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

Department of General and Bioorganic Chemistry

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

Topic 5: Redox titration. Permanganatometric titration

Time: 2 hours

Approved at the meeting of the Department
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THE TRAINING AND EDUCATIONAL GOAL, TASKS, MOTIVATION TO STUDY THE TOPIC

Training purpose:

– formation of students' basic professional competence to solve diagnostic, research and other tasks of professional activity based on knowledge about theoretical basis of permanganatometry as one of the leading methods of oxidimetry, widely used in biomedical research.

Educational goal:

– to develop your personal, spiritual potential;

– to form the qualities of a patriot and a citizen who is ready to actively participate in the economic, industrial, socio-cultural and social life of the country;

– learn to observe academic and labor discipline, the norms of medical ethics and deontology;

– to realize the social significance of their future professional activities.

Tasks:

As a result of the training session, the student should

know:

– general characteristics and classification of methods of redox titration (oxidimetry);

– application of oxidimetry methods in clinical and biochemical investigations;

– 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;

be able to:

– calculate the results of permanganatometric titration based on the Equivalent Law involving the rules of significant figures;

– perform static treatment of experimental data;

– solve computational problems in permanganometry;

possess:

– skills in preparing and standardization a solution of potassium permanganate of a certain concentration;

– skills of conducting non-indicator permanganatometric titration.

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 (φ^0 ($MnO_4^-|Mn^{2+}$) = 1.51 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.

The practical application of permanganometry is very diverse. Reducing agents are determined permanganometrically by direct titration, oxidants by reverse titration, and some substances that do not have redox properties by substitution titration. Permanganometry is used to determine the total oxidizability of water or soil. In biochemistry and in clinical analysis, the content of uric acid in urine, Ca^{2+} ions in blood serum, and blood sugar are determined by permanganometry. The main objects analyzed permanganatometric titration, among medicines, are solutions of hydrogen peroxide.

NECESSARY EQUIPMENT

1. Methodological manual for students on the topic "Redox titration. Permanganatometric titration".
2. Training tables:
a) Periodic Table of chemical elements by D.I. Mendeleev;
b) table of solubility of acids, bases and salts.
3. Reference materials of basic physico-chemical constants.
4. 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:

$$5H_2C_2O_4 + 2KMnO_4 + 6H_2SO_4 \rightarrow 10CO_2 + 2MnSO_4 + K_2SO_4 + 8H_20$$

– ***dichromate titration*** *(dichromatometry)* is the method of redox titration that uses oxidation reactions with potassium dichromate $K_2Cr_2O_7$. 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:

$$K_2Cr_2O_7 + 6Fe(NH_4)_2(SO_4)_2 + 7H_2SO_4 \rightarrow$$
$$3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + K_2SO_4 + 6(NH_4)_2SO_4 + 7H_2O$$

– ***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 $Ce(SO_4)_2$, 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):

$$Na_2S + I_{2\ (excess)} + 2HCl \rightarrow S + 2NaCl + 2HI$$
$$I_{2\ (rest)} + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6$$
$$n_e(Na_2S) = n_e(I_2) - n_e(Na_2S_2O_3)$$

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 $KMnO_4$:

$$Ca^{2+} + C_2O_4^{2-} \rightarrow CaC_2O_4$$
$$CaC_2O_4 + 2H^+ \rightarrow H_2C_2O_4 + Ca^{2+}.$$
$$5C_2O_4^{2-} + 2MnO_4^- + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$
$$n_e(Ca^{2+}) = n_e(CaC_2O_4) = n_e(H_2C_2O_4) = n_e(KMnO_4)$$

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:

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

To create acidic medium, dilute H_2SO_4 solution is used, since HCl is a reducing agent (can react with $KMnO_4$), HNO_3 is an oxidizer (can react with the substance being determined).

The reddish violet color of $KMnO_4$ 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:

MnO_4^- *(reddish violet (purple) color)* →
- *acidic medium:* ***Mn^{2+}*** *(colorless)*
- *basic medium:* ***MnO_4^{2-}*** *(green color)*
- *neutral medium:* ***MnO_2*** *(brown ppt)*

Permanganatometric titration is carried out in an acidic medium where MnO_4^- exhibits the strongest oxidizing properties; the value of its standard potential:

$$\varphi^0 (MnO_4^-|Mn^{2+}) = 1.51 \text{ V}$$

The $KMnO_4$ working solution is prepared in advance with an approximately known concentration, left for several days until MnO_2 (usually $KMnO_4$ contains traces of MnO_2 in the form of admixtures) is completely precipitated, and then the solution is thoroughly filtered. To determine the exact concentration of $KMnO_4$, standard solutions prepared from $H_2C_2O_4 \times 2H_2O$ (oxalic acid dihydrate) or $Na_2C_2O_4$ (sodium oxalate) are used.

