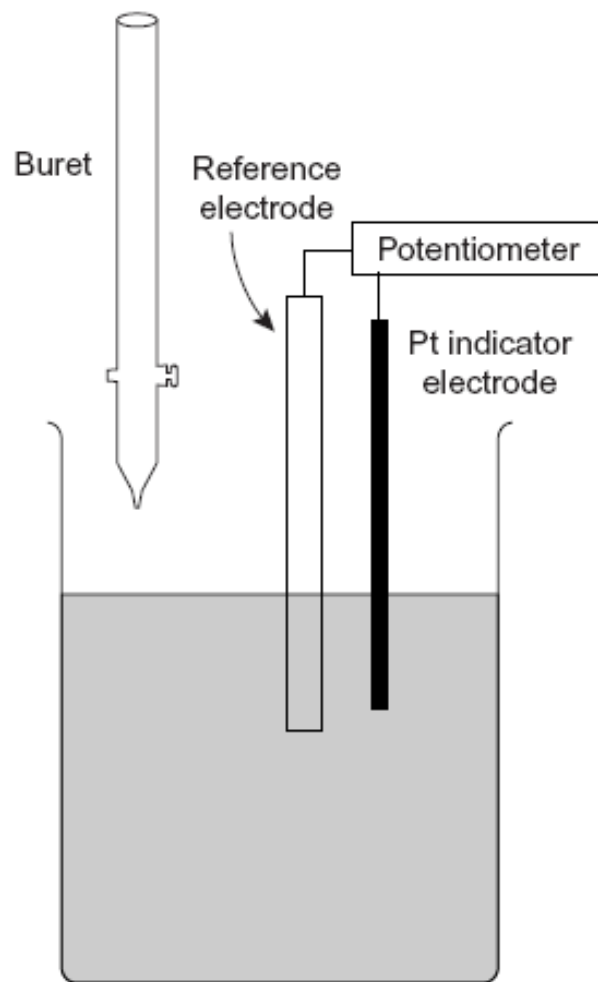
# The types of visual indicators are used to signal the end point in a redox titration:

---

**Titration without indicator**, if titrant has colour (when  $\text{MnO}_4^-$  is used as an oxidizing titrant, the solution remains colorless until the first drop of excess  $\text{MnO}_4^-$  is added)

**Titration with indicator**

**Physico-chemical methods** of equivalence point fixing (potentiometric, amperometric, voltamperometric)



Experimental arrangement for recording a potentiometric redox titration curve.

### 3. Indicators, which use in redoxometry.

---

**Specific indicator** (the completion of a reaction in which  $I_3^-$  is consumed (color change: blue to colorless); thiocyanate, which forms a soluble red-colored complex,  $Fe(SCN)^{2+}$ , with  $Fe^{3+}$ )

**Redox indicator** - a visual indicator used to signal the end point in a redox titration.

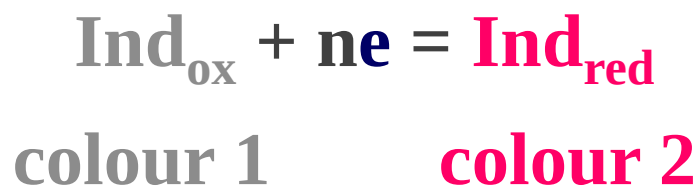
**External indicators** – iodostarchy paper in nitritometry

**The irreversible specific indicators** - methyl orange in bromatometry

# Redox-indicators

---

The most important class of redox indicators, however, are substances that do not participate in the redox titration, but whose oxidized and reduced forms differ in color. When added to a solution containing the analyte, the indicator imparts a color that depends on the solution's electrochemical potential. Since the indicator changes color in response to the electrochemical potential, and not to the presence or absence of a specific species, these compounds are called general **redox indicators**.



$$E = E^{\circ} + \frac{0,059}{n} \lg \frac{[\text{Ind}_{\text{ox}}]}{[\text{Ind}_{\text{red}}]},$$

where  $E^0$  – standard redox potentials.

If we assume that the indicator's color in solution changes from that of  $\text{Ind}_{\text{ox}}$  to that of  $\text{Ind}_{\text{red}}$  when the ratio  $[\text{Ind}_{\text{red}}]/[\text{Ind}_{\text{ox}}]$  changes from 0.1 to 10, then the end point occurs when the solution's electrochemical potential is within the range

$$pT = E^{\circ} \pm \frac{0,059}{n}.$$

(transformation range of indicator)

