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Zaporizhzhia State Medical and Pharmaceutical University
Department of Physical, Colloid and Analytical Chemistry

ANALYTICAL CHEMISTRY
COLLECTION OF TESTS WITH EXPLANATIONS
«KROK 1. PHARMACY»

Study guide
for 2-nd year students of
Speciality «Pharmacy, Industrial Pharmacy»

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PREFACE

Analytical Chemistry is studied according to the model curriculum approved by the Ministry of Health of Ukraine on April 19, 2017, and on the basis of the working academic plan approved by the Academic Council of ZDMPhU (Protocol No. 11 of May 28, 2024), and the working program of the academic discipline «Analytical Chemistry» from 2024.

The relevance and expediency of this study guide are due to the change in the structure of the KROK 1 licensure examination, Pharmacy.

This study guide contains material that ensures the acquisition of general and professional competencies and program learning outcomes. The tests were taken from the official database of the testing center.

According to the curriculum, analytical chemistry is studied in the III and IV semesters.

Analytical chemistry as an academic discipline is based on knowledge of inorganic chemistry, physics and mathematics and integrates with organic, pharmaceutical, toxicological, physicochemical and biological chemistry; lays the foundations for the study of pharmaceutical and toxicological chemistry and provides for the formation of skills in the application of acquired knowledge for the study of special disciplines and in professional activities.

The collection of tests covers all sections of analytical chemistry, namely «Qualitative analysis», «Quantitative analysis», «Instrumental methods of analysis», and is designed to prepare students for the integrated test exam «STEP 1. Pharmacy», which is a test component of the Unified state qualification exam for holders of a master's degree in the field of knowledge «Health care».

QUALITATIVE ANALYSIS

**Chemistry of the Ist analytical group cations
(acid-base classification)**

Acid-base classification is based on using aqueous solutions of acids and bases as group reagents. Cations detected according to the acid-base classification are divided into six analytical groups.

Acid-base classification of cations

| Group | Cations | Group reagent |
|-----------------|--|---|
| I (soluble) | K^+ , Na^+ , NH_4^+ | No |
| II (chloride) | Ag^+ , Hg_2^{2+} , Pb^{2+} | 2 M solution HCl |
| III (sulphate) | Ca^{2+} , Ba^{2+} , Sr^{2+} | 1 M solution H_2SO_4 |
| IV (ampholytic) | Al^{3+} , Cr^{3+} , Zn^{2+} , As^{III} , As^V , Sn^{2+} , Sn^{IV} | 2 M solution NaOH in the presence H_2O_2 |
| V (hydroxide) | Mg^{2+} , Mn^{2+} , Fe^{2+} , Fe^{3+} , Bi^{3+} , Sb^{III} , Sb^V | 2 M solution NaOH or 25 % solution NH_4OH |
| VI (ammonia) | Cu^{2+} , Cd^{2+} , Hg^{2+} , Co^{2+} , Ni^{2+} | 25 % solution NH_4OH |

K^+ , Na^+ , NH_4^+ form compounds with the ionic type of the chemical bond and most of them are readily soluble in water. Therefore, the Ist analytical group cations have no group reactant.

1. A solution being analyzed contains ammonium and sodium cations. What reagent can detect sodium cations in this solution?
 - A. Potassium oxalate
 - B. Uranyl zinc acetate*
 - C. Potassium hydrotartrate
 - D. Potassium tetraiodomercurate(II)
 - E. Potassium benzoate

