Analytical chemistry

Lecture № 15

REDOX titration
Part III

The quantitative estimations of a number of pharmaceutical substances may be carried out by using a variety of potential oxidizing agents as stated below:

- **Permanganate Methods:**

a) Direct Titration Methods,
b) Indirect Titration Methods, and
c) Residual Titration Methods.

- **Dichromate Methods:**

Direct titrations with Potassium Dichromate.

- **Ceric Sulphate Titration Methods:**

Direct Titrations with Ceric Sulphate

Permanganatometric titration titrant is $KMnO_4$

The term "***manganimetry***" groups all the titrimetric determinations based on the oxidizing power of permanganate ions MnO_4^- toward several reductors. Manganimetry is usually achieved in acidic medium, but some determinations are also performed in neutral and alkaline media.

Manganese exhibits the following oxidation states:

- +VII in permanganate ion MnO_4^- (permanganic acid is a strong acid);
- +VI in manganate ion MnO_4^{2-};
- +V in hypomanganous ion MnO_4^{3-} ;
- +IV in manganese dioxide MnO_2;
- +III in manganic oxide Mn_2O_3;
- +II in the manganous cation Mn^{2+} and in the manganous hydroxide $Mn(OH)_2$;
- 0 in the metal.

Potassium permanganate is a strong oxidant with an intense violet colour. In strongly acidic solutions (pH ≲1), it is reduced to colourless Mn^{2+}

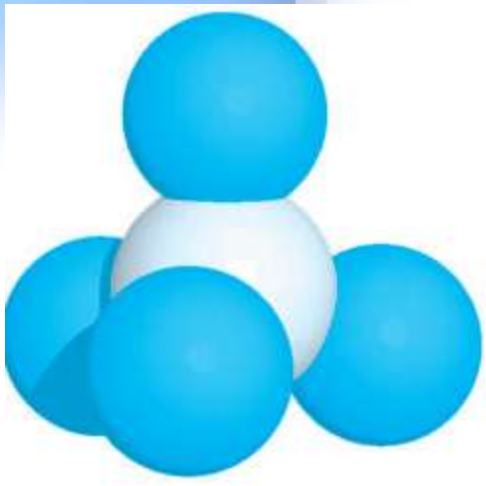
$$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O, \qquad E^\circ(MnO_4^-/Mn^{2+}) = 1.507\,V,$$

In neutral or alkaline solution, the product is the **brown solid, MnO_2.**

$$MnO_4^- + 4H^+ + 3e^- \rightleftharpoons MnO_{2(s)} + 2H_2O, \qquad E^\circ(MnO_4^-/MnO_{2(s)}) = 1.70\,V,$$

In strong basic solution (e.g., 2M NaOH), the **green manganate ion is produced:**

$$MnO_4^- + e^- \rightleftharpoons MnO_4^{2-}, \qquad E^\circ(MnO_4^-/MnO_4^{2-}) = 0.56\,V.$$



In addition to its use as an analytical reagent, usually in the form of its potassium salt, permanganate is very useful as an oxidizing agent in synthetic organic chemistry. It is used as a bleaching agent with fats, oils, cotton, silk, and other fibers. It has also been used as an antiseptic and anti-infective and as a component in outdoor survival kits, as well as for destroying organic matter in fish ponds, in manufacturing printed wiring boards, for neutralizing the effects of the pesticide rotenone, and for scrubbing flue gases in the determination of mercury.

The Preparation and Stability of Standard Solutions

Aqueous solutions of permanganate are not entirely stable because of water oxidation:

$$MnO_4^- + 2H_2O + 3e^- \rightleftharpoons MnO_{2(s)} + 4OH^-$$

Preparation of a solution of permanganate involves heating on a steam bath for about an hour and then filtering the solution before storing in a dark coloured glass storage bottle as light promotes the decomposition of the solution. Before filtration, the reagent solution is allowed to stand for about 24 hours or is heated for a brief period to hasten oxidation of the organic species generally present in small amounts in distilled and deionized water. Paper cannot be used for filtering because permanganate ion reacts with it to form additional manganese dioxide.
Sulfuric acid (0.5-1.0M) is the acid of choice for a redox reaction with permanganate. Using hydrochloric acid poses a problem as the permanganate may react with the chloride ion forming chlorine gas.

Solutions of permanganate ions are purple. This is one of the advantages of manganimetry. The reactant is its own indicator. During the titration of a colorless or slightly colored reductor with a permanganate solution, a drop in excess imparts a pale-pink color to the titrand solution.

Preparation of 0.1 N Potassium Permanganate Solution

Materials Required: Potassium permanganate: 3.5 g.

