Ministry of Health of the Russian Federation

Volgograd State Medical University

Department of Pharmaceutical and Toxicological Chemistry

GENERAL PHARMACEUTICAL CHEMISTRY

Redox Titration.

Permanganatometry.

Lesson 12

V term

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QUESTIONS FOR THE LESSON

1. Redox titration
2. Classification of redox titration methods
3. Permanganometry. Essence of the method
4. Permanganatometry in acid medium
5. Permanganatometry in neutral or slightly alkaline medium:
6. Permanganatometry in strongly alkaline medium:
7. Determination of the titration end point in permanganatometry
8. Preparation of standard potassium permanganate solution
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REDOX TITRATION

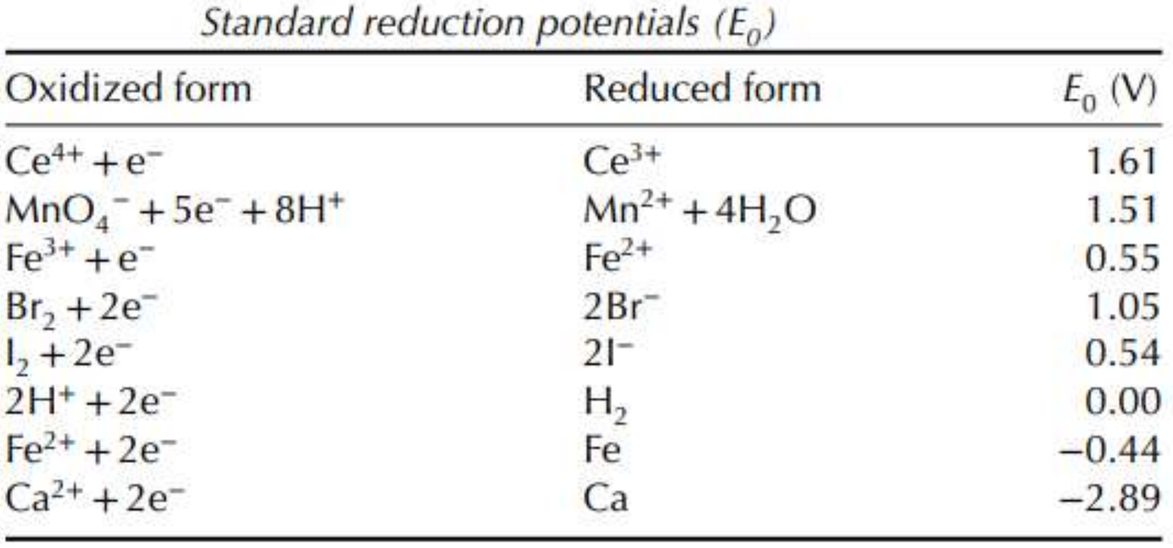
The oxidation and reduction processes essentially take place simultaneously in a reaction, thus one entity gets reduced in the process of oxidizing the second. ‘Redox’ - is the abbreviated form of reduction-oxidation systems. In the oxidation-reduction methods of analysis a change in valence of the reacting products is a must which is contrary to precipitation and neutralization methods of analysis where no change in valence occur.

As a number of elements are capable of exhibiting more than one oxidation state, hence volumetric titration methods based on redox reactions are usually employed widely.

In oxidation-reduction titration method, a reducing substance is titrated with standard solution of an oxidizing agent (e.g., potassium permanganate) or an oxidizing substance is titrated with the standard solution of the reducing agent (e.g., sodium thiosulfate).

A redox titration can be described by the following equation:

$$\mathrm{Ox1} + \mathrm{Red2} \rightarrow \mathrm{Red1} + \mathrm{Ox2}$$



Standard reduction potentials (E_0)

Oxidized form	Reduced form	E_0 (V)
$Ce^{4+} + e^-$	Ce^{3+}	1.61
$MnO_4^- + 5e^- + 8H^+$	$Mn^{2+} + 4H_2O$	1.51
$Fe^{3+} + e^-$	Fe^{2+}	0.55
$Br_2 + 2e^-$	$2Br^-$	1.05
$I_2 + 2e^-$	$2I^-$	0.54
$2H^+ + 2e^-$	H_2	0.00
$Fe^{2+} + 2e^-$	Fe	−0.44
$Ca^{2+} + 2e^-$	Ca	−2.89

The reduction potential of a given substance is an expression of the extent to which the substance may take up electrons. A high positive value for the reduction potential indicates:

- The substance is easily reduced.
- The substance is a powerful oxidizing agent.
- The substance easily removes electrons from other substances with a lower reduction potential.

A substance with a higher reduction potential oxidizes a compound with a lower reduction potential. For titrations in general, the equilibrium constant should be high to ensure a complete reaction. In redox titration, the equilibrium constant is determined by the difference (ΔE) between the reduction potentials of the two substances:

$$\Delta E = E_0^{\mathrm{T}} - E_0^{\mathrm{A}}$$

E_0^T is the reduction potential of the titrant

E_0^A is the reduction potential of the analyte (titrate).