2. Reaction of sodium ions with potassium hexahydroxoantimonate (V) in neutral medium produces precipitate. Specify the color of this precipitate:
- A. White *
 - B. Blue
 - C. Green
 - D. Red
 - E. Yellow
3. Microcrystalloscopy reaction for detecting potassium ions is the following one:
- A. With sodium hydrotartrate
 - B. With sodium tetraphenylborate
 - C. With sodium hexanitrocobaltate
 - D. With sodium lead (II) hexanitrocuprate *
 - E. Flame colour test
4. In order to bind hydrogen ions with tartaric acid during identification of potassium ions the following solution is used:
- A. Sodium acetate *
 - B. Ammonia
 - C. Sulfuric acid
 - D. Hydrochloric acid
 - E. Sodium hydroxide
5. Ammonium ions (NH_4^+) must be removed from a mixture during the detection of sodium (Na^+) and potassium (K^+) cations of the first analytical group. Why is it necessary?
- A. The solution pH becomes >7 , because of hydrolysis of these ions
 - B. The solution pH becomes <7 , because of hydrolysis of these ions
 - C. They interfere with the determination of potassium and sodium ions *
 - D. Compounds with K^+ and Na^+ ions form supersaturated solutions
 - E. Ammonium salts decompose at high temperatures

6. Sodium hexanitrocobaltate(III) is used to determine the presence of potassium cations in a solution. What visual analytical effect is observed in this case?
- A. Formation of a white precipitate
 - B. Formation of a yellow precipitate *
 - C. Formation of a blue precipitate
 - D. Formation of a violet precipitate
 - E. Formation of a black precipitate
7. What cation is present in the solution, if its heating with an alkali produces a gas with pungent odor?
- A. Lead(II)
 - B. Silver(I)
 - C. Mercury(II)
 - D. Ammonium*
 - E. Mercury(I)
8. If addition of an alkali solution and heating provokes the release of ammonia in an analyzed solution, it indicates that the analyzed solution contains the following ions:
- A. NH_4^{+} *
 - B. Na^{+}
 - C. NO_3^{-}
 - D. K^{+}
 - E. NO_2^{-}
9. One of the cations of the 1st group hinders detection of the others. Therefore, it should be detected first and then extracted. Name this cation:
- A. Ca^{2+}
 - B. Na^{+}
 - C. K^{+}
 - D. Li^{+}
 - E. NH_4^{+} *

10. Specific reactions used in qualitative analysis make it possible to:

- A. Detect only anions
- B. Detect only cations
- C. Detect an ion without previous separation of other ions *
- D. Detect an ion with previous separation
- E. Detect only a certain group of ions

11. Name the reactions and reagents that under certain conditions allow determination of certain ions in the presence of other ions:

- A. Characteristic
- B. Specific*
- C. General
- D. Selective
- E. Group

12. An alkali was added into the solution being analyzed. When heated, the solution produced a gas. This gas changes the color of a moist litmus paper from red to blue, which indicates the presence of the following ions in the solution:

- A. Cl^-
- B. Pb^{2+}
- C. Bi^{3+}
- D. CO_3^{2-}
- E. NH_4^{+*}

13. What reagent must be used for identification of sodium cations in a sodium thiosulfate substance according to the regulations of the State Pharmacopoeia of Ukraine, second edition?

- A. Silver nitrate
- B. Barium chloride
- C. Ammonium oxalate
- D. Potassium pyroantimonate *
- E. Potassium hexacyanoferrate (III)

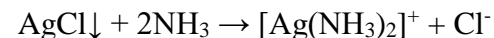
Chemistry of the II^d analytical group cations (acid-base classification)

The second analytical group includes silver Ag^+ , mercury(I) Hg_2^{2+} , and lead Pb^{2+} cations. The group reagent for the second analytical group cations is an aqueous hydrochloric acid. The group reagent precipitates the second analytical group cations from aqueous solutions in the form of silver AgCl , mercury(I) Hg_2Cl_2 , and lead Pb_2Cl_2 precipitates.

The precipitates of chlorides of the IInd analytical group cations are partially dissolved in the excess of concentrated hydrochloric acid with complex ions: $[\text{AgCl}_2]^-$, $[\text{HgCl}_3]^-$, $[\text{PbCl}_3]^-$.

Lead (II) chloride has the highest solubility among chlorides of the IInd analytical group cations, therefore, it is completely dissolved in hot water.

Silver chloride as opposed to mercury (I) chloride is dissolved in ammonia solution.



