

**Ministry of Health of the Republic of Belarus
Educational institution
"Gomel State Medical University"**

Department of General and Bioorganic Chemistry

Author:

A.K. Dovnar, senior lecturer of the Department
of General and Bioorganic Chemistry

METHODOLOGICAL MANUAL

for conducting the laboratory class with the first-year students
of the Faculty of International Students
studying in the specialty 7-07-0911-01 "Medical business" (FIS)
English-speaking students
in the discipline "Medical chemistry"

Topic 5: REDOX TITRATION. PERMANGANATOMETRIC TITRATION

Time: 2 hours

Gomel, 2023

THE TRAINING AND EDUCATIONAL GOALS, MOTIVATION TO STUDY THE TOPIC

The purpose of the class:

To familiarize students with the theoretical basis of permanganatometry as one of the leading methods of oxidimetry, widely used in biomedical research.

The tasks of the class:

As a result of the class, the student *must know*:

- 1) general characteristics and classification of methods of redox titration (oxidimetry);
- 2) application of oxidimetry methods in clinical and biochemical investigations;
- 3) theoretical basis of the permanganatometric titration method: working solution (features of its preparation), standard solutions, determination of the accurate concentration of KMnO_4 in solution using oxalic acid solution as primary standard, autocatalytic nature of the reaction, fixing the equivalence point.

The student *must be able to*:

- 1) carry out non-indicator permanganatometric titration;
- 2) calculate the results of permanganatometric titration based on the Equivalent Law involving the rules of significant figures;
- 3) perform static treatment of experimental data.

Motivation to study the topic:

Redox processes play an important role in the metabolism and energy exchange occurring in humans and animals.

The use of redox reactions is the basis for many methods applied in quantitative analysis and commonly referred to as methods of redox titration (oxidimetry). In the practice of clinical, forensic research, as well as in the testing of pharmacological materials, methods of permanganatometry, iodometry, bromatometry, etc. have become widespread.

Permanganatometric titration is a method of redox titration based on potassium permanganate reduction in acidic medium. Due to the high value of the standard potential of potassium permanganate in acidic medium ($\varphi^0 (\text{MnO}_4^-|\text{Mn}^{2+}) = 1.51 \text{ V}$), it can be used to determine a wide range of substances that can be oxidized: sulfide, sulfite, nitrite, arsenide anions, Fe^{2+} cation, hydrazine, a number of organic acids.

NECESSARY EQUIPMENT

1. Methodological manual for students on the topic "Redox titration. Permanganatometric titration".
2. Reference materials of physico-chemical constants for the 1st year education international students.
3. Chemical reagents and equipment necessary for laboratory work.

CONTROL QUESTIONS ON THE TOPIC OF THE CLASS

1. General characteristics of redox titration methods.
2. Theoretical basis of the permanganatometric titration method.

COURSE OF THE CLASS

The theoretical part

1. GENERAL CHARACTERISTICS OF REDOX TITRATION METHODS

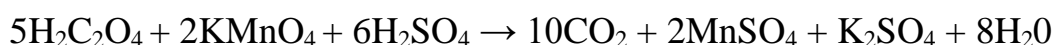
Redox titration methods are based on oxidation-reduction reactions between the analyte and titrant. Like in other titration methods, the quantitative determination of the analyzed component is carried out by accurately measuring the volumes of solutions entering into a chemical reaction with each other.

In oxidation-reduction titration method, a reducing substance is titrated with working solution of an oxidizing agent (*oxidative titration, oxidimetry*) or an oxidizing substance is titrated with the working solution of the reducing agent (*reducing titration, reductometry*). Since the working solutions of reducing agents are unstable due to oxidation in air, reducing titration is used less often.

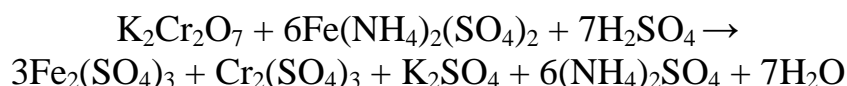
The analytical characteristics of redox methods are close to those of acid-base titration, but analysis often takes longer due to lower rates of redox reactions.