Procedure: Weigh accurately about 3.2 g of potassium permanganate on a watch-glass. Transfer the contents to a 250 ml beaker containing cold water and stir vigorously with a glass rod to effect rapid dissolution.

Decant the solution through a small plug of glass wool supported by a funnel, into a 1 litre volumetric flask thereby leaving the undissolved residues in the beaker. Add more DW to the beaker and repeat the above process till all the potassium permanganate gets dissolved. Finally make up the volume to the graduated mark and shake well so as to effect uniform mixing.

Note: 1) $KMnO_4$ must be weighed on a watch-glass and not on any kind of paper since cellulose fibers are corrosively attacked by it,

2) Likewise, filtration of $KMnO_4$ solution must be done though cleaned glass wool and not cotton wool, and

3) Avoid heat in the preparation of $KMnO_4$ solution because traces of grease or other possible contaminants on the glass vessels used can catalyse its decomposition.

Standardisation of permanganate may be against the primary standards, sodium oxalate or arsenic III oxide (very toxic), although a number of secondary standards could also be used.
The reaction between oxalate and permanganate is initially slow, but is catalysed by the presence of Mn^{2+} formed during the reaction.

$$2MnO_4^- + 5(COOH)_2 + 6H^+ \rightarrow 2Mn^{2+} + 10CO_{2(g)} + 8H_2O.$$

Standardization with Arsenious Acid. The reaction to standardize arsenious acid is slow. It occurs in a concentrated acid medium. It is catalyzed by chloride ions in sufficiently high concentrations.

$$2MnO_4^- + 5H_3AsO_3 + 6H^+ \rightarrow 2Mn^{2+} + 5H_3AsO_4 + 3H_2O.$$

Standardization with Ferrous Iron (Mohr's Salt) Mohr's salt is the iron + II and ammonium double sulfate, $FeSO_4$, $(NH_4)_2SO_4 \times 6H_2O$. The standardization reaction is

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

Standardization of 0.1 N Potassium Permanganate Solution

Materials Required: Oxalic acid: 6.3 g; sulphuric acid concentrated: 5 ml.

Theory: The standardization of potassium permanganate solution is based upon the following equations:

$$\begin{matrix} COOH \\ | \\ COOH \end{matrix} \longrightarrow 2CO_2 + 2H^+ + 2e$$

Procedure: Weigh accurately about 6.3 g of pure oxalic acid into a 1 litre volumetric flask, dissolve in sufficient DW and make up the volume upto the mark. Pipette out 25.00 ml of this solution, add to it 5 ml of concentrated sulphuric acid along the side of the flask, swirl the contents carefully and warm upto 70°C. Titrate this against the potassium permanganate solution from the burette till the pink colour persists for about 20 seconds.

Precautions:

1) Sufficient acid must be present, otherwise formation of a brown colour during titration may be observed,

2) Similar brown colouration can also be observed by using too high a temperature or by using a dirty flask,

3) To avoid such anomalies always rinse the flask with solution of H_2O_2 and dilute H_2SO_4 before performing the titrations.

Applications of Manganimetry in Acidic Medium

Determination of Inorganic Reductors

• Determination of Nitrites

Nitrites are oxidized by permanganate ions in acidic medium with the formation of nitrate ions. The determination consists of a ***back*** titration. The nitrite solution is progressively added into the solution of permanganate ions in excess. The medium consists of a diluted sulfuric acid solution heated at 50°C since the reaction is slow. Permanganate ions in excess are titrated with a Mohr's salt solution.

$$2MnO_4^- + 5NO_2^- + 6H^+ \rightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O$$

• Determination of Persulfate Ions

Persulfate ion is a powerful oxidizing agent. It easily oxidizes ferrous ions into ferric ions:

$$S_2O_8^{2-} + 2Fe^{2+} + 2H^+ \rightarrow 2Fe^{3+} + 2HSO_4^-$$

The determination is a back titration. Ferrous ions in excess are determined by manganimetry. An analogous titration can be achieved by replacing ferrous ions by oxalic acid.

• Determination of Hydrogen Peroxide

Hydrogen peroxide is a reducing agent with respect to permanganate ions. The half-redox couple is

$$2MnO_4^- + 5H_2O_2 + 6H^+ \rightarrow 5O_{2(g)} + 2Mn^{2+} + 8H_2O$$

• Determination of Calcium Ion

An interesting extension of the oxidization reaction of oxalic acid is the determination of calcium ions. The latter are precipitated as calcium oxalate in hot acetic acid. *The precipitate is separated* out from the solution, washed, and dissolved into a 2 mol/L sulfuric acid solution. After heating, the liberated oxalic acid is titrated with permanganate.