ΔE is termed the reaction potential.

In practice, ΔE should not be less than 0.1–0.2 V. Throughout titration, the potential changes gradually with addition of the titrant, and at the equivalence point the potential increases or decreases very sharply as a function of the added titrant.

Redox reactions

Reduction Reaction

A substance undergoes a reduction in the following ways:

- The addition of hydrogen.
- The process of removing oxygen.
- Acceptance of electrons.
- A reduction in overall oxidation state.

Oxidation Reaction

A substance undergoes oxidation in the following ways:

- The addition of oxygen.
- The hydrogen that was connected to the species was removed.
- Electron donation and loss
- An increase in the oxidation state of the material

The redox reactions underlying redox methods are subject to the following ***requirements:***

- reactions run to the completion,
- are fast and stoichiometric,
- form products of a certain composition,
- do not react with by-products,
- allow the equivalence point to be accurately fixed.

Classification of redox titration methods

There are different types of redox titrations, and these are commonly named after the reagent being used.

- ***Permanganometry*** is a redox titration that uses potassium permanganate as an oxidizing agent.
- ***Cerimetry*** is a type of redox titration that uses ammonium ceric sulphate as an oxidizing agent.
- ***Dichrometry*** uses potassium dichromate.
- ***Bromatometry*** is a redox titration that uses potassium bromate as an oxidizing agent.
- ***Iodimetric titrations*** use iodine as an oxidizing agent to titrate reducing agents.

- ***Iodometric titrations***, on the other hand, uses iodide ion as a weak reducing agent.

PERMANGANOMETRY

Permanganatometry is one of the most frequently used methods of redox titration.

A solution of ***potassium permanganate*** $KMnO_4$ is used as the ***titrant***. The oxidising properties of the titrant can be adjusted depending on the acidity of the solution.

The indicator in the permanganatometry method is $KMnO_4$ solution itself, which has a crimson-purple colour due to the MnO_4^- ion; the resulting Mn^{2+} cation is colourless after the reaction. The use of potassium permanganate makes it possible to fix the point of equivalence by the appearance of a pink colour from just one extra drop of solution.

The essence of the method is the oxidation of reducing agents with potassium permanganate solution. The oxidation is carried out in different media. The method is based on the reduction of the permanganate ion to different degrees of oxidation depending on the acidity of the medium.

The permanganatometric method is the most widely used in analytical practice in acidic media.

Acidic medium:

In acidic media, manganese ions can exist in different oxidation states: Mn^{2+}, Mn^{3+} , Mn^{4+} , Mn^{5+} and Mn^{7+}. Low-charged manganese ions are capable of oxidising to higher oxidation degrees. In order to avoid the formation of intermediate oxidation forms of manganese ions it is recommended to carry out the titration slowly, in very acidic pH values, and at certain temperatures (heating). The reduction reaction can be observed by a ***colour change*** - the **red-violet** colour changes to **brown** (IV and III) and then **decolourises** (II):

$$MnO_4^- \longrightarrow MnO_2 \longrightarrow Mn^{3+} \longrightarrow Mn^{2+}$$

The summary process proceeds as follows:

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

- ✓ A special feature of the method is the strong effect of pH. When titrating in strongly acidic media, sulphuric acid is most commonly used. Hydrochloric and nitric acids should not be used, as in their presence there may be competing redox reactions.

- ✓ Manganese ions of lower oxidation states, are catalysts of the reaction. For more accurate titration a reverse titration method is often used, where a known excess of permanganate is added and after a short time the residue is titrated with a reducing agent.

A neutral or slightly alkaline medium:

The reduction of permanganate in a neutral or slightly alkaline medium is no less complicated than in an acidic medium. In the first stage of the redox reaction, manganate is formed first:

$$MnO_4^- + e^- \longrightarrow MnO_4^{2-}$$

In the second redox stage the manganate is reduced to Mn (IV):

$$MnO_4^{2-} + 2H_2O + 2e^- \longrightarrow MnO_2\downarrow + 4OH^-$$

The ***colouring changes*** from **red-violet** to **green** and turns to a **brownish-black** MnO_2 precipitate. The total process proceeds as follows:

$$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2\downarrow + 4OH^-$$

Strongly alkaline medium:

The reduction of permanganate in a strongly alkaline medium takes place in in one stage, with a ***colour change*** from **red-violet** to **green**:

$$MnO_4^- + e^- \longrightarrow MnO_4^{2-}$$

The oxidising power of permanganate in neutral and alkaline media is much lower than in acidic media. Therefore, the determination of reducing agents is mainly carried out in an acidic medium.