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

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

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	2	$f_e = 1/5$
$H_2C_2O_4 - 2e^- \rightarrow 2CO_2 + 2H^+$	5	$f_e = 1/2$

$$2MnO_4^- + 6H^+ + 5H_2C_2O_4 \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

The considered reaction is *autocatalytic* and is catalyzed by one of the reaction products, i.e. by Mn^{2+} cations. Since the initial concentration of Mn^{2+} 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 H_2O_2 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 Fe^{2+} mass in a test solution

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

$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 \rightarrow 2MnSO_4 + 5Fe_2(SO_4)_3 + K_2SO_4 + 8H_2O$$

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O \quad | \quad 2 \quad f_e = 1/5$$

$$2Fe^{2+} - 2e^- \rightarrow 2Fe^{3+} \quad | \quad 5 \quad f_e = 1$$

$$2MnO_4^- + 10Fe^{2+} + 16H^+ \rightarrow 2Mn^{2+} + 10Fe^{3+} + 8H_2O$$

Carry out an experiment in the following sequence of operations:

a) 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_{overal} = 50 ml);

b) 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;

c) pour $KMnO_4$ solution into the burette up to the zero mark;

d) 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*;

i) repeat such titration two times stating from zero mark of burette; the results must not differ greatly from each other;

f) fill in the table 1 below with the obtained data.

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

№	$V(Fe^{2+})$, ml	$V(KMnO_4)$, ml	$C_N(Fe^{2+})$, mol /l	$T(Fe^{2+})$, g/ml	$m(Fe^{2+})$, g
1	10.0				
2	10.0				
3	10.0				

3. Calculation of the results of the experiment:

According to the Equivalent Law: $n_e(KMnO_4) = n_e(Fe^{2+})$

$$C_N(KMnO_4) \times V(KMnO_4) = C_N(Fe^{2+}) \times V(Fe^{2+})$$

• $C_N(Fe^{2+}) = \dfrac{C_N(KMnO_4) \times V(KMnO_4)}{V(Fe^{2+})}$; $V(Fe^{2+}) = 10$ ml

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

• $m(Fe^{2+}) = T(Fe^{2+}) \times V_{overal}(Fe^{2+})$; $V_{overal}(Fe^{2+}) = 50$ *ml*

Sample 1:	***Sample 2:***	***Sample 3:***
$C_N(Fe^{2+})_1 = \frac{C_N(KMnO_4) \times V(KMnO_4)_1}{V(Fe^{2+})}$	$C_N(Fe^{2+})_2 = \frac{C_N(KMnO_4) \times V(KMnO_4)_2}{V(Fe^{2+})}$	$C_N(Fe^{2+})_3 = \frac{C_N(KMnO_4) \times V(KMnO_4)_3}{V(Fe^{2+})}$
$T(Fe^{2+})_1 = \frac{C_N(Fe^{2+})_1 \times M_e(Fe^{2+})}{1000}$	$T(Fe^{2+})_2 = \frac{C_N(Fe^{2+})_2 \times M_e(Fe^{2+})}{1000}$	$T(Fe^{2+})_3 = \frac{C_N(Fe^{2+})_3 \times M_e(Fe^{2+})}{1000}$
$m(Fe^{2+})_1 = T(Fe^{2+})_1 \times V_{ov}(Fe^{2+})$	$m(Fe^{2+})_2 = T(Fe^{2+})_2 \times V_{ov}(Fe^{2+})$	$m(Fe^{2+})_3 = T(Fe^{2+})_3 \times V_{ov}(Fe^{2+})$

4. Fulfill the statistic treatment of the experimental data:

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

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

4.2. The deviation from the average value:

$$d_1 = m_1 - \overline{m}\left(Fe^{2+}\right) = x.xxxx$$
$$d_2 = m_2 - \overline{m}\left(Fe^{2+}\right) = x.xxxx$$
$$d_3 = m_3 - \overline{m}\left(Fe^{2+}\right) = x.xxxx$$

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

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

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:

$m(Fe^{2+}) = \overline{m}\left(Fe^{2+}\right) \pm \varepsilon_\alpha = x.xxxx \pm x.xxxx$ *(g)*

Control over the assimilation of the topic

It is conducted in the form of an oral conversation with students.

METHODOLOGICAL RECOMMENDATIONS FOR THE ORGANIZATION AND PERFORMING OF INDEPENDENT WORK OF STUDENT (IWS)

The time allotted for independent work can be used by students for:

– preparation for laboratory classes;
– taking notes of educational literature;
– performing tasks for self-control of knowledge;
– preparation of thematic reports, abstracts, presentations.

The main methods of organizing independent work:

– studying topics and problems that are not covered in the classroom;

– writing an abstract and making a presentation;
– performing tasks for self-control of knowledge.

List of tasks of IWS:

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

a) $H_2C_2O_4 + KMnO_4 + H_2SO_4 \rightarrow CO_2 + \ldots$
b) $H_2O_2 + KMnO_4 + H_2SO_4 \rightarrow O_2 + \ldots$
c) $K_2Cr_2O_7 + KI + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + I_2 + \ldots$
d) $K_2Cr_2O_7 + KNO_2 + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + \ldots$

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

The control of the IWS is carried out in the form of:
– evaluation of an oral answer to a question, message, report or presentation;
– individual conversation.

LIST OF SOURCES USED

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