Redox titration methods can be classified depending on the titrant used. The main types include:

– *permanganate titration (permanganatometry)* is the type of redox titration uses potassium permanganate (KMnO_4) as the titrant and oxidizer. Its solution is used to estimate reducing agents including hydrogen peroxide, oxalic acid, ferrous salt, oxalates, and many more. It acts as self-indicator during the titration analysis. For example, during the titration between potassium permanganate and oxalic acid potassium permanganate becomes colourless at the end point:



– *dichromate titration (dichromatometry)* is the method of redox titration that uses oxidation reactions with potassium dichromate $\text{K}_2\text{Cr}_2\text{O}_7$. Although potassium dichromate is a weaker oxidizing agent than potassium permanganate it has several advantages. It can be used as a primary standard substance. Additionally, the solution of dichromate is quite stable. For example, determination of Fe^{2+} by using potassium dichromate:



– *iodimetric and iodometric titration (iodimetry and iodometry)* is the method of redox titration that uses oxidation reactions with iodine or reduction with iodide ions;

– *bromatometry* is the method of redox titration that uses oxidation reactions with potassium bromate KBrO_3 ; potassium bromate is usually used as the oxidizing agent for the determination of various pharmaceutical compounds;

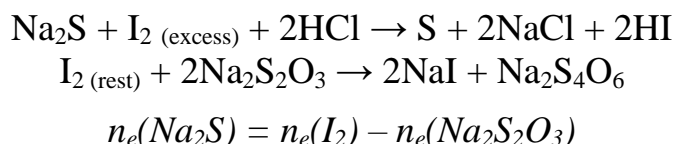
– *cerimetry* is a method that uses oxidation reactions with cerium (IV) sulfate $\text{Ce}(\text{SO}_4)_2$, etc.

The analytical possibilities of redox titration methods allow the determination of oxidants, reducing agents and substances that do not exhibit redox properties by themselves, but react with oxidants and reducing agents to form precipitates or complex compounds.

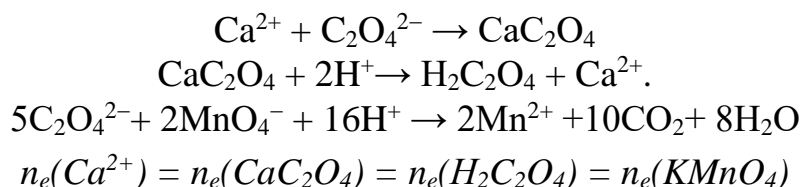
Depending on the analytical problem being solved, redoximetry uses direct, back and displacement titration.

Direct redox titration is carried out when the redox reaction meets the general requirements for reactions in titration analysis (reaction runs quickly, quantitatively, stoichiometrically, there is a possibility of fixing the equivalence point).

Back redox titration is carried out when the use of direct titration is impractical for one reason or another, for example, due to the low reaction rate. For example, when determining sulfides, an excess solution of I_2 is added (titrant 1), and then its rest amount is titrated with a solution of $Na_2S_2O_3$ (titrant 2):



Displacement redox titration can be used to determine substances that do not have redox properties. For example, when determining the content of Ca^{2+} , calcium ions are precipitated as a hardly soluble oxalate, acting with an excess of ammonium oxalate; the precipitate is separated from the solution, washed and dissolved in sulfuric acid; the resulting $H_2C_2O_4$ is titrated with a working solution of $KMnO_4$:



Determination of the endpoint of titration in the redox titration methods is carried out by a non-indicator method or using specific and redox indicators.

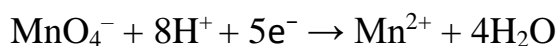
Non-indicator titration is used in cases where the oxidized and reduced forms of the working solution have different colors. For example, MnO_4^- (purple) – Mn^{2+} (colorless), I_2 (brown) – I^- (colorless). In this case, a small excess of the titrant after the equivalence point causes the appearance of color of the solution and titration is completed.

Specific indicators are substances that form intensely colored compounds with one of the components of the redox pair. For example, starch is a specific indicator for I_2 (a blue compound is formed), the thiocyanate ion CNS^- – for Fe^{3+} ions (a blood-red complex).

Redox indicators are organic compounds capable of oxidation and reduction, and their oxidized and reduced forms have different colors. These include, for example, diphenylamine and anthranilic acid [1-4].