Determination of the titration end point

The end of the titration is indicated by a slightly pink colour of the excess $KMnO_4$ titrant. Therefore, if the titrated solution is colourless, reaching the point of equivalence can be indicated by the ***appearance of a slightly pink colour*** of the excess KMnO4 titrant in the ***direct titration*** or by ***the disappearance of the colour*** in the ***reverse titration***. The use of the indicator ferroin is recommended for the analysis of coloured solutions.

Preparation of standard Potassium Permanganate Solution

The permanganatometric method uses 0.05 N or 0.1 N $KMnO_4$ solution as a standard solution.

A standard solution of potassium permanganate cannot be prepared from an exact sample weight, as there are always impurities in the salt and there are organic substances oxidised by the permanganate in the water. The titer of potassium permanganate can be set by ***oxalic acid*** and by ***ammonium or sodium oxalate***.

The oxalic acid standardisation of the solution is carried out in an acidic medium. The following reaction takes place:

$$5H_2C_2O_4 + 2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$$

Applications of permanganatometry in pharmaceutical analysis

Permanganatometric titration is not widely used in pharmaceutical analysis. This is due to the rather narrow range of substances to be determined and the instability of the $KMnO_4$ solution. In addition, the interaction of KMnO4 with organic substances proceeds by complex mechanisms and is slow. Therefore, the main pharmaceutical targets of permanganatometry are hydrogen peroxide solutions of different concentrations and metal peroxides as well as some other compounds.

Permanganatometry is used for the following purposes:

1. Determination of the reducing agents.

If the redox reaction between the reducing agent to be determined and MnO_4^- is fast, the titration is carried out by the ***direct method***.

Oxalates, hydrogen peroxide, iron (II), ferrocyanides, arsenic acid etc. are determined in this way, e.g:

Assay of Hydrogen Peroxide Solution

Procedure: Sulfuric acid is added to the hydrogen peroxide solution and titrated with a solution of potassium permanganate to a constant pink endpoint.

Equations :

$$\begin{array}{rcl} 2KMnO_4 + 3H_2SO_4 & \longrightarrow & K_2SO + 2MnSO_4 + 3H_2O + 5(O) \\ 5H_2O_2 + 5(O) & \longrightarrow & 5O_2 + 5H_2O \\ \hline \textbf{Summing up :}\ 5H_2O_2 + 2KMnO_4 + 3H_2SO_4 & \longrightarrow & K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2 \uparrow \end{array}$$

In the case of delayed reactions the determination is made by ***reverse titration*** of an excess of permanganate.

2. Determination of the oxidizing agents.

An excess of a standard reducing agent solution is added and then the remainder is titrated with $KMnO_4$ solution (reverse titration method).

For example dichromates, persulfates, chlorides and other oxidants can be determined using the permanganatometric method by first exposing the excess Fe^{2+} standard solution and then titrating the unreacted Fe^{2+} with $KMnO_4$ solution:

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

The excess Fe^{2+} ions are titrated with permanganate:

$$5Fe^{2+} + MnO^-_4 + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$$

3. Determination of substances which do not have redox properties

This analysis is carried out indirectly, e.g. by substitution titration. To do this, the constituent to be determined is converted into a compound with reducing or oxidising properties and then titrated. For example calcium, zinc, cadmium and cobalt ions are precipitated as low soluble oxalates.

4. Identification of organic compounds

A characteristic feature of reactions of organic compounds with MnO_4^- is their low speed. Determination is possible by reverse titration. The analysed compound is pretreated with an excess of strong alkaline permanganate solution and allowed to react for the required period of time. The permanganate residue is titrated with a sodium oxalate solution.

This is how formic, poly- and oxycarboxylic acids are determined, aldehydes and other organic compounds, e.g:

$$HCOO^- + 2MnO_4^- + 3OH^- \rightarrow CO_3^{2-} + 2MnO_4^{2-} + 2H_2O$$

The excess permanganate is then titrated with oxalic acid or oxalates:

$$5H_2C_2O_4 + 2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$$

Advantages and disadvantages of the permanganatometric method

The permanganatometric method has several *advantages*:

1. In this method the working solution is the indicator - one drop of the working solution stains the solution pink.
2. The possibility of titration by KMnO4 solution can be carried out both in acidic and alkaline environment.
3. Permanganate is a cheap and accessible reagent.

4. Stoichiometricity and fairly high rate of most redox reactions involving permanganate.

In addition to the listed advantages, the permanganatometric method has a number of *disadvantage*s:

1. Potassium permanganate is difficult to obtain in chemically pure form, because it contains many impurities and it is not possible to take an exact sample.
2. Standard solutions are unstable and the titre must be checked periodically during use.
3. In hydrochloric acid, the determination cannot be carried out as the chloride ion is oxidised to free chlorine.
4. Some oxidation reactions are very slow and therefore require heating; but in this case the test substances may decompose.