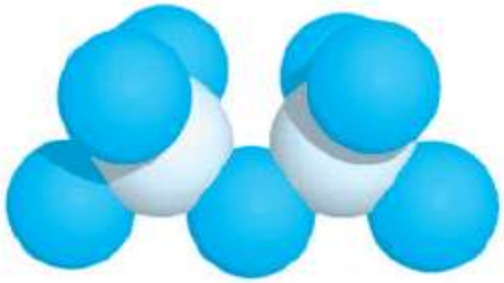
Organic Analysis

In organic analysis, the oxidizing power of permanganate ions in neutral or weakly alkaline medium permits the determination of some alcohols, oxalic and formic acids, and their salts with the production of carbon dioxide. In these pH conditions, permanganate ions react faster than in acidic medium.

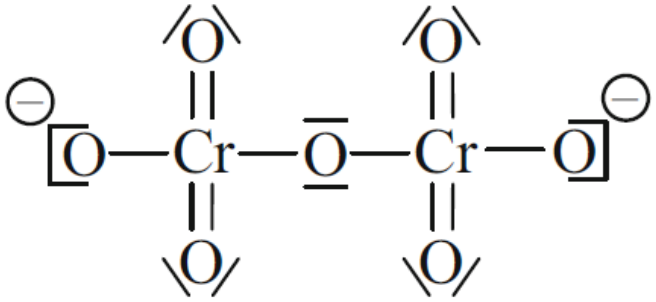
The residual titration method for pharmaceutical substances using potassium permanganate solution are mainly of *two categories, namely:* 1) titration wherein an excess of standard oxalic acid is added to the substance and then the excess of oxalic acid is back titrated with KMnO4, and 2) titration wherein an excess of standard $KMnO_4$ solution is used to oxidize the product, and then the amount in excess is estimated by reduction with either: a) excess ferrous ammonium sulphate and back titrated with more of standard $KMnO_4$, or b) excess standard oxalic acid.

DICHROMATOMETRIC TITRATION titrant $K_2Cr_2O_7$

Potassium dichromate is not such a powerful oxidizing agent as potassium permanganate, but it has several advantages over the latter substance. It can be obtained pure, it is stable, and it is therefore an excellent primary standard. Standard solution of exactly known concentration can be prepared by weighing out the pure dry salt and dissolving it in the proper volume of water. Furthermore, the aqueous solutions are stable indefinitely if adequately protected from evaporation. Potassium dichromate is used only in acid solution (even HCl can be used), and is reduced rapidly at the ordinary temperature to a green chromium (III) salt. $E^0 = 1.33\ B\ E^{o\prime} = (E^\circ - 0.14\text{pH})\,\text{V}.$



$$Cr_2O_7^{2-} + 14H^+ + 6\bar{e} \rightarrow 2Cr^{3+} + 7H_2O$$



dichromate ion

For many years, dichromate in the form of its ammonium, potassium, or sodium salts was used in nearly all areas of chemistry as a powerful oxidizing agent. In addition to its use as a primary standard in analytical chemistry, it has been used as an oxidizing agent in synthetic organic chemistry; as a pigment in the paint, dye, and photographic industries; as a bleaching agent; and as a corrosion inhibitor. The use of chromium compounds in general and dichromate in particular has decreased over the last decade because of the discovery that chromium compounds are carcinogenic.

Potassium dichromate can be obtained as a primary standard reagent and hence, standard solutions may be prepared determinately and stored for long periods of time.

Standardization of 0.1 N Potassium Dichromate Solution

It can be achieved by following these steps, namely:

1*)* Preparation of Standard Solution of Mohr's Salt $FeSO_4(NH_4)_2SO_4 \times 6H_2O$

Materials Required: Mohr's salt: 4.9 g; dilute sulphuric acid (9 N): 20 ml.

Procedure : Weigh accurately about 4.9 g of pure sample of Mohr's salt and transfer it to a 250 ml volumetric flask. Add 20 ml of dilute sulphuric acid and make up the volume to the mark with DW and finally mix the contents of the flask thoroughly.

2) **Standardization** of 0.1 N $K_2Cr_2O_7$ Solution

Materials Required: Standard solution of Mohr's salt (0.05 N):250 ml, sulphuric acid (2 N):20 ml; potassium dichromate solution (0.1 N):1 litre.