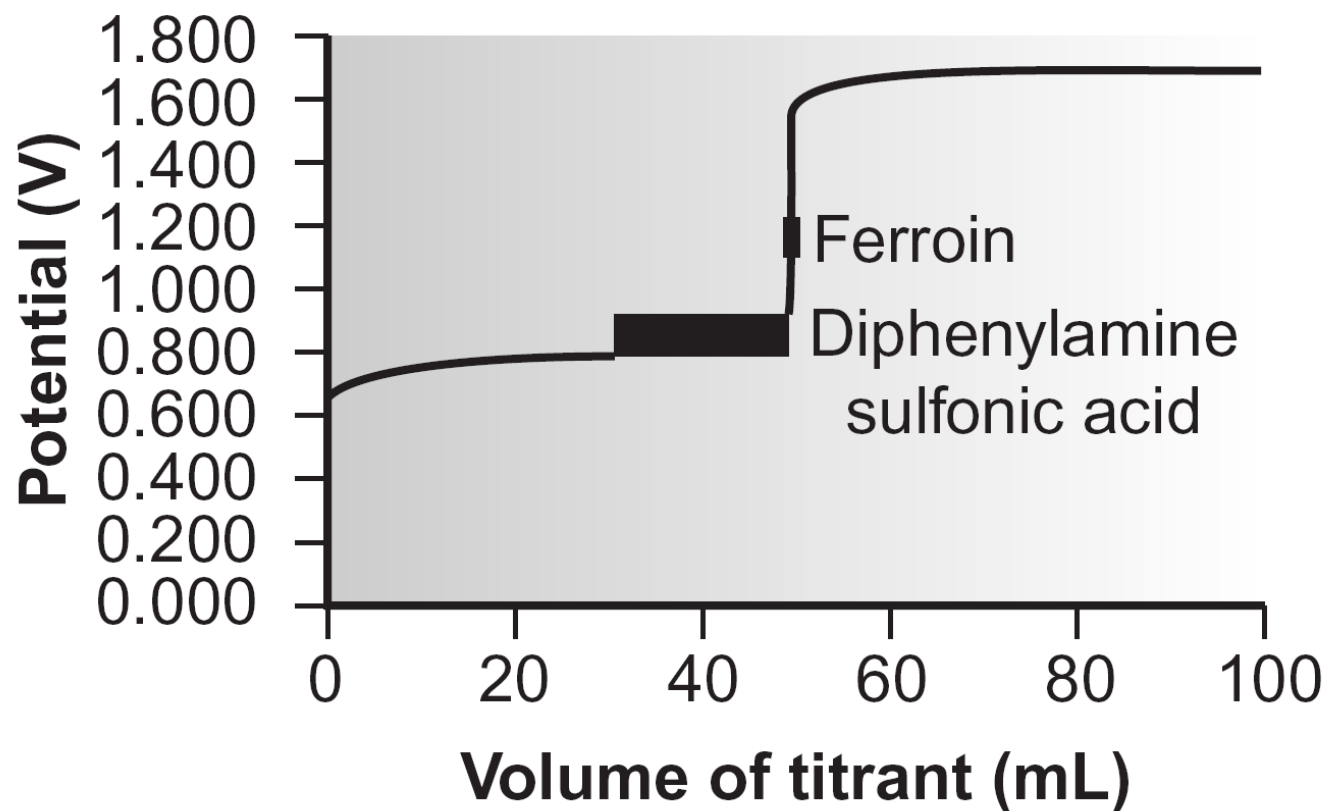
# Redox indicators

| <b>Indicator</b>                                    | <b>Colour of Ind<sub>ox</sub></b> | <b>Colour of Ind<sub>red</sub></b> | <b>E°, by [H<sup>+</sup>] = 1 mol/L, V</b> |
|-----------------------------------------------------|-----------------------------------|------------------------------------|--------------------------------------------|
| diphenylamine                                       | violet                            | colorless                          | + 0,76                                     |
| Phenylanthranilic acid                              | Red-violet                        | colorless                          | +1,08                                      |
| o-phenanthroline-Fe <sup>2+</sup> complex (ferroin) | pale blue                         | red                                | +1,06                                      |
| o,o'-diphenylaminodicarboxylic acid                 | Dark blue-violet                  | colorless                          | +1,26                                      |
| Diphenylaminazo-sulfonic acid                       | Red-violet                        | colorless                          | +0,84                                      |

# Rules of a redox indicator choice

---

*That colouring of the oxidation-reduction indicator changed at titration sharply and indicator error of titration was insignificant, the interval of the indicator transition should be in limits of inflection point (change of potential) on a titration curve*



Titration curve for 50.00 mL of 0.0500 M  $\text{Fe}^{2+}$  with 0.0500 M  $\text{Ce}^{4+}$  showing the range of  $E$  and volume of titrant over which the indicators ferroin and diphenylamine sulfonic acid are expected to change color

**ferroin is appropriate and diphenylamine sulfonic is inappropriate indicators**

## 4. Permanganatometry

---

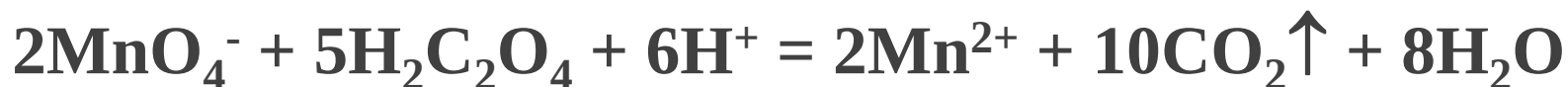
**Titrant:**  $\text{KMnO}_4$  – secondary standard solution



**Reaction of method:**



**Standardization:** on standard substances  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ,  
 $\text{Na}_2\text{C}_2\text{O}_4$ ,  $\text{As}_2\text{O}_3$ ,  $\text{KI}$ ,  $\text{Fe}$ ,  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ ,  
 $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$

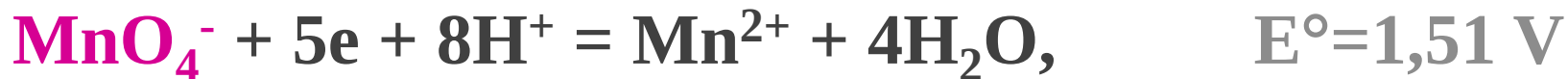


**Medium:** in presence of sulphatic acid

**Indicators:** without indicator (on occurrence of roze colour)

# Titration conditions:

In very acidic medium  $\text{pH} \ll 7$



In neutral medium:



In very basic medium:



Medium of titration must be very acidic.  $[\text{H}^+]$  ( $\text{H}_2\text{SO}_4$ ) = 1-2 mol/L. ( $\text{HNO}_3$ ,  $\text{HCl}$  – don't use)

Heating of solutions

Ware only glass (including buret without rubber shutter)

# Determinate substance in permanganatometry:

---

**reducers:**  $\text{H}_2\text{O}_2$ , Fe (metal.),  $\text{MgO}_2$ ,  $\text{NaNO}_2$ , carboxylic acids, compounds with hydrazo-groups  $\text{R}-\text{NH}-\text{NH}-\text{R}$ .

**oxidizers:**  $\text{Fe}^{3+}$ ,  $\text{Ce}^{\text{IV}}$ ,  $\text{MnO}_2$ ,  $\text{PbO}_2$ ,  $\text{NO}_3^-$ ,  $\text{BrO}_3^-$ ,  $\text{ClO}_3^-$ ,  $\text{S}_2\text{O}_3^{2-}$  и др.

# Advantages of permanganatometry

---

Titration without indicator

Possibility of use of a wide interval of pH

High value of  $E^\circ$

Cheap and accessible reagent

Possibility of definition of substances which haven't oxidation-reduction properties

# Lacks of permanganatometry

---

**secondary** standard solution

**instability** of standard solution

**It is impossible** titrate **at presence  $\text{Cl}^-$**  (for speed reduction of chloride-ion oxidation by titrant use mix Rhinegard - Cimmerman  $\text{H}_2\text{SO}_4 + \text{MnSO}_4 + \text{H}_3\text{PO}_4$ )

**Heating** is often **necessary**

**Strict keeping of the conditions** described in a technique

# 5. Dichromatometry

---

**Titrant:**  $\text{K}_2\text{Cr}_2\text{O}_7$  – primary standard solution; or  $\text{CrO}_3$  in  $\text{CH}_3\text{COOH}$  (concentrated)

**Reaction of method:**



**Medium:** acidic (sulphatic, chloridic or phosphatic)

## Indicators:

- **internal redox indicators:** diphenylamine, N-phenylanthranilic acid, diphenylamine sulphonatic acid
- **chemiluminescent** (siloxen)
- **external redox indicators:** leucomethylene blue

# Determinate substance:

**reducers** — direct titration:  $\text{Fe}^{2+}$ ,  $\text{SO}_3^{2-}$ ,  $\text{I}^-$ ,  $\text{AsO}_3^{3-}$ , ascorbic acid, glycerine,  $\text{CH}_3\text{OH}$

**oxidizers** — back-titration:  $\text{NO}_3^-$ ,  $\text{ClO}_3^-$ ,  $\text{MnO}_4^-$ , etc.

# Advantages of dichromatometry

$\text{K}_2\text{Cr}_2\text{O}_7$  – primary standard solution

The long-term stability of its solutions

May titrate at presence of  $\text{Cl}^-$  ions

$\text{Cr}_2\text{O}_7^{2-}$  - slowly react with organic substances, which may be in distilled water

