Ministry of Health of the Russian Federation

Volgograd State Medical University

Department of Pharmaceutical and Toxicological Chemistry

GENERAL PHARMACEUTICAL CHEMISTRY

Redox Titration.

Cerimetry. Dichromatometry.

Lesson 14

V term

Volgograd, 2022

QUESTIONS FOR THE LESSON

1. Cerimetry.
   a) Preparation and standardisation of cerium sulphate solution
   b) Fixing the titration end-point
   c) The advantages and disadvantages of cerimetry
   d) Application of cerimetry in pharmaceutical analysis
2. Dichromatometry
   a) Preparation of a standard solution of potassium bichromate
   b) Fixing the titration end-point
   c) Advantages and disadvantages of bichromatometry
   d) Application of dichromatometry in pharmaceutical analysis

CERIMETRY

Cerimetry is a method of titrimetric analysis, based on the use of cerium (IV) compounds as an oxidant. Cerium (IV) compounds. It is based on a half reaction:

$$Ce^{4+} + \bar{e} = Ce^{3+}$$

Preparation and standardisation of cerium sulphate solution

The titrants of the method are 0.1 and 0.01 mol/ml of cerium (IV) sulfate $Ce(SO_4)_2 \cdot 4H_2O$ or cerium (IV)-ammonium sulfate $[Ce(SO_4)_2 \cdot 2(NH_4)_2SO_4] \cdot 2H_2O$. These titrants are *secondary* standards. The titrants are standardized according to the standard substances $Na_2C_2O_4$ or $(NH_4)_2S_2O_4$ solution are standardized.

Fixing the titration end-point

The titration end point is determined as follows

- **<u>without indicator</u>** - by the colour change of the titrated mixture (unreliable method). The method is based on visual observation of the colour change of the titrated solution, which turns yellow in the presence of excess titrant. This method is not applicable when titrating stained or turbid solutions, or when colouring due to the formation of coloured reaction products occurs.
- With the help **<u>of redox indicators</u>** such as diphenylamine, ferroin, etc;

- with the **acid-base indicators** methyl orange, methyl red. At the point of equivalence, the indicator is irreversibly oxidised by the titrant and a colour change occurs.
- **instrumental methods** - potentiometric, photometric, amperometric, etc.

The advantages of cerimetry

- ✓ Standard solutions retain a constant concentration for a long time and are very resistant to environmental components.
- ✓ Titration with solutions of cerium (IV) salts can be carried out not only in sulphuric but also in hydrochloric acid media.
- ✓ The titration with solutions of cerium (IV) salts usually does not produce intermediate products or by-products which reduce accuracy or slow down the titration process.
- ✓ Cerimetry can be used to determine a wide variety of objects that cannot be determined by other redox methods.

Cerimetry also has some disadvantages

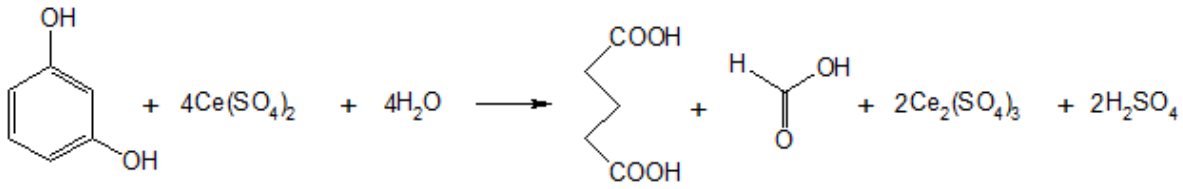
- ✓ In cerimetry, indicators are needed because the titration end-point is difficult to detect by the colour change of the solution when an excess of titrant is added.
- ✓ Do not use in the presence of phosphates and fluorides, as stable complexes are formed.
- ✓ Titration with solutions of cerium (IV) salts often has to be carried out when heated to 50-75 C. This leads to difficulties in the case of the determination of volatile organic compounds.

Application of cerimetry in pharmaceutical analysis

Cerimetric is used for the determination of reducing agents: tin (II), arsenic (III), antimony (III), iron (II), H_2O_2, iodides, nitrites, etc. Organic compounds such as phenols, carbohydrates, oxalic acid, ascorbic acid.

Resorcinol assay

The method is based on the oxidation of resorcinol with an excess of 0.1 M cerium (IV) sulphate in an acidic environment at room temperature. The oxidation of resorcinol produces glutaric and formic acid:



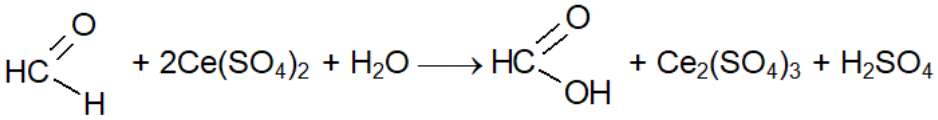
The excess titrant is determined by the iodometric method (indicator - starch):

$$2Ce(SO_4)_2 + 2KI \rightarrow I_2 + Ce_2(SO_4)_3 + K_2SO_4$$

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

Formaldehyde assay

Action with an excess of titrated cerium (IV) sulphate solution:



The excess is titrated with a solution of Mohr's salt: $(NH_4)_2SO_4 * FeSO_4 * 6H_2O$