2. THEORETICAL BASIS OF THE PERMANGANATOMETRIC TITRATION METHOD

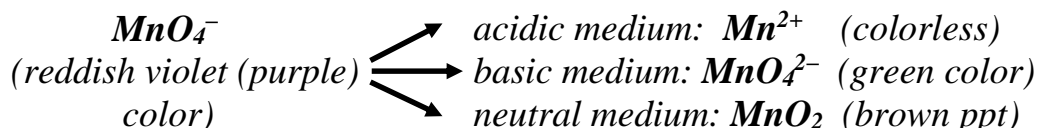
Permanganatometric titration is a method of redox titration based on potassium permanganate reduction in acidic medium according to the following half-reaction:



To create acidic medium, dilute H₂SO₄ solution is used, since HCl is a reducing agent (can react with KMnO₄), HNO₃ is an oxidizer (can react with the substance being determined).

The reddish violet color of KMnO₄ solution turns colorless at the endpoint of titration, so *no indicator* is required for analyses.

Potassium permanganate exhibits its oxidizing properties in all media: acidic, basic and neutral as well. The reduction products depend upon the medium:

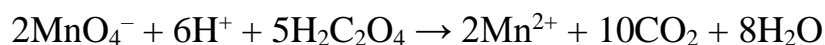
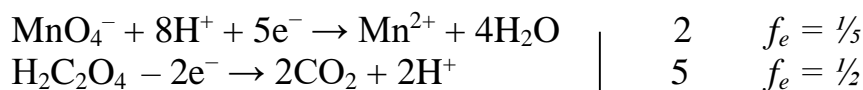
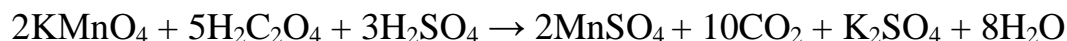


Permanganatometric titration is carried out in an acidic medium where MnO₄⁻ exhibits the strongest oxidizing properties; the value of its standard potential:

$$\varphi^0 (\text{MnO}_4^-|\text{Mn}^{2+}) = 1.51 \text{ V}$$

The KMnO₄ working solution is prepared in advance with an approximately known concentration, left for several days until MnO₂ (usually KMnO₄ contains traces of MnO₂ in the form of admixtures) is completely precipitated, and then the solution is thoroughly filtered. To determine the exact concentration of KMnO₄, standard solutions prepared from H₂C₂O₄·2H₂O (oxalic acid dihydrate) or Na₂C₂O₄ (sodium oxalate) are used.

Potassium permanganate in an acidic medium is quantitatively reduced by oxalic acid:



The considered reaction is *autocatalytic* and is catalyzed by one of the reaction products, i.e. by Mn²⁺ cations. Since the initial concentration of Mn²⁺ cations is negligible, the reaction rate is quite low. To speed up the process, titration is carried out in hot solutions. For this purpose, the solutions containing a mixture of oxalic and sulfuric acids should be heated to boiling point, but never boiled to avoid oxalic acid decomposition. Addition a new portion of a titrant should be done only after the previous portion becomes colorless.

Permanganatometric titration is widely used for medical and biological investigations. Determination of essential metals, some vitamins, hydrogen peroxide H₂O₂ and metal peroxides are illustrative examples of this type of volumetric analysis [1-4].

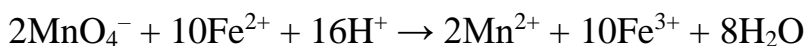
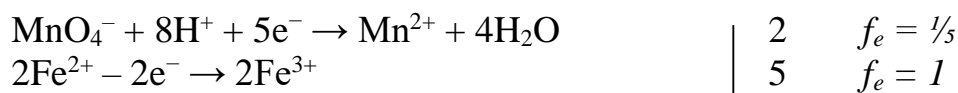
The practical part

Safety instructions before laboratory work.

LABORATORY WORK

Determination of Fe²⁺ mass in a test solution

1. Iron (Fe^{2+}) determination is based on the following redox reaction:



Carry out an experiment in the following sequence of operations:

- take the analyzed FeSO_4 solution of an unknown volume contained in a 50 ml volumetric flask and add distilled water up to the round mark to get the exact volume of the analyzed solution ($V_{\text{overall}} = 50 \text{ ml}$);
- take an analytical pipette and pour 10 ml of FeSO_4 solution into each flask for titration; treat the solutions with approximately 10 ml of sulfuric acid;
- pour KMnO_4 solution into the burette up to the zero mark;
- titrate FeSO_4 solution against KMnO_4 up to the endpoint *when colorless FeSO_4 solution turns reddish violet (purplish-pink) after one drop of a titrant addition*;
- repeat such titration two times starting from zero mark of burette; the results must not differ greatly from each other;
- fill in the table 1 below with the obtained data.

