

Potassium Permanganate

- Permanganate ion is a strong oxidizing reagent. Half-reaction is,



The half-reaction shown for permanganate ion occurs only in solutions that are 0.1 M or greater in strong acid. In less acidic media, the product may be Mn(III), Mn(IV), or Mn(VI), depending on conditions.

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



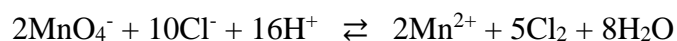
Permanganate solutions, when properly prepared, are reasonably stable because the decomposition reaction is slow. It is catalyzed by

- light,
- heat,
- acids,
- bases,
- manganese(II),
- manganese dioxide.

- Permanganate solutions are moderately stable provided they are free of manganese dioxide and stored in a dark container.

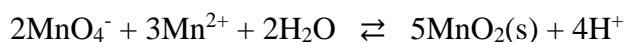
Removal of manganese dioxide by filtration before standardization markedly improves the stability of standard permanganate solutions. Before filtration, the reagent solution is allowed to stand for about 24 hours or is heated for a brief period to hasten oxidation of the organic species generally present 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.

- Permanganate solutions oxidize chloride ion and cannot be used with hydrochloric acid solutions unless special precautions are taken to prevent the slow oxidation of chloride ion that leads to overconsumption of the standard reagent.



- A useful property of a potassium permanganate solution is its intense purple color, which is sufficient to serve as an indicator for most titrations.

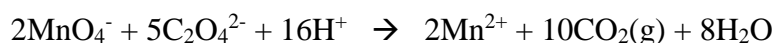
- The permanganate end point is not permanent because excess permanganate ions react slowly with the relatively large concentration of manganese(II) ions present at the end point, according to the reaction



The rate at which this equilibrium is approached is so slow that the end point fades only gradually over a period of perhaps 30 seconds.

Standardizing Permanganate Solution

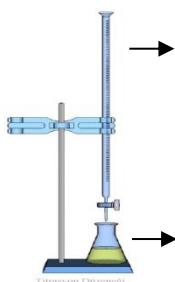
- Sodium oxalate** is a widely used primary standard. In acidic solutions, the oxalate ion is converted to the undissociated acid. Thus, its reaction with permanganate can be described by



The reaction between permanganate ion and oxalic acid is complex and proceeds slowly even at elevated temperature unless manganese(II) is present as a catalyst. Therefore, when the first few milliliters of standard permanganate are added to a hot solution of oxalic acid, several seconds are required before the color of the permanganate ion disappears. As the concentration of manganese(II) builds up, however, the reaction proceeds more and more rapidly as a result of **autocatalysis**.

Autocatalysis is a type of catalysis in which the product of a reaction catalyses the reaction. This phenomenon causes the rate of the reaction to increase as the reaction proceeds.

Experimental Procedure:



→ KMnO_4 solution

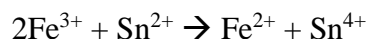
- 4-5 mL $\text{Na}_2\text{C}_2\text{O}_4$ solution + 30 mL ~ 3 M H_2SO_4 + $\text{MnSO}_4(\text{s})$
- After the color of the first drop disappears, second drop is added.
- The solution is titrated until permanent pink color is obtained for 30 seconds

Fe (III) Determination with Zimmermann - Reinhardt Method

This method is used when there is a large amount of Cl^- in the medium.

Permanganate solutions oxidize chloride ion and some precautions should be taken to prevent this oxidation.

- The Fe (III) ions are reduced with SnCl_2 in hot medium containing concentrated HCl.



The end of this reduction is understood by the disappearance of the yellow color of the solution (FeCl_4^- is yellow).

Since the yellow color is not too sharp, 1-2 drops of additional SnCl_2 are added.

- The excess of SnCl_2 is oxidized to Sn^{4+} with HgCl_2 . HgCl_2 should be added quickly.

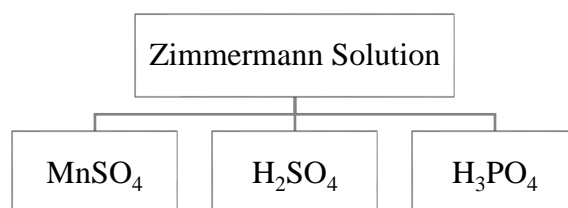


If Sn^{2+} remains in the medium, it is oxidized with KMnO_4 and that leads to overconsumption of KMnO_4 .

Mercury (I) chloride is very slightly soluble in water, forms a separate phase and does not participate in the titration.

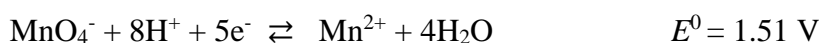
HgCl_2 should be added quickly. If the addition of HgCl_2 is slow, mercury (II) ions can be reduced to metallic mercury (Hg^0) by tin (II) ions. Hg^0 oxidizes the reduced Fe^{2+} to Fe^{3+} .

- Zimmermann solution is added to the iron (II) solution.



MnSO₄

The abundant Mn^{2+} added to the solution reduces the oxidizing potential of the permanganate. Thus, permanganate is prevented from raising chloride.



Nernst Equation:

$$E = E^0 - \frac{0.0592}{5} \log \frac{[Mn^{2+}]}{[MnO_4^-][H^+]^8}$$

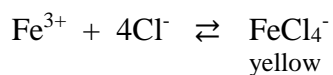
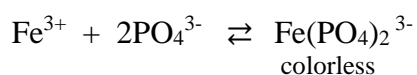
As Mn^{2+} concentration increases, the electrode potential decreases. Thus, the oxidation of the chloride ions is prevented.

H₂SO₄

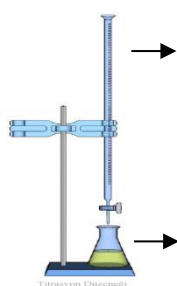
It provides acidic solution.

H₃PO₄

It is used as a PO_4^{3-} source to form the $Fe(PO_4)_2^{3-}$ complex. The formation of the $FeCl_4^-$ complex is prevented.



Experimental Procedure:



KMnO₄ solution

- 4-5 drops of concentrated HCl is added to the sample and the solution is heated (the color of the solution becomes orange)
- SnCl₂ is added dropwise while the solution is warm (until the yellow color of the solution disappears).
- After the yellow color disappears, 2 drops of additional SnCl₂ are added.
- The solution is diluted to 20 milliliters.
- The solution is cooled under tap water.
- 10 mL of 5% HgCl₂ solution is added rapidly (Hg₂Cl₂ is formed).
- 25 mL of Zimmermann solution is added.
- The solution is titrated until permanent pink color is obtained for 30 seconds