Procedure: Transfer 20 ml of the primary standard solution (Mohr's salt) to the titration flask and add 20 ml of 2 N sulphuric acid. Take the potassium dichromate solution in the burette. Put drops of freshly prepared potassium ferricyanide, $K_3[Fe(CN)_6]$, solution in the grooves of a porcelain tile. Now, proceed with the titration of Mohr's salt solution against $K_2Cr_2O_7$ solution. Presoaked and dried filter paper with $K_3[Fe(CN)_6]$ solution can also be used in place of the groove-tile method. In order to arrive at the exact end-point the above titration may be carried out at *three stages,*namely:

Stage 1: Spot tests are carried out at intervals of 1-2 ml until a blue colour is no longer produced with $K_3[Fe(CN)_6]$, which provides an altogether rough estimate of the $K_2Cr_2O_7$ solution required for the titration,

Stage 2 : Spot tests are only performed near the approach of the end of titration at intervals of 0.1-0.2 ml, and

Stage 3 : Spot tests are finally done only at the end-point. The above sequential steps give fairly accurate results because the error caused by the removal of part of the solution for the spot tests is made negligibly small. However, the titration is repeated to get a set of concordant readings.

To ascertain the end point of a dichromate titration a redox indicator should be employed which gives a strong and unmistakable colour change. Suitable indicators for use with dichromate titrations include N-phenylanthranilic acid (0,1% solution in 0,005 M NaOH) and diphenylamine (0,2% aqueous solution).

Examples of determinations:

Determination of CH_3OH

$$K_2Cr_2O_7 + CH_3OH + 4H_2SO_4 = Cr_2(SO_4)_3 + K_2SO_4 + CO_2\uparrow + 6H_2O$$

Determination of $FeSO_4$

$$K_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 = Cr_2(SO_4)_3 + K_2SO_4 + 3Fe_2(SO_4)_3 + 7H_2O$$

When phosphoric acid, which complexes ferric iron, is added, there is a decrease in the equivalence point potential value and the color change of the sulfonated diphenylamine at the equivalence point becomes very sharp.

Determination of $K_4[Fe(CN)_6]$

$$K_2Cr_2O_7 + 6K_4[Fe(CN)_6] + 7H_2SO_4 = Cr_2(SO_4)_3 + 4K_2SO_4 + 6K_3[Fe(CN)_6] + 7H_2O$$

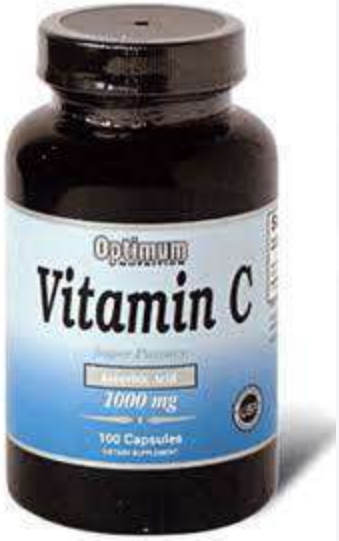
Determination of Vitamin C

$$K_2Cr_2O_7 + 3C_6H_8O_6 + 4H_2SO_4 = Cr_2(SO_4)_3 + K_2SO_4 + 3C_6H_6O_6 + 7H_2O$$

At equivalence point:

Ind = starch

$$K_2Cr_2O_7 + 6KI + 7H_2SO_4 = Cr_2(SO_4)_3 + K_2SO_4 + 3I_2 + 7H_2O$$

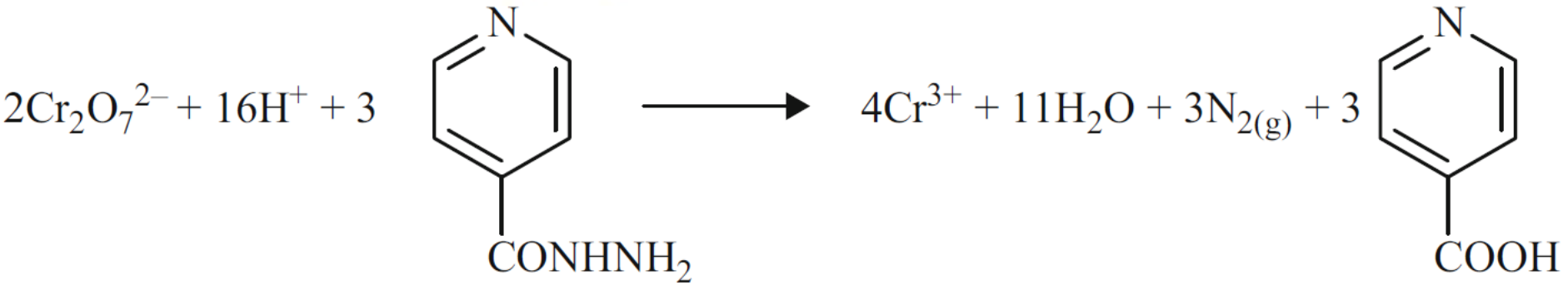


A 5.00-mL sample of brandy was diluted to 1.000 L in a volumetric flask. The ethanol (C_2H_5OH) in a 25.00-mL aliquot of the diluted solution was distilled into 50.00 mL of 0.02000 M $K_2Cr_2O_7$ and oxidized to acetic acid with heating:

$$3C_2H_5OH + 2Cr_2O_7^{2-} + 16H^+ \rightarrow 4Cr^{3+} + 3CH_3COOH + 11H_2O$$

After cooling, 20.00 mL of 0.1253 M Fe21 was pipetted into the flask. The excess Fe21 was then titrated with 7.46 mL of the standard $K_2Cr_2O_7$ to a diphenylamine sulfonic acid end point. Calculate the percent (w/v) C_2H_5OH (46.07 g/mol) in the brandy.

isoniazid



Chromimetry is used in inorganic and organic analysis. We mention the following examples:

• determination of ferrous iron;

• determination of ferric iron. Fe^{3+} ions are quantitatively reduced into Fe^{2+} ions, which are then titrated by dichromate ions. Fe^{3+} ions are reduced as in manganimetry, that is, by an excess of stannous chloride. The stannous ions in excess are oxidized into stannic ions with mercury(II) chloride;

• determination of uranyl salts. Uranyl salts can be determined by chromimetry but only after reduction into uranous ions U^{4+}.

$$Cr_2O_7^{2-} + 2H^+ + 3U^{4+} \rightarrow 2Cr^{3+} + 3UO_2^{2+} + H_2O.$$

• In organic analysis, most of the time the determinations involving dichromate ions are back titrations. The dichromate in excess is determined by indirect iodometry. Several organic compounds can be determined by chromimetry, including ethylenics, alcohols, carboxylic acids, and aldehydes. The reaction products are usually water and carbon dioxide. Ethanol gives acetic acid. This reaction is used to determine the alcohol level in blood.

CERIMETRIC TITRATION titrant $Ce(SO_4)_2$

Cerium (IV) sulphate is a powerful oxidizing agent. It can be used only in acidic solutions, best in 0,5 M or higher concentrations. The solution has an intense yellow colour, and in hot solutions which are not too dilute the end point may be detected without an indicator.

$$Ce^{4+} + \bar{e} \rightarrow Ce^{3+} \qquad E^0 = 1.45\ B$$

Standardized Solutions

They are prepared

• either by starting from ceric sulfate, which is not a standard,

• or by starting from ammonium and cerium double sulfate, which may be purchased in a state of warranted purity,

• or from hexanitratocerate IV, also called ceria mmonic nitrate $[Ce(NO_3)_6](NH_4)_2]$, which is a nitrato complex of cerium IV. It exhibits the interesting property to be soluble in water. It may be considered a primary standard. It is dissolved into a 1 mol/L sulfuric acid in order to prepare solutions.

The advantages of cerium (IV) sulphate as a standard oxidizing agent

1.Cerium (IV) sulphate solutions are remarkably stable over prolonged periods. They need not to be protected from light, and may be even be boiled for a short time without appreciable change in concentration.

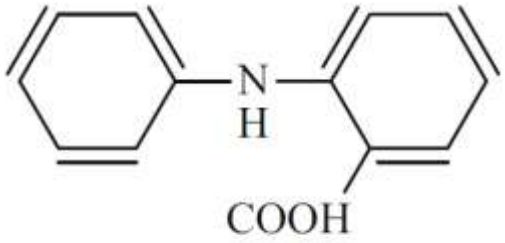
2.Cerium(IV) sulphate may be employed in the determination of reducing agents in the presence of a high concentration of HCl.

3.Cerium(IV) solutions in 0,1 M solution are not too highly coloured to obstruct vision when reading the meniscus in burettes and other titrimetric apparatus.

4.In the reaction of cerium (IV) salts in acid solution with reducing agents, the simple change is assumed to take place. With permanganate a number of reduction products are produced according to the experimental conditions.

Standardization of cerium (IV) sulphate (1 variant)

The most trustworthy method for standardizing cerium (IV) sulphate solution is application of iodometric titration. Cerium (IV) sulphate is reacted with an excess of potassium iodide, producing iodine. The iodine that is produced is then titrated against sodium thiosulphate, to find how much iodine was produced by the reaction of cerium (IV) sulphate with potassium iodide. Once the amount of iodine has been found, the amount of the cerium (IV) sulphate solution can be calculated.