Potassium dichromate is a relatively strong oxidizing agent and it may oxidize many organic substances

Titration is made without heating

The titration may use for determination of oxidizers and reduces

2- и 3-componental mixes may titrate at presence concentrated  $\text{H}_3\text{PO}_4$

# Lacks of dichromatometry

---

Potassium dichromate is weaker oxidizer, than  $\text{KMnO}_4$

Slow pass of reaction

Necessary to use indicators

Often back-titration, because low speed of reaction

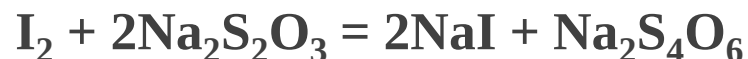
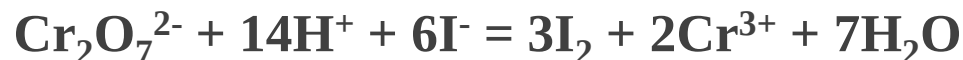
# 6. Iodometry

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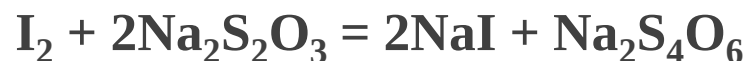
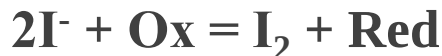
**Iodometry** – the method of oxidizers determination

**Titrant:**  $\text{Na}_2\text{S}_2\text{O}_3$  - secondary standard solution

**Standardization:** on primary standard solution of  $\text{KIO}_3$ ,  $\text{KBrO}_3$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$



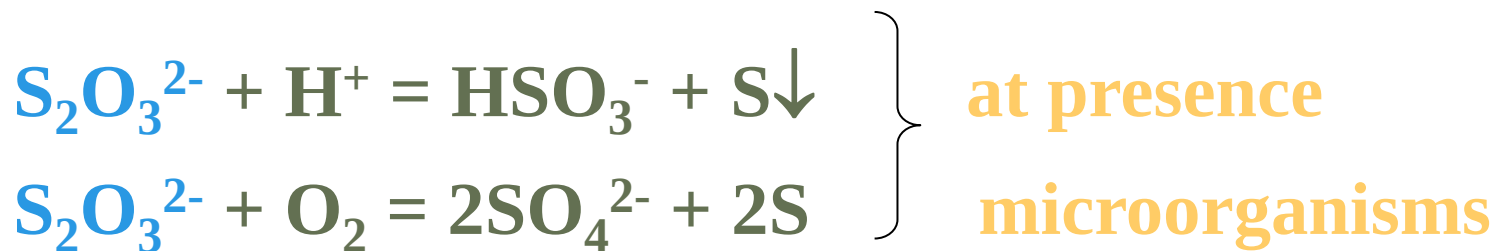
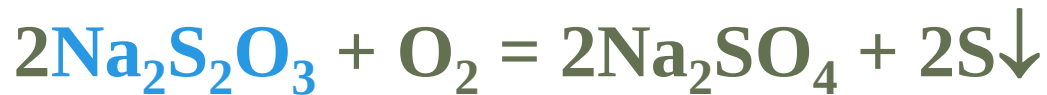
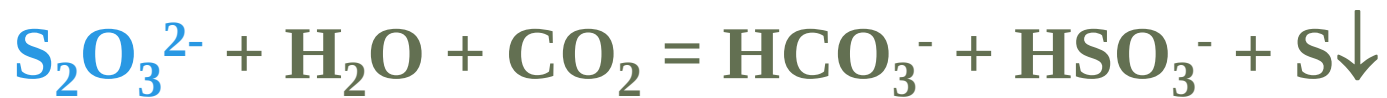
**Reaction of method:**



# Features of preparation sodium thiosulphate and starch

---

$\text{Na}_2\text{S}_2\text{O}_3 + \text{Na}_2\text{CO}_3$  – standardization in 1 day



- Decomposition by thiobacterias

**1% starch** is stabilised with the help **HgI<sub>2</sub>**

---

**Indicators:** 1 % starch solution (it is added in the end of titration, when colour of solution will be straw-yellow, the solution titrated to disappearance of dark blue colour)

**Determinate substance:** oxidizers -  $\text{H}_2\text{O}_2$ ,  $\text{Na}_2\text{O}_2$ ,  $\text{MgO}_2$ ,  $\text{BaO}_2$ ,  $\text{Cu(II)}$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{KMnO}_4$ ,  $\text{Na}_3\text{AsO}_4$ ,  $\text{I}_2$ .

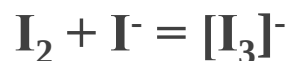
# 7. Iodimetry

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**Iodimetry** – this is method of reducers determination by direct titration iodine

**Titrant:**  $\text{I}_2$  – secondary standard solution

**Reaction of method:**

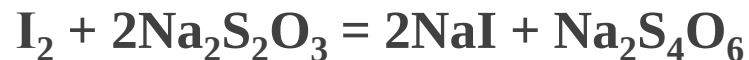


**On light**

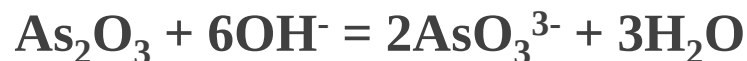


# Standardization:

---



on  $\text{As}_2\text{O}_3$ :



# Conditions iodimetric titration

---

Titration is made on a cold

Titration is made in the presence of substances which will link reaction products

**pH < 8**



# Indicators:

- ✓ **Without indicators** (in e.p. yellow colour of  $I_2$ , if it is extracted by  $CHCl_3$  or  $CCl_4$  - pale **rose-violet colour**)
- ✓ **1% starch** to occurrence **dark blue colour** (3 days it is suitable)

**Determinate substance:** reducers and water (Fisher),  $As(III)$ ,  $Na_2SO_3$ ,  $Hg_2Cl_2$ , Analginum, Antipyrinum, Acidum ascorbinicum, hydrazines, Isoniazidum, coffeine, methionine, sum of Penicillinum, K and Na salts of benzylpenicilinum,  $HCHO$ , etc.