DICHROMATOMETRY

The most important feature of dichromate, which has led to its wide use in oxidimetry, is the instability of the intermediate oxidation degrees of chromium +5 and +4 and the high value of the standard electrode potential of the half-reaction in acidic solution:

$$Cr_2O_7^{2-} + 14H^+ + 6\bar{e} = 2Cr^{3+} + 7H_2O$$
$$E^0 = 1{,}33\ V$$

In neutral or alkaline solutions, the Cr^{3+} ion or $[Cr(H2O)6]^{3+}$ forms an insoluble hydroxide and the dichromate becomes chromate:

$$Cr_2O_7^{2-} + 2OH^- = 2CrO_4^{2-} + H_2O$$

An acidic medium for titration is usually created by using solutions of sulphuric or orthophosphoric acid. A solution of HCl can also be used at a concentration not exceeding 2 mol/l, as under these conditions the chloride ions are not oxidised to chlorine by the dichromate ions.

Preparation of a standard solution of potassium bichromate

The titrant for the method is a 0.1 mol/l $K_2Cr_2O_7$ solution.

Since $K_2Cr_2O_7$ is the standard substance, it is used to is prepared as a *primary* standardisation titrant.

The standard solution is prepared by dissolving a exact weight of potassium dichromate in water. It dissolves easily in water.

The obtained solutions are stable for many years if they are protected against evaporation. Potassium dichromate solutions should be stored in closed containers

Fixing the titration end-point

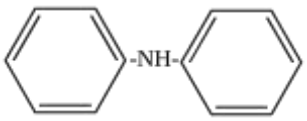
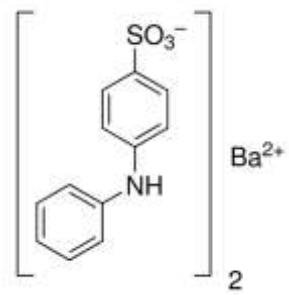
The fixing of the titration end-point in this method is carried out as follows:

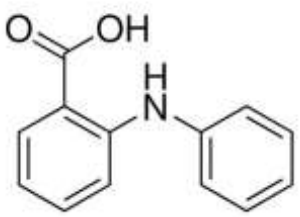
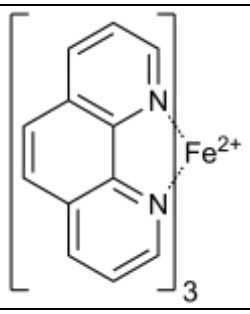
Without indicator - by the change in colour of the titrated solution when an excess of titrant is added (green to yellow-green transition of Cr^{3+}). The method is unreliable.

By instrumental methods - potentiometry.

With the use of redox indicators such as diphenylamine, phenylanthranilic acid, diphenylamine sulphonic acid, etc;

The most important indicators in dichromatometry

Indicator	Formula	Colouring	
		Reduced form	Oxidised form
Diphenylamine		Colourless	Violet
Diphenylamine sulphonates Na and Ba		Colourless	Blue

N-phenylanthranilic acid		Colourless	Purple-red
Ferroin (complex with Fe^{2+} 5,6- dimethyl-1,10-Phenanthroline)		Red	Yellow-green

Advantages and disadvantages of bichromatometry

Dichromatometry has some ***advantages***:

1. $K_2Cr_2O_7$ is easily obtained chemically pure by recrystallisation from an aqueous solution. A standard 0.1 n potassium dichromate solution can be prepared from an exact sample weight.
2. Potassium dichromate solution is very stable. It does not decompose even when boiling in an acidified solution. Because of this its titre does not change during storage.
3. Potassium dichromate titration can be carried out both in sulphuric acid and in hydrochloric acid solution, because dichromate does not react with chloride ions in cold conditions.

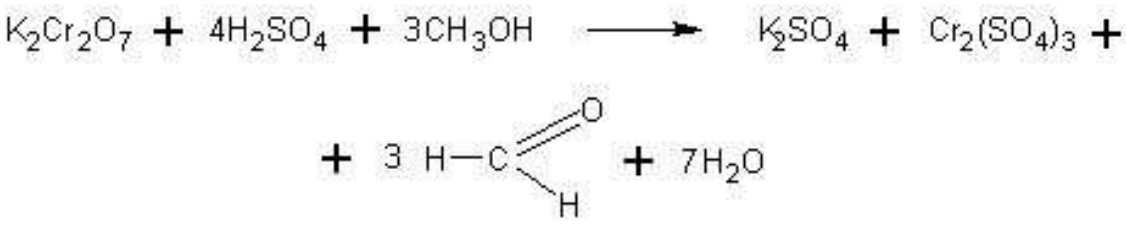
A ***disadvantage*** of the dichromatometric titration method is that the titration produces Cr3+ -ions which give the solution a green colour making it difficult to fix the equivalence point.

Application of dichromatometry in pharmaceutical analysis

The oxidation of most organic compounds by dichromate is too slow to be used for practical purposes. Exceptions are the dichromatometric determination of ethanol, methanol, ascorbic acid, glycerol and some other substances. Potassium dichromate is also widely used for the standardisation of other redox titrants, such as sodium thiosulphate.

Methanol assay

Methanol is analysed by heating it in sulphuric acid sulphuric acid.



Ethanol assay

The quantity of ethyl alcohol is also determined by a chemical method based on the oxidation of alcohol to acetaldehyde using a 0.1 M solution of potassium dichromate. The excess of the latter is determined by the iodometric method (indicator starch):