N-phenylanthranilic acid

$$2Ce(SO_4)_2 + 2KI(excess) = Ce_2(SO_4)_3 + K_2SO_4 + I_2$$

$$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$$

$$n(Ce(SO_4)_2) = n(Na_2S_2O_3)$$

Standardization of cerium (IV) sulphate (2 variant)

Standardization may also be carried out with sodium oxalate. It is possible to carry out a direct titration.

$$2Ce(SO_4)_2 + Na_2C_2O_4 = Ce_2(SO_4)_3 + Na_2SO_4 + 2CO_2$$

Cerium(IV) standardizations against sodium oxalate are usually performed at 50°C in a hydrochloric acid solution containing iodine monochloride as a catalyst.

Ind = N-phenylanthranilic acid

Applications of Cerimetry

In Inorganic Analysis

$$2Ce^{4+} + H_2O_2 = 2Ce^{3+} + 2H^+ + O_2 \uparrow$$

- ferrous salts (see standardization);
- hydrazine. The reaction is

$$N_2H_4 + 4Ce^{IV} \rightarrow N_{2(g)} + 4H^+ + 4Ce^{III}$$

Hydrazine is oxidized with an excess of boiling ceric sulfate in excess. The excess is titrated with a ferrous salt.

- hydrazoic acid and hydrazoates;

This is a back titration. The oxidization reaction of hydrazoic acid is

$$2N_3H + 2Ce^{IV} \rightarrow 3N_2 + 2Ce^{III} + 2H^+$$

The excess of ceric salt is titrated with ferrous sulfate in sulfuric acid with ferroin as the indicator;

- nitrites; The nitrite solution is added to a known quantity in excess of ceric sulfate. The excess is titrated with a ferrous salt solution or with an oxalate solution with ferroin or N-phenylanthranilic acid as the indicator. The oxidization reaction is

$$2Ce^{IV} + HNO_2 + H_2O \rightarrow 2Ce^{III} + NO_3^- + 3H^+$$

• hydroxylamine;

This is a back titration. The ceric salt oxidizes hydroxylamine according to thereaction

$$2NH_2OH + 4Ce^{IV} \rightarrow N_2O + 4Ce^{III} + 4H^+$$

The excess of ceric salt is titrated with an arsenious acid solution with ferroin as the indicator;

• hexacyanoferrate II (ferrocyanide);

This is a direct titration that is achieved in 1 mol/L sulfuric acid:

$$Fe(CN)_6^{4-} + Ce^{IV} \rightarrow Ce^{III} + Fe(CN)_6^{3-}$$

• hydrogen peroxide;

This is a direct titration with ceric sulfate with ferroin or N-phenylanthranilic acid as the indicator:

$$2Ce^{IV} + H_2O_2 \rightarrow 2Ce^{III} + O_{2(g)} + 2H^+$$

• antimony III;

Antimony III can be directly titrated with ceric sulfate with ferroin as the indicator. The reaction must be achieved at 50◦C.

$$4Ce^{IV} + 2SbO^+ + 3H_2O \rightarrow 4Ce^{III} + Sb_2O_{5(s)} + 6H^+$$

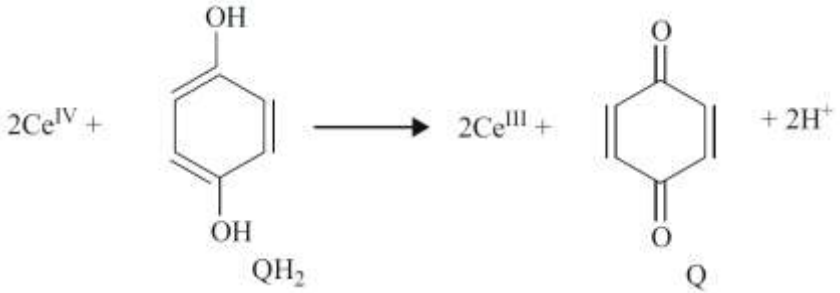
In Organic Analysis

• Determination of organic acids;

The ceric oxidization of organic acids has been the matter of several studies. Except for oxalic acid, which can be directly titrated, other organic acids are back-titrated. They are oxidized with an excess of ceric sulfate in a sulfuric acid medium heated with a heat bath for about one hour. After cooling at room temperature, the ceric sulfate in excess is titrated with a solution of Mohr's salt with N-phenylanthranilic acid as the indicator.