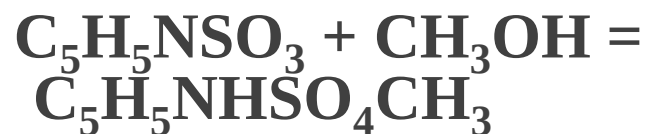
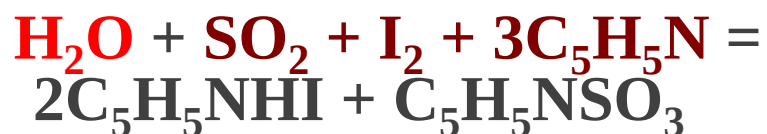


# Iodimetric determination of water on Fisher

**Fisher** reagent



Reaction of method:



Automatic waters titrator on  
Fisher by firm Mettler Toledo



# Advantages of iodimetry

---

It is used for definition of many substances

**The highest accuracy** among all oxidation-reduction methods

It is possible to titrate without indicator

Not water solutions of iodine are possible because it is well dissolved in organic solvents

# Lacks of iodimetry

---

volatility of standard solutions

Secondary standard solutions

It is impossible to titrate in very acidic and basic solutions

Special conditions because  $E^\circ$  is small and often reactions are reversible

Often we use back titration

Sometimes results are deformed through adsorption of iodine *on a precipitate surface*

Change of standard solution titre

The order of addition can't be changed

## 8. CHLORIODOMETRY

---

**Titrant:**  $\text{ICl}$  (solid substance, which it has red color and (melting point  $t = 27^\circ\text{C}$ )) – secondary standard solution



**Basic reaction of method:**

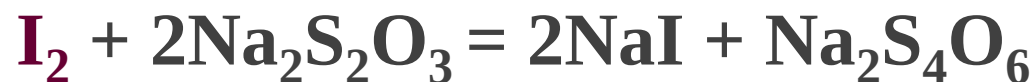
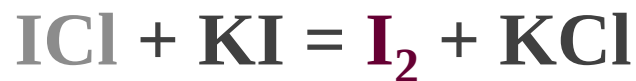


or



(1) equation + (3) equation = (2) equation

**Standardization:** on standard solution of  $\text{Na}_2\text{S}_2\text{O}_3$



**Methods of titration:** direct, back and indirect (displacement) titration

**Conditions of titration:** basic, neutral, weak basic medium

*In the strong basic medium:*



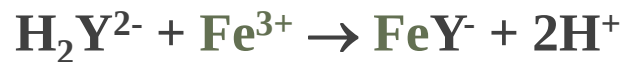
**Indicator:** 1) 1% starch solution ( $\text{ICl} + \text{KI} = \text{I}_2 + \text{KCl}$ )  
2) potentiometric method

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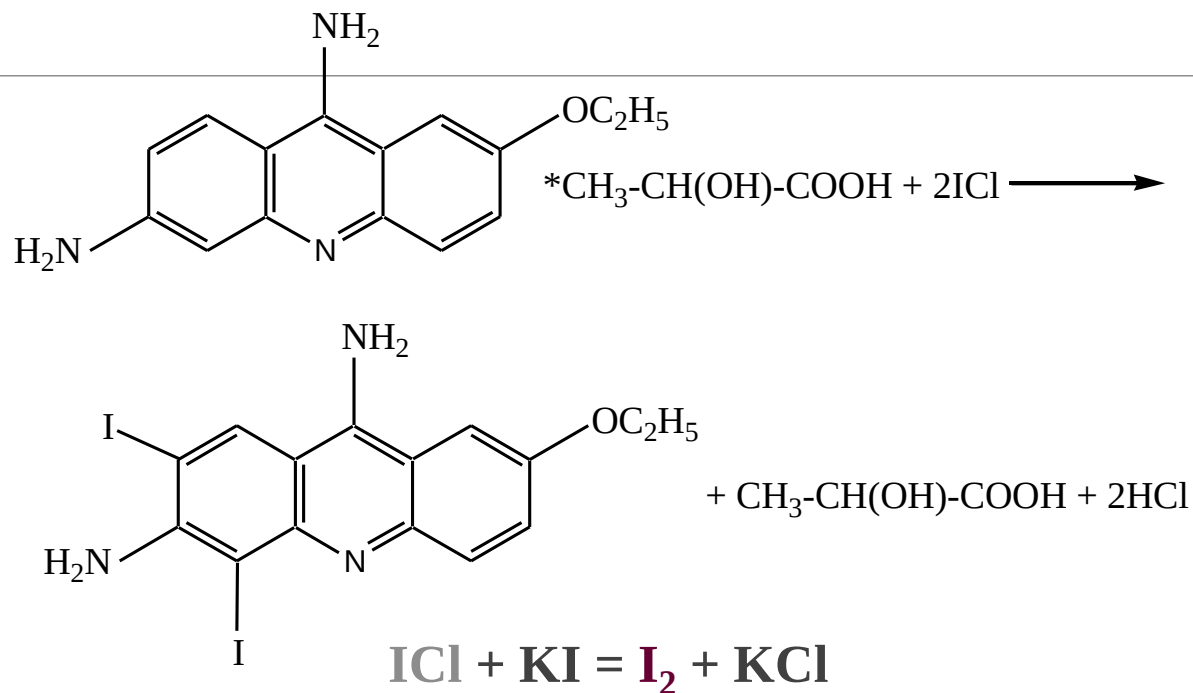
**Defined substances:** reducers – sulfanilamidum drugs, barbiturate, thio barbiturate, novocainum, rivanolum; salts of Hg(I), Sn(II), As(III), Sb(III), Fe(II), I<sup>-</sup>, SO<sub>3</sub><sup>2-</sup>, SCN<sup>-</sup>, ascorbic acid, hydrazine, hydroquinone, methionine.



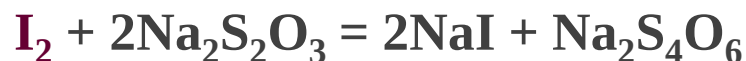
pH = 0,5 – 1,0 at the presence H<sub>2</sub>Y<sup>2-</sup> for linkage of Fe<sup>3+</sup>-ions:



# Back chloriodometric determination of Aethacridinum lactate



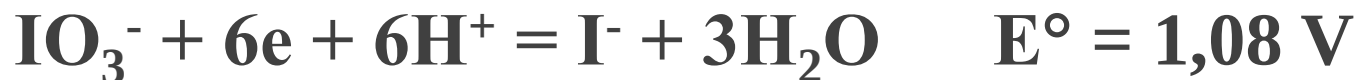
rest



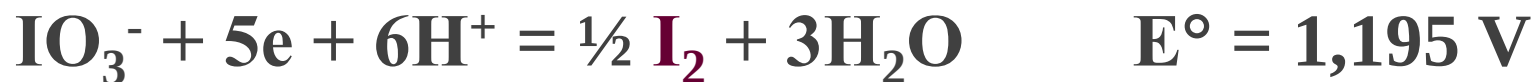
## 9. IODATOMETRY

**Titrant:**  $\text{KIO}_3$  – primary standard or secondary standard solution

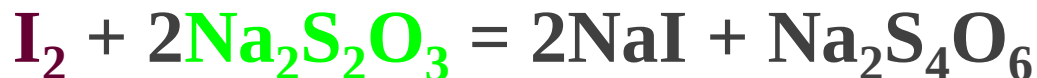
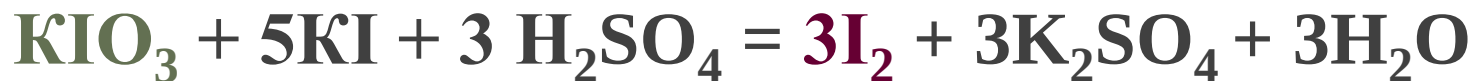
**Basic equation of method:**