Mercury (I) chloride become black in ammonia solution owing to formation of fine-dispersed metallic mercury:



1. In the process of silver cations identification reaction HCl and then ammonia solution have been added to the solution. What compound has been produced as a result?
 - A. $[\text{Ag}_2(\text{NH}_3)_3]\text{Cl}$
 - B. AgCl
 - C. $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$ *
 - D. $[\text{Ag}(\text{NH}_3)_3]\text{Cl}$
 - E. AgOH
2. To determine the qualitative content of a drug, a sample of the analyte solution was processed with 2M solution of HCl. A white

precipitate, soluble in aqueous ammonia solution, was formed. This analytical effect indicates of the presence of the following cations:

- A. Mercury(II) cations
- B. Tin(II) cations
- C. Silver(I) cations *
- D. Lead(II) cations
- E. Mercury(I) cations

3. In order to carry out the silver cations identification, HCl was added to the solution. Later, the formed solution was followed by adding the solution of ammonia. Specify which of the below-mentioned compounds are formed in such case?

- A. AgCl
- B. $[\text{Ag}_2(\text{NH}_3)_3]\text{Cl}$
- C. $[\text{Ag}(\text{NH}_3)_3]\text{Cl}$
- D. AgOH
- E. $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$ *

4. A solution of an alkali was added into the analyte solution and the resulting solution was heated. In the process, a black precipitate formed and a pungent-smelling gas was released. It indicates the presence of the following in the solution:

- A. Ammonium and mercury(II) ions
- B. Ammonium and calcium ions
- C. Ammonium and mercury(I) ions*
- D. Ammonium and stanium(II) ions
- E. Ammonium and lead(II) ions

5. In the process of systematic analysis there is a need to separate PbSO_4 from mixture of the 3rd analytical group cation sulphates. Which of the following suits most towards this end?

- A. Processing precipitate with acetate acid solution
- B. Processing precipitate with ammonia solution
- C. Precipitate recrystallization

- D. Processing precipitate with 30% ammonium acetate solution *
- E. Processing precipitate with concentrated sulfate acid
6. A 2 M solution of HCl was added into the studied solution, resulting in formation of a white precipitate that dissolved when heated. What cations are present in the solution?
- A. Pb^{2+} *
 - B. Ba^{2+}
 - C. Mg^{2+}
 - D. Hg_2^{2+}
 - E. Ag^+
7. To identify iodide ions in a solution, a reaction with lead cations was conducted. The obtained precipitate was dissolved in water by means of heating; afterwards the test glass was cooled. What analytical effect could be observed in the process?
- A. Brown precipitate
 - B. Golden scales *
 - C. Blue precipitate
 - D. White precipitate
 - E. Gas bubbles
8. To determine a certain second group cation, the «golden rain» reaction is used with slow cooling of the preheated reagents. What reaction product is formed during the slow precipitation?
- A. AgI
 - B. PbI_2 *
 - C. Hg_2I_2
 - D. PbCl_2
 - E. HgI_2
9. Hydrochloric acid was added into the solution under investigation. The resulting precipitate was filtered, then this filter cake was processed with hot water; after the filtrate cooled,

KI solution was added into it. What cation was present in the solution, if the precipitate was colored yellow?

- A. Ca^{2+}
- B. Ag^+
- C. Ba^{2+}
- D. Hg^{2+}
- E. Pb^{2+*}

Chemistry of the III^d analytical group cations (acid-base classification)

The third analytical group includes calcium Ca^{2+} , strontium Sr^{2+} , and barium Ba^{2+} cations. The group reagent for cations of the III^d analytical group is 1 M solution of H_2SO_4 in the presence of ethanol providing cations precipitation as sulphates. The third analytical group cations are precipitated by the group reagent in the form of calcium CaSO_4 , strontium SrSO_4 , and barium BaSO_4 sulfate precipitates, which are slightly soluble in water.

The further analysis of the III^d analytical group cations is based on transformation of the precipitates of sulphates cations of this group into carbonates, solubility of these carbonates in CH_3COOH solution and on using different precipitation reactions for determining barium, calcium and strontium ions.