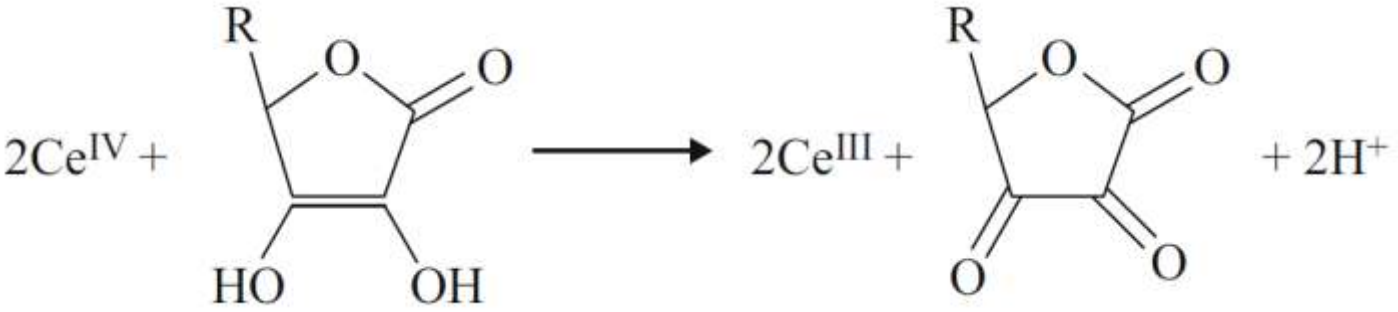
• determination of hydroquinol

Hydroquinol is quantitatively and fastly oxidized into p-quinone with ceric sulfate



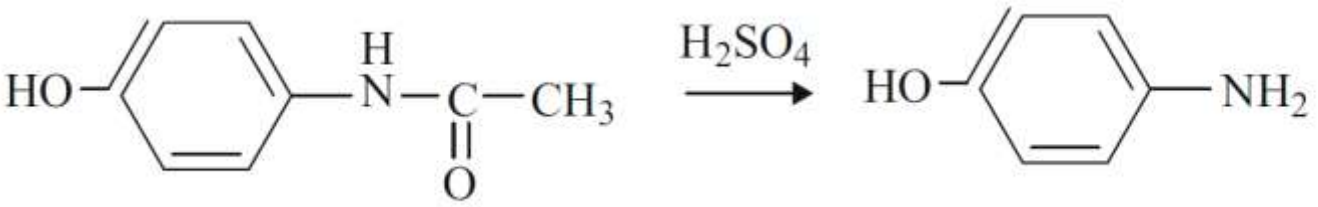
• determination of vitamin C;

There is formation of dehydroascorbic acid by direct titration with ceric sulfate



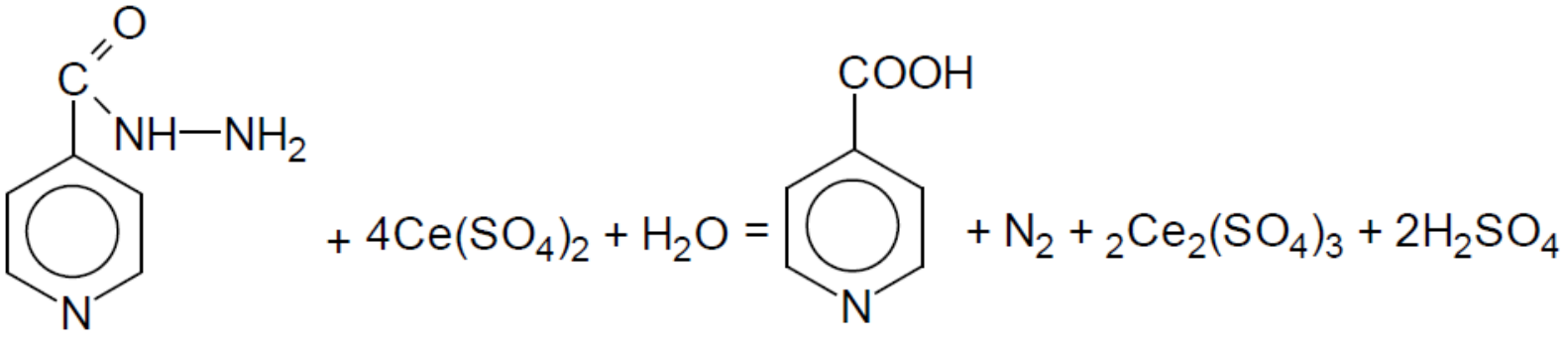
• determination of paracetamol;

At first, paracetamol is quantitatively hydrolyzed into 4-aminophenol in sulfuric acid medium. Then 4-aminophenol is directly titrated with the ceric salt to give 1,4-benzoquinonimine:



• determination of isoniazid;

As in other redox titrations of isoniazid, nitrogen of the hydrazide group passes from oxidation state −II to 0.