Iodate-ion is capable to reduce in the acidic medium also to iodine:



**Standardization:** on standard solution of  $\text{Na}_2\text{S}_2\text{O}_3$



**Indicator:** 1) 1% starch solution

2) extraction by chloroform

# IODATOMETRY

## Defined substances:

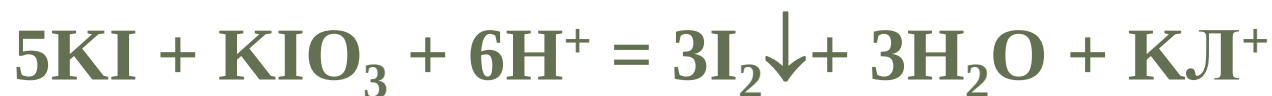
**In the direct titration** – reducers:  $\text{I}^-$ ,  $\text{SO}_3^{2-}$ ,  $\text{SCN}^-$ ,  
 $\text{S}_2\text{O}_3^{2-}$ ,  $\text{C}_6\text{H}_8\text{O}_6$

**In back titration** – oxidizers:  $\text{Sn(II)}$ ,  $\text{Sb(III)}$ ,  $\text{As(III)}$ .

## Determination of iodides:



## Determination of ascorbic acid:

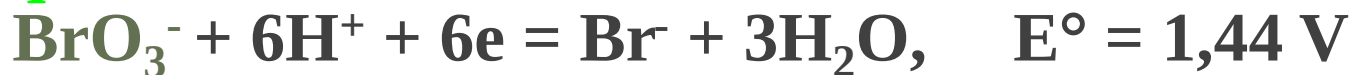


## 10. BROMATOMERTY

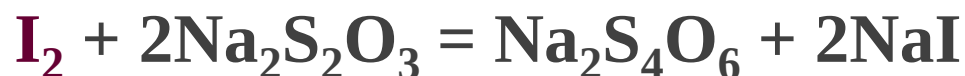
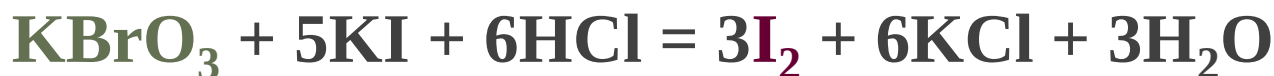
**Titrant:**  $\text{KBrO}_3$  – primary standard or secondary standard solution

---

**Basic equation of method:**



**Standardization:** iodometric method or on standard substance  $\text{As}_2\text{O}_3$ , or on standard solution of  $\text{Na}_2\text{S}_2\text{O}_3$ .



**Conditions of titration :**

Acidic medium ( $C_{\text{HCl}} > 1 \text{ mol/L}$ )

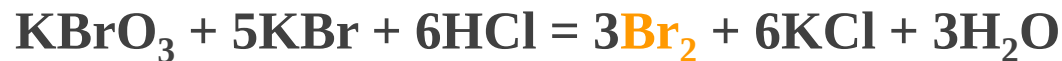
sometimes  $t \approx 70^\circ\text{C}$  (reaction speed is low)

sometimes use catalyst (for example,  $\text{Hg}^{2+}$  ions).

# BROMATOMETRY

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**Indicators:** methyl orange , methyl orange. Titrate in the cold!!!



**Defined substances:** Sn(II), As(III), Sb(III), Fe(II), H<sub>2</sub>O<sub>2</sub>, NO<sub>2</sub><sup>-</sup>, SCN<sup>-</sup>, As<sub>2</sub>O<sub>3</sub> (drugs, which are contained arsenic), hydrogen peroxide, nitrites, thiocyanides, hydrazines, hydroxylamine.

# BROMATOMERTY

## Advantage:

Not only for determination oxidizers and reducers but also many organic substances

KBrO<sub>3</sub> is primary standard solution and it is steady at storage

Ion [HgBr<sub>4</sub>]<sup>2-</sup> forms after eddyng of Hg<sup>2+</sup>, therefore a potential of system of BrO<sub>3</sub><sup>-</sup>/Br<sup>-</sup> increases.

## Disadvantage

Sometimes H<sub>2</sub>O, which forms in the reaction, interferes determination of many organic substances

Oxidization of some organic substances is accompanied by hydrolysis, displacement, addition.

A reaction can be not stoichiometrical.

# 11. BROMOMETRY

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**Titrant:**  $\text{Br}_2$ , which obtain in reaction between  $\text{KBrO}_3$  and  $\text{KBr}$  in acidic medium



**Basic equation of method:**



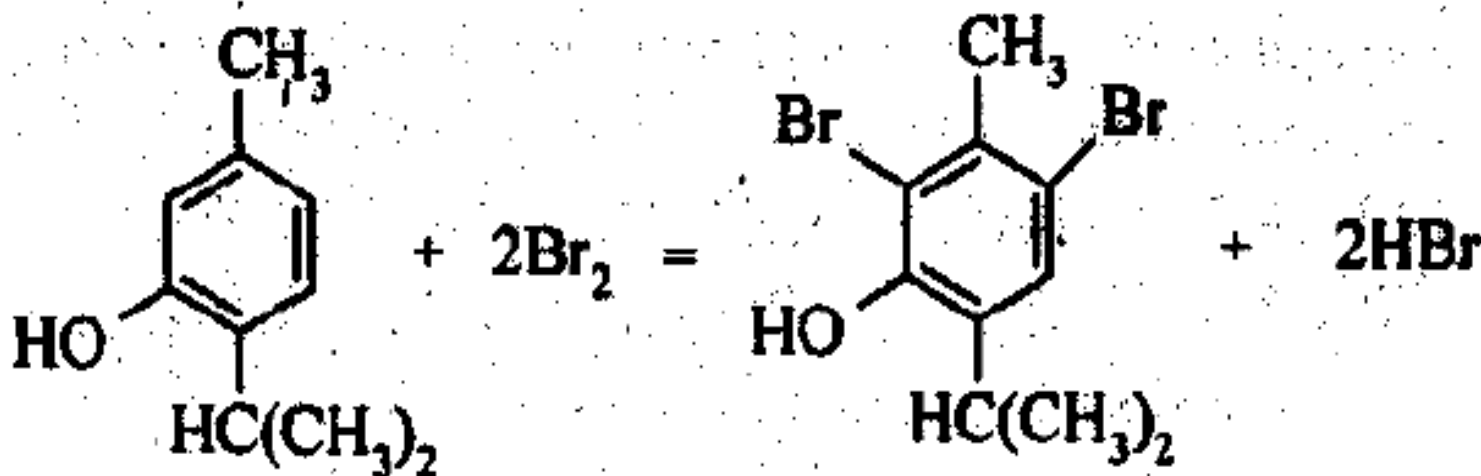
**Methods of determination:** direct titration, back titration, indirect (displacement) titration.