Solubility product of calcium sulfate is not very low; calcium cations are partially precipitated by the group reagent from the aqueous solution in the form of calcium sulfate precipitate, while some calcium Ca^{2+} ions remain in the solution. Ethanol, which decreases calcium sulfate solubility, is added to the analyzed solution to achieve more complete calcium cations precipitation in the form of calcium sulfate by the action of the group reagent.

1. The third analytical group of cations (acid-base classification) includes Ca^{2+} , Sr^{2+} , Ba^{2+} . What acid can function as a precipitator agent (group reagent) for these cations?
 - A. HCl
 - B. H_2SO_4 *
 - C. HNO_3
 - D. HClO_4
 - E. CH_3COOH
2. In the qualitative analysis which involves precipitation of sulphates of the third analytical group cations (Ca^{2+} , Sr^{2+} , Ba^{2+}) the solubility of sulphates can be reduced by adding:

- A. Amyl alcohol
- B. Chloroform
- C. Benzene
- D. Distilled water
- E. Ethyl alcohol*

3. The researcher while conducting the qualitative analysis that involves sulfates precipitation of the third analytical group cations (Ca^{2+} , Sr^{2+} , Ba^{2+}) has to reduce solubility of sulfates. What substance should be used for this purpose?

- A. Chloroform
- B. Amyl alcohol
- C. Benzene
- D. Ethyl alcohol *
- E. Distilled wated

4. Calcium cations can be used as components of pharmaceuticals. Pharmacopoeial reaction for the detection of calcium cations is a reaction with a solution of:

- A. Sodium hydroxide
- B. Ammonium hydroxide
- C. Potassium iodide
- D. Hydrochloric acid
- E. Ammonium oxalate*

5. A solution being analyzed contains calcium chloride and sodium bromide. What solution must be added to the solution being analyzed, to identify the calcium ions?

- A. Barium chloride
- B. Potassium iodide
- C. Sodium chloride
- D. Ammonium oxalate *
- E. Ammonium acetate

6. Gypsum water is added to a test solution for analytical determination of barium ions. What visual effect is observed in this case?
- A. Production of a brown gas
 - B. Yellow coloring of the solution
 - C. Formation of a white precipitate *
 - D. A characteristic odor appearing
 - E. Formation of a blue precipitate
7. A potassium chromate solution was added into the solution being analyzed, which resulted in the formation of a yellow precipitate, soluble in acetic acid. What cations were present in the solution, as indicated by this qualitative reaction?
- A. Sodium cations
 - B. Magnesium cations
 - C. Ammonium cations
 - D. Potassium cations
 - E. Strontium cations *
8. When dividing cations into analytical groups according to the acid-base classification, the group reagents can be acids or bases. What acids are used as group reagents?
- A. H_2CO_3
 - B. HNO_3 , CH_3COOH
 - C. H_3PO_4 , $\text{H}_2\text{C}_2\text{O}_4$
 - D. HCl , H_2SO_4^*
 - E. HClO_4
9. A heated nichrome wire was immersed in the solution that is being studied and then placed in the flame of a gas burner. The flame colored yellow-green as a result. What cations are present in the solution?
- A. Potassium cations
 - B. Sodium cations
 - C. Calcium cations

D. Ammonium cations

E. Barium cations*

Chemistry of the IVth analytical group cations (acid-base classification)

The fourth analytical group includes aluminum Al^{3+} , chromium Cr^{3+} , zinc Zn^{2+} , arsenic As^{3+} and As^{5+} , tin Sn^{2+} and Sn^{4+} cations. The group reagent is an aqueous sodium hydroxide NaOH (or potassium KOH) solution in the presence of hydrogen peroxide H_2O_2 . The fourth analytical group cations are precipitated by the group reagent from an aqueous solution in the form of amphoteric hydroxides, soluble in excess alkali with the formation of hydroxocomplexes.