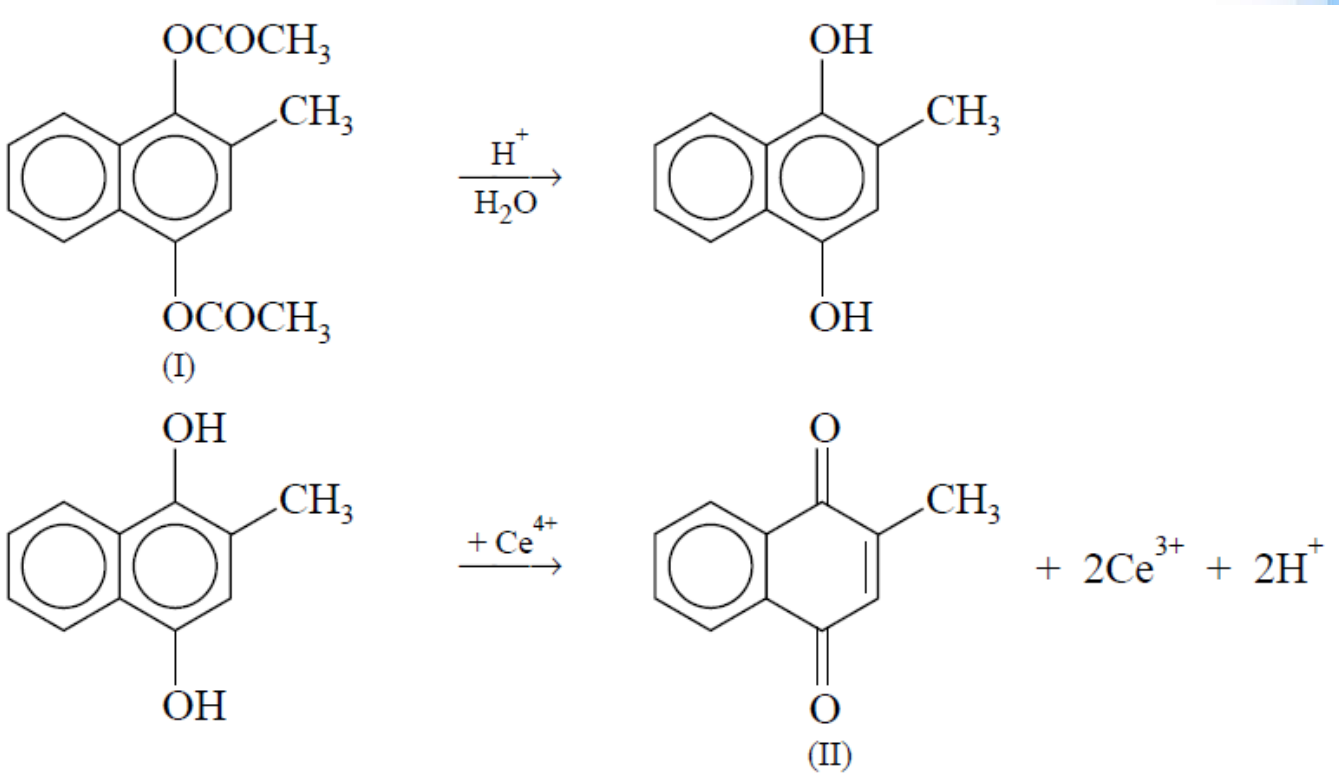


• Acetomenaphthone

Materials Required: Acetomenaphthone: 0.2g; glacial acetic acid:15 ml; dilute hydrochloric acid (10% w/v):15 ml; ammonium ceric sulphate 0.05 N; ferroin sulphate solution.

Procedure: Weigh accurately about 0.2g of acetomenaphthone and boil it with 15 ml of glacial acetic acid and 15 ml of dilute hydrochloric acid under a reflux condenser for 15 minutes. Cool the contents carefully and taking adequate precautions to avoid any atmospheric oxidation. Add 0.1 ml of ferroin sulphate solution as indicator and titrate with 0.05 N ammonium ceric sulphate. Repeat the assay without the substance being examined (blank determination) and incorporate the correction, if any.

Equations -



First, acetamenaphthone (I) undergoes hydrolysis in acidic medium to yield the corresponding phenol and secondly, this phenol is oxidised quantitatively with ammonium ceric sulphate to give the resulting 1, 4-dione derivative (II).