**Defined substances:** organic substances and drugs: isoniazidum, resorcinum, streptocidum, thymolum and others.

# BROMOMETRY

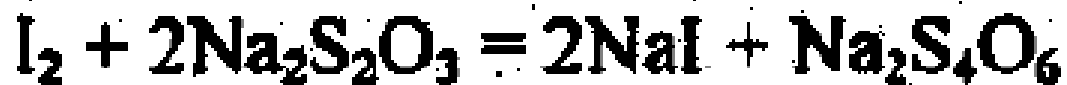
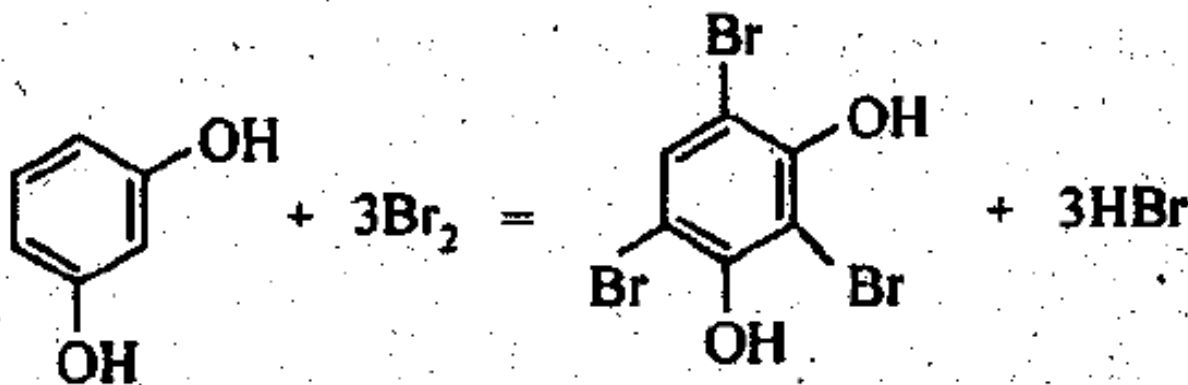
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## Direct determination of thymolum



# BROMOMETRY

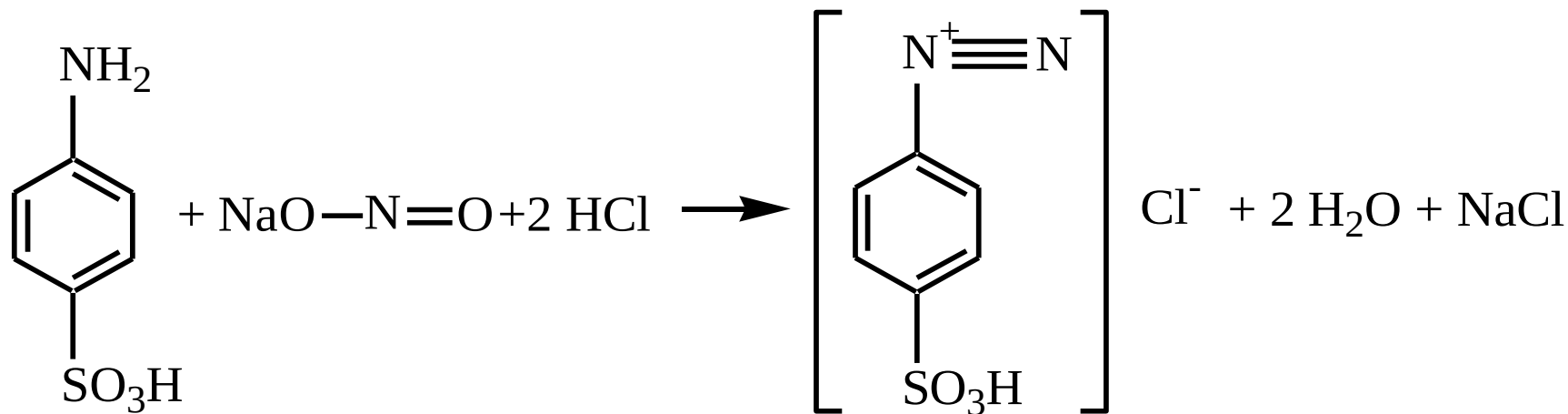
Indirect (displacement) titration of **resorcinum**



## 12. NITRITOMETRY

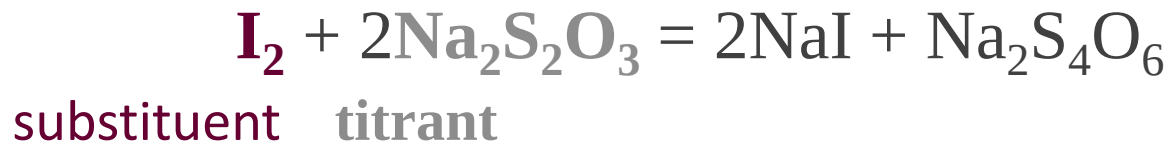
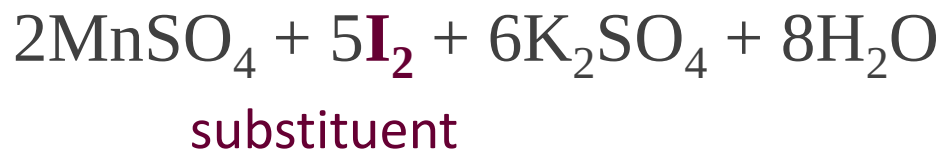
**Titrant:**  $\text{NaNO}_2$  - secondary standard solution

**Standardization:** on sulfanilic acid or potassium permanganate and others.



# Standardization sodium nitrite on potassium permanganate solution

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# NITRITOMETRY

The method is based on reaction which passes in the acidic medium:

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The majority of **nitritometric titrations** are based on:

**diazotization of primary amines:**



**formation of nitroso-compounds of secondary amines:**



# Conditions of nitritometric determinations:

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The **big excess** of **hydrochloric acid** (double).

Titration on a cold **0 - 10°C**.

**Catalyst** addition – crystal potassium bromide **KBr**.

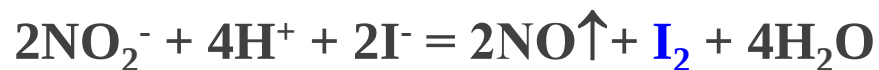
**Titration** to spend **very slowly** (1 drop for a minute near the end point).

Often it is impossible to use the internal indicator, but it gives advantage.