The presence of H_2O_2 promotes the formation of hydroxoanions and oxoanions of these elements with the highest degree of oxidation. Under these conditions the cations of the Vth and VIth analytical groups are precipitated as hydroxides, but hydroxoanions and oxoanions of the IVth analytical group remain in the solution. These anions can be hydrolysed, but to different degree that is used in the systematic course of analysis for the separation of $[\text{Al}(\text{OH})_6]^{3-}$ and $[\text{Sn}(\text{OH})_6]^{2-}$ ions as respective hydroxides.

Under the action of the group reagent at first the precipitates of hydroxides cations are formed white precipitates, except $\text{Cr}(\text{OH})_3 \downarrow$ (green).

1. A chemist-analyst performs a qualitative analysis of group IV cations. Why is a 3% hydrogen peroxide solution added in the process?
 - A. Conversion of ions to a lower degree of oxidation
 - B. Gas removal
 - C. Formation of colored compounds
 - D. Sediment formation
 - E. Conversion of ions to a higher degree of oxidation *
2. During the analysis of the cations that belong to the fourth analytical group (acid-base classification), their processing with a

group reagent makes it possible not only to separate, but also to identify the following ions:

- A. Cr(III) ions *
- B. As(III) ions
- C. Sn(IV) ions
- D. Al(III) ions
- E. Zn(II) ions

3. What reaction must be conducted by an analytical chemist during the preliminary tests to determine chromium(III) ions?

- A. Reaction with sodium hydroxide and hydrogen peroxide
- B. Reaction with potassium permanganate
- C. Reaction with sodium hydroxide
- D. Reaction with ammonia
- E. Reaction for formation of a perchromic acid after preliminary oxidation of chromium *

4. A characteristic reaction between sodium sulfide and the salts of an unknown cation has produced a white precipitate. What cation was it?

- A. Zinc *
- B. Lead
- C. Copper
- D. Mercury
- E. Magnesium

5. Pharmacopoeia reaction of potassium ferrocyanide with zinc cations produces:

- A. Red precipitate
- B. Black precipitate
- C. White precipitate *
- D. Yellow precipitate
- E. Violet precipitate

6. An analytical chemist conducts qualitative analysis of IV group cations. What reagent can be used to determine zinc?
- A. Murexide
 - B. Thiourea
 - C. Dithizone *
 - D. Alizarin
 - E. Diphenylamine
7. A dithizone solution was added into the studied alkaline solution of cations that belong to the IV analytical group. As a result, a compound formed that was coloring not only the organic but also the aqueous phase in red. What cations are present in the solution, as indicated by this analytical effect?
- A. Bi^{3+}
 - B. Fe^{3+}
 - C. Zn^{2+*}
 - D. Cr^{3+}
 - E. Al^{3+}
8. In order to identify the cations of zinc (II) an analytical chemist used the reagent solution of hexacyanoferrate (II) potassium (Pharmacopeia reaction). What colour would the precipitate have in this reaction?
- A. Black
 - B. Green
 - C. Yellow
 - D. Red
 - E. White*

Chemistry of the V analytical group cations (acid-base classification)

The fifth analytical group includes magnesium Mg^{2+} , manganese Mn^{2+} , iron Fe^{2+} and Fe^{3+} , antimony Sb^{3+} and Sb^{5+} , bismuth(III) Bi^{3+} cations. The group reagent is an aqueous alkali solution, or 25% aqueous ammonia solution. The group reagent precipitates the fifth analytical group cations from an aqueous solution in the form of $\text{Mg}(\text{OH})_2$, $\text{Mn}(\text{OH})_2$, $\text{Fe}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$, $\text{Sb}(\text{OH})_3$, $\text{SbO}(\text{OH})_3$, $\text{Bi}(\text{OH})_3$ hydroxides. The fifth analytical group, cations hydroxides are insoluble in excess of the group reagent, in contrast to the fourth analytical group cations.