2. Table 1 – Iron (Fe^{2+}) mass determination in a test solution

Nº	$V(\text{Fe}^{2+})$, ml	$V(\text{KMnO}_4)$, ml	$C_N(\text{Fe}^{2+})$, mol/l	$T(\text{Fe}^{2+})$, g/ml	$m(\text{Fe}^{2+})$, g
1	10.0				
2	10.0				
3	10.0				

3. Calculation of the results of the experiment:

According to the Equivalent Law: $n_e(\text{KMnO}_4) = n_e(\text{Fe}^{2+})$

$$C_N(\text{KMnO}_4) \times V(\text{KMnO}_4) = C_N(\text{Fe}^{2+}) \times V(\text{Fe}^{2+})$$

$$\bullet C_N(\text{Fe}^{2+}) = \frac{C_N(\text{KMnO}_4) \times V(\text{KMnO}_4)}{V(\text{Fe}^{2+})}; \quad V(\text{Fe}^{2+}) = 10 \text{ ml}$$

$$\bullet T(\text{Fe}^{2+}) = \frac{C_N(\text{Fe}^{2+}) \times M_e(\text{Fe}^{2+})}{1000}; \quad M_e(\text{Fe}^{2+}) = 56 \text{ g/mol}$$

$$\bullet m(\text{Fe}^{2+}) = T(\text{Fe}^{2+}) \times V_{\text{overall}}(\text{Fe}^{2+}); \quad V_{\text{overall}}(\text{Fe}^{2+}) = 50 \text{ ml}$$

Sample 1:	Sample 2:	Sample 3:
$C_N(\text{Fe}^{2+})_1 = \frac{C_N(\text{KMnO}_4) \times V(\text{KMnO}_4)_1}{V(\text{Fe}^{2+})}$	$C_N(\text{Fe}^{2+})_2 = \frac{C_N(\text{KMnO}_4) \times V(\text{KMnO}_4)_2}{V(\text{Fe}^{2+})}$	$C_N(\text{Fe}^{2+})_3 = \frac{C_N(\text{KMnO}_4) \times V(\text{KMnO}_4)_3}{V(\text{Fe}^{2+})}$
$T(\text{Fe}^{2+})_1 = \frac{C_N(\text{Fe}^{2+})_1 \times M_e(\text{Fe}^{2+})}{1000}$	$T(\text{Fe}^{2+})_2 = \frac{C_N(\text{Fe}^{2+})_2 \times M_e(\text{Fe}^{2+})}{1000}$	$T(\text{Fe}^{2+})_3 = \frac{C_N(\text{Fe}^{2+})_3 \times M_e(\text{Fe}^{2+})}{1000}$
$m(\text{Fe}^{2+})_1 = T(\text{Fe}^{2+})_1 \times V_{\text{ov}}(\text{Fe}^{2+})$	$m(\text{Fe}^{2+})_2 = T(\text{Fe}^{2+})_2 \times V_{\text{ov}}(\text{Fe}^{2+})$	$m(\text{Fe}^{2+})_3 = T(\text{Fe}^{2+})_3 \times V_{\text{ov}}(\text{Fe}^{2+})$

4. Fulfill the statistic treatment of the experimental data:

4.1. The average value of Fe^{2+} mass:

$$\bar{m}(\text{Fe}^{2+}) = \frac{m_1 + m_2 + m_3}{3} = x.xxxx$$

4.2. The deviation from the average value:

$$d_1 = m_1 - \bar{m}(\text{Fe}^{2+}) = x.xxxx$$

$$d_2 = m_2 - \bar{m}(\text{Fe}^{2+}) = x.xxxx$$

$$d_3 = m_3 - \bar{m}(\text{Fe}^{2+}) = x.xxxx$$

4.3. Measurement variance (s^2) and measurement standard deviation (s):

$$s^2 = \frac{d_1^2 + d_2^2 + d_3^2}{n \times (n - 1)} = \quad s = \sqrt{s^2} =$$

4.4 Confidence interval: $\varepsilon_\alpha = t \times s = 4.30 \times s = x.xxxx$

(t is a Student's t -number; $t = 4.30$ for a 95 % confidence level and 3 of measurements)

4.5 The result of Fe^{2+} mass determination:

$$m(\text{Fe}^{2+}) = \bar{m}(\text{Fe}^{2+}) \pm \varepsilon_\alpha = x.xxxx \pm x.xxxx \text{ (g)}$$

Control over the assimilation of the topic

It is conducted in the form of written independent work of students.