# Indicators of nitritometry:

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**External indicator**— iodine-starch paper



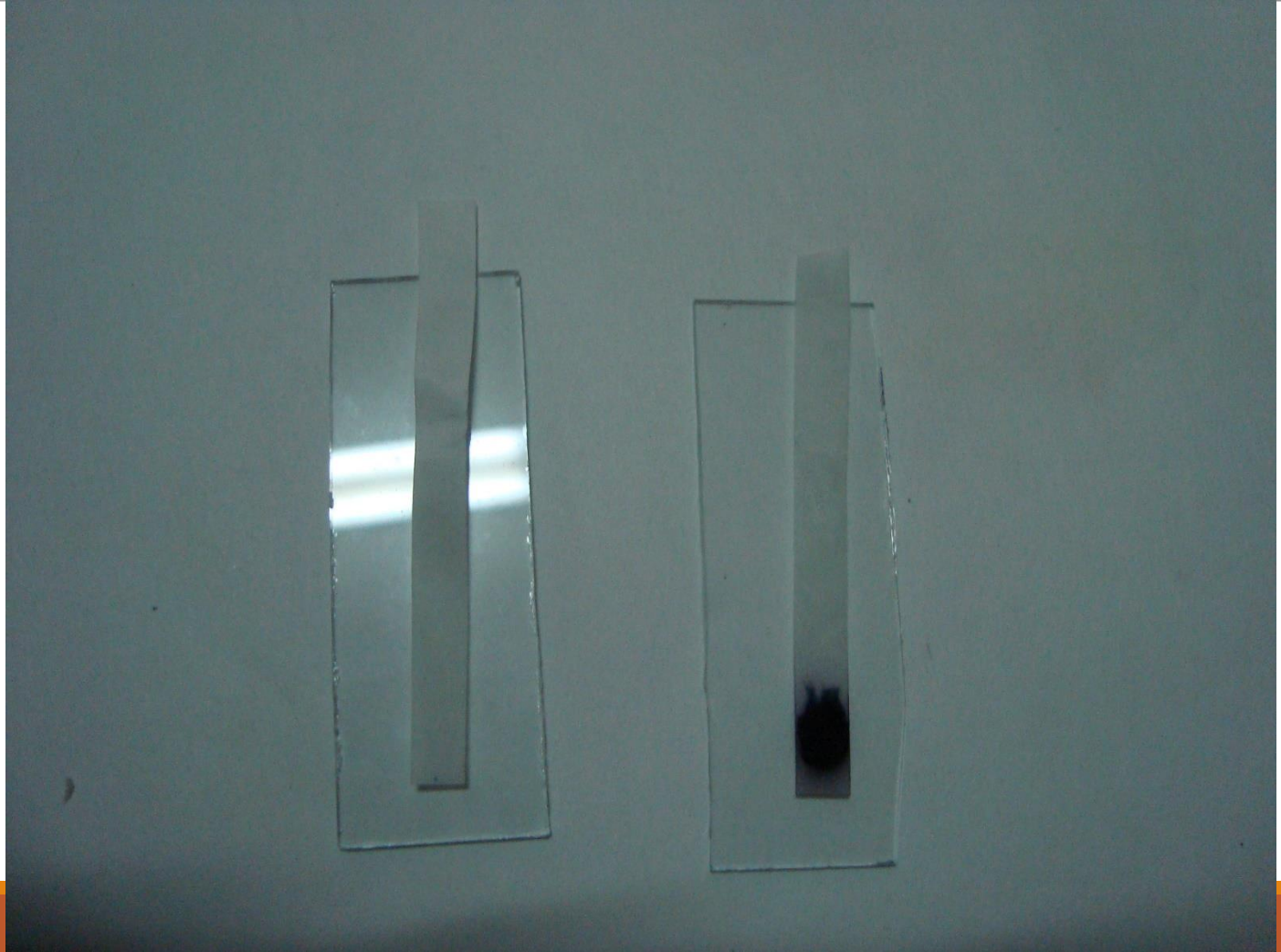
Free iodine with starch give blue color on the paper.

**Internal indicator:** diphenylamine, tropeolin-00, safranile.

Instrumental **methods** (potentiometry with platinic electrode)

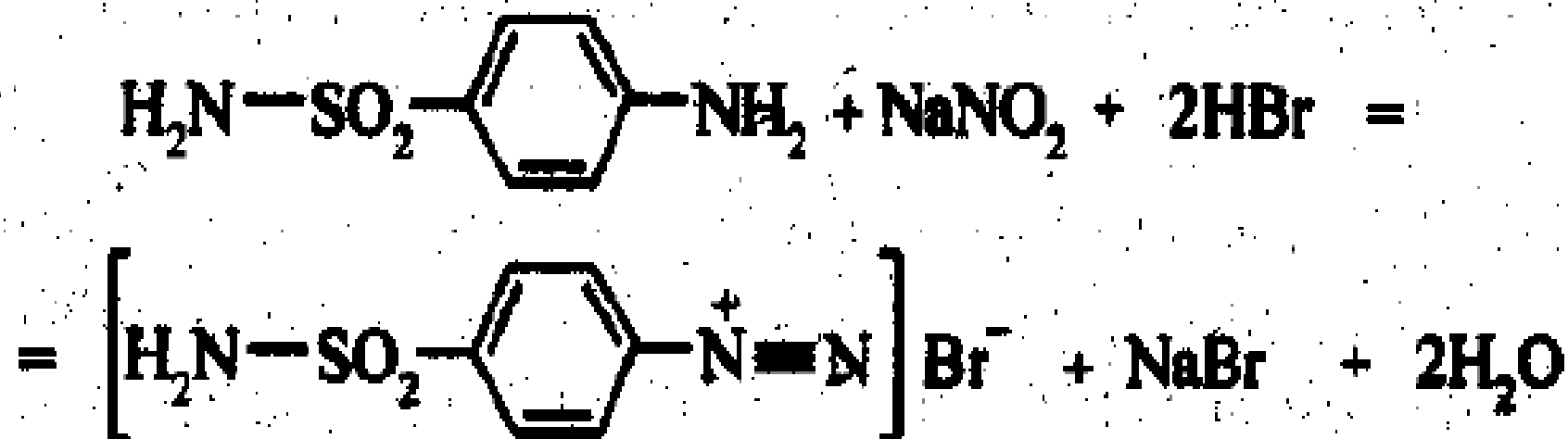
Using external indicator— iodine-starch paper  
to end-point after end-point

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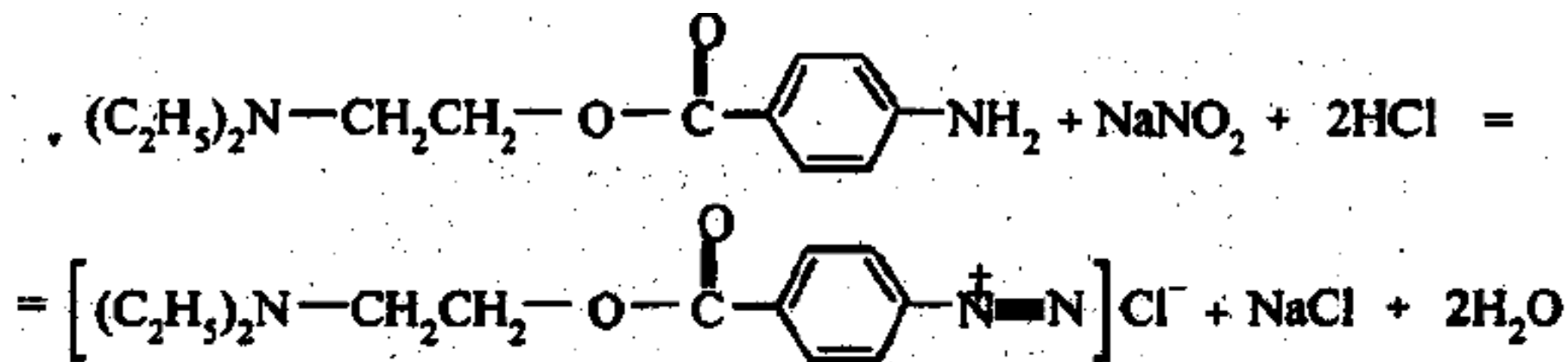
## Nitritometric determination of Streptocidum

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## Nitritometric determination of Novocainum

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# 13. Cerimetry

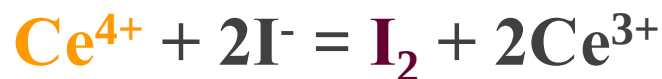
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**Basic equation of methods:**

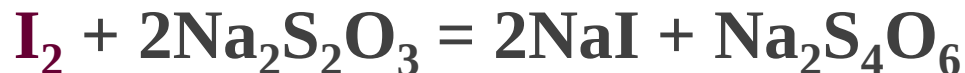


**Titrant:** secondary standard solution of  $\text{Ce}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$

**Standardization:** on standard solution of sodium thiosulfate



Defined titrant     substituent



Substituent     Standard titrant

# Indicators of cerimetry:

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## **Nonindicator method**

**Redox indicator:** ferroin, diphenylamine

sulfonic acid, ortho-phenantroline, diphenylamine

**Physico-chemical methods:** potentiometric, photometric, amperometric

# Advantages of cerimetry:

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Standard solution is stable in time.

Titration is possible at presence chloride ions.

Auxiliary products are not formed.

The dependence of real potential on reaction of medium and concentration of ligands allows to use this method for definition of different substances.

Is possibility use cerimetry in physico-chemical methods of the analysis.

# Lacks of cerimetry:

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Necessity of use of indicators

Possibility of complexing with  $F^-$  - ions ( $[CeF_6]^{2-}$ ) and of sedimentation with  $PO_4^{3-}(Ce_3(PO_4)_4^{4-})$

Sometimes at presence hydrochloric acids probably formation  $CeCl^{3+} \rightarrow CeCl^{2+} + Cl_2$

In hydrochloric medium solutions photochemical **reduction**  $Ce^{4+}$  to  $Ce^{3+}$  is observed

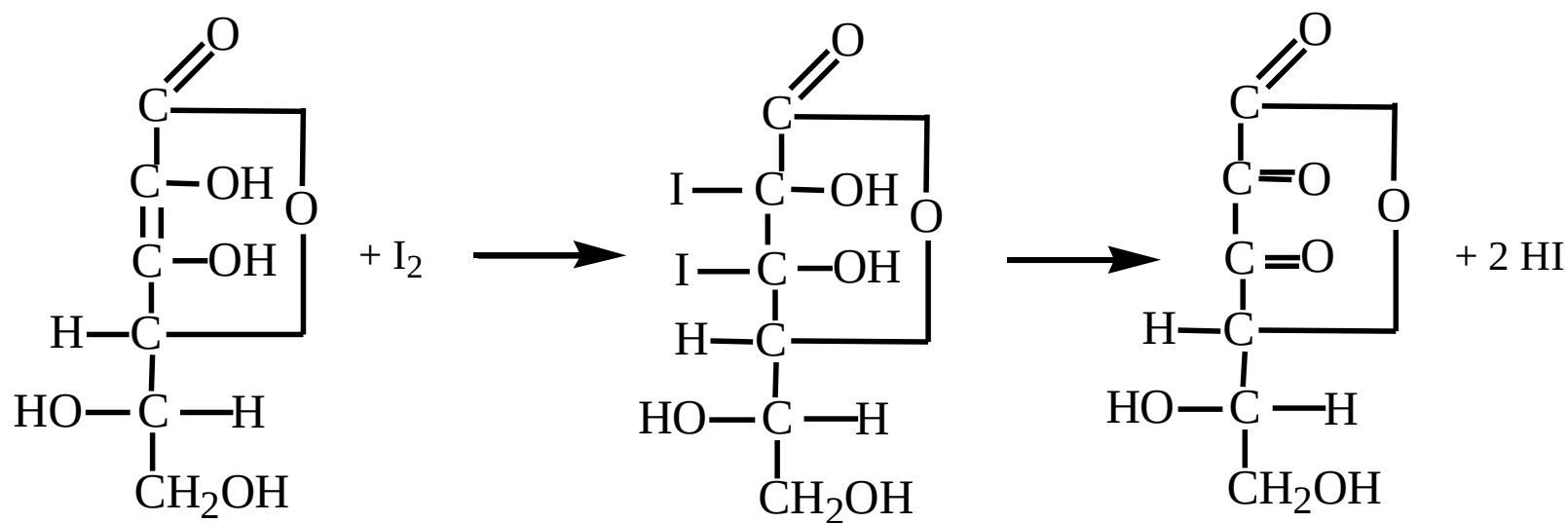
Heating (50-75 °C) is often necessary because is impossible sometimes (**fugitive** organic substances)

## 14. Ascorbinometry, titanometry

**Titrant:** standard solution of ascorbic acid.

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**Basic reaction of method:**



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### Advantages of ascorbinometry:

- Solution of ascorbic acids does not need to be stored during titration in inert atmosphere ( $H_2$ ,  $N_2$ ), in difference to solutions of salts Cr (II), Ti (III).

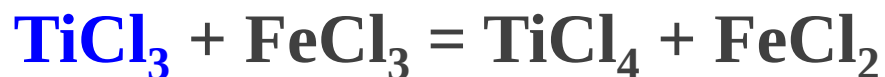
### Lacks of ascorbinometry:

Concentration of standard solution of ascorbic acids decreases as a result of action of enzymes, Uf-radiations.

For **stabilisation of ascorbic acids solutions** use **EDTA** and **HCOOH**.

- 
- **Titanometry** is a method of titration by solutions of compounds of Ti (III) which have strong **reduction** properties:

$$E^0 = +0,1 \text{ B}$$



#### Lacks of titanometry:

- Titration in inert atmosphere for standardization  $\text{TiCl}_3$  on  $\text{K}_2\text{Cr}_2\text{O}_7$ , difficult conditions of storage, standardization before each use.