QUESTIONS FOR SELF-CONTROL OF KNOWLEDGE

1. Classification of redox titration methods.
2. Theoretical basis of the permanganatometric titration method.
3. What is the difference between the course of the potassium permanganate reduction in an acidic medium and the course of this reaction in a basic (or neutral) medium and how is this difference explained? What are the equivalent molar masses of KMnO_4 in all cases?
4. Write the equations of reactions of potassium permanganate interaction with sodium sulfite in various media. Balance the redox reactions using the half-reaction method.
5. Why do the first drops of potassium permanganate solution slowly become colorless when oxalic acid is titrated, whereas in the future this discoloration occurs almost instantly? What can be done to instantly discolor the first drops of KMnO_4 ?

Exercises for the self – control

1. Complete the following redox reactions and balance them using the half-reaction method:

- a) $\text{H}_2\text{C}_2\text{O}_4 + \text{KMnO}_4 + \text{H}_2\text{SO}_4 \rightarrow \text{CO}_2 + \dots$
- b) $\text{H}_2\text{O}_2 + \text{KMnO}_4 + \text{H}_2\text{SO}_4 \rightarrow \text{O}_2 + \dots$
- c) $\text{K}_2\text{Cr}_2\text{O}_7 + \text{KI} + \text{H}_2\text{SO}_4 \rightarrow \text{Cr}_2(\text{SO}_4)_3 + \text{I}_2 + \dots$
- d) $\text{K}_2\text{Cr}_2\text{O}_7 + \text{KNO}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{Cr}_2(\text{SO}_4)_3 + \dots$

2. 2.5 g of hydrogen peroxide solution were diluted with water to 200 ml. To titrate 5.0 ml of the obtained solution in the acidic medium was used 20.0 ml of KMnO_4 solution

with normality 0.05 mol/l. What is the mass percent of H_2O_2 in the initial concentrated solution?

Answer: 27.2 %

3. For titration 25 ml of potassium permanganate solution with normality 0.05 mol/l in an acidic medium, 10.2 ml of sodium nitrite solution was used. Calculate the mass of sodium nitrate contained in 100 ml of the solution.

Answer: 0.423 g

4. To titrate 0.0244 g of $\text{H}_2\text{C}_2\text{O}_4 \times 2\text{H}_2\text{O}$ was used 19.5 ml of KMnO_4 solution. Calculate the normality of KMnO_4 in the solution.

Answer: 0.0199 mol/l

5. To titrate 25.0 ml 0.0500 N of KMnO_4 solution in the acidic medium was used 10.2 ml of sodium nitrite solution. How many grams of NaNO_2 are in 100 ml of its solution?

Answer: 0.4228 g

QUESTIONS FOR INDEPENDENT WORK OF STUDENTS (IWS)

1. Types of permanganatometric titration (direct, back, displacement) and their application in analytical practice.
2. The use of oxidimetry methods in clinical and biochemical investigations.

LIST OF SOURCES USED

1. Medical chemistry : textbook for students of higher education establishments – med. univ., inst. and acad. / V.O. Kalibabchuk, V.I. Halynska, L.I. Hryshchenko et al. ; ed. by V.O. Kalibabchuk. – 6th ed., corr. – Kyiv : AUS Medicine Publishing, 2018. – P. 103-107.

2. Основы химии для иностранных студентов = Essential chemistry for foreign students : учебно-методическое пособие / С. В. Ткачѳв [и др.]. – 5-е изд. – Минск : БГМУ, 2018. – 168 с. – Режим доступа: <http://rep.bsmu.by:8080/handle/BSMU/21054>.

3. Филиппова, В. А. Общая химия : учеб. пособие для студентов лечеб. факта, обуч. на англ. яз. : в 2 ч. = General Chemistry : Educational guidance for students medical department in English medium / В. А. Филиппова, А. В. Лысенкова, Л. В. Чернышева. – Гомель : ГомГМУ, 2009. – Ч. 1. – 192 с. URI: <https://elib.gsmu.by/handle/GomSMU/2679>.

4. Chang, Raymond. Chemistry / R. Chang. – 4th ed. – USA : University Science Books, 1991. – 1065 p.