The further course of analysis of the Vth analytical group cations is based on different solubility of these cations hydroxides in the concentrated solutions of ammonium salts, acids, as well as on using different oxidation-reduction reactions and reactions of these cations precipitation.

Compounds of iron(III)-cation are of a yellow-brown colour, and iron(II)-cation are of a light-green colour; the compounds of other cations are of a white colour, but their solutions are colourless.

1. Ammoniacal buffer and 8-oxyquinoline solution were added into the solution containing cations of the V analytical group, which resulted in production of a green-yellow precipitate. What cations were in the solution?
 - A. Iron(II).
 - B. Manganese.
 - C. Calcium.
 - D. Magnesium.*
 - E. Ammonium.
2. Crystalline lead(IV) dioxide in the presence of concentrated nitric acid is used to detect the presence of manganese(II) cations in a solution. What visual analytical effect is observed in the process?
 - A. A blue precipitate is formed

- B. The solution colors pink *
 - C. The solution colors yellow
 - D. The solution colors green
 - E. A white precipitate is formed
3. In the process of systematic analysis of a cation mixture, iron(III) cations can be determined using the fractional method. What reagent is used for this purpose?
- A. Nitric acid
 - B. Sodium dihydrogen phosphate
 - C. Potassium hexacyanoferrate(II) *
 - D. Potassium chloride
 - E. Hydrochloric acid
4. What cations of the fifth analytical group (acid-base classification) form colored hydroxides when precipitated with a group reagent?
- A. Ca^{2+} , Ba^{2+}
 - B. Ag^+ , Al^{3+}
 - C. Fe^{2+} , Fe^{3+} *
 - D. Sn^{2+} , Sb^{2+}
 - E. Na^+ , K^+
5. Name the method of binding foreign ions in an analysis:
- A. Analytical coprecipitation
 - B. Analytical separation
 - C. Analytical concentration
 - D. Analytical masking*
 - E. Analytical extraction
6. Ammonium thiocyanate solution was added into the solution being studied. The resulting solution colored red. This analytical effect indicates the presence of the following cation:
- A. Mercury(I)
 - B. Mercury(II)

C. Iron(III) *

D. Silver

E. Lead(II)

9. What cation of the V analytical group (acid-base classification) is present in the solution, if a black precipitate is produced when tin(II) chloride dissolved in an alkaline medium is added into this solution?

A. Bismuth(III)*

B. Antimony(III)

C. Iron(II)

D. Manganese(II)

E. Iron(III)

Chemistry of the VIth analytical group cations (acid-base classification)

The sixth analytical group includes copper(II) Cu^{2+} , cadmium Cd^{2+} , mercury(II) Hg^{2+} , cobalt(II) Co^{2+} , and nickel(II) Ni^{2+} cations. The group reagent is 25% aqueous ammonia solution. Initially, the action of the group reagent on aqueous solutions comprising the sixth analytical group cations leads to the precipitation of various compositions, which dissolved in an excess of the group reagent.

Detection of the VIth analytical group cations is based on using complex formation and oxidation-reduction reactions. All cations of the VIth analytical group (except Hg^{2+} -cations) are coloured and form coloured compounds.

1. Potassium iodide solution has been added to the solution containing cations of the sixth analytical group (acid-base classification). It resulted in the red precipitate soluble in excess of reagent. What cations are present in the solution?
 - A. Cadmium
 - B. Cobalt (II)
 - C. Bismuth
 - D. Nickel
 - E. Mercury (II) *
2. An analytical chemist performs a qualitative analysis of cations that belong to the 6th analytical group. If nickel ions are processed with Chugaiev's reagent (dimethylglyoxime), a colored substance is produced. What is the color of the resulting substance?
 - A. Violet
 - B. Green
 - C. Red *
 - D. Yellow
 - E. Blue

3. What cation can be detected with Chugaiev's agent (Dimethylglyoxime)?
- A. Co^{2+}
 - B. Ca^{2+}
 - C. Mn^{2+}
 - D. Ni^{2+} *
 - E. K^+
4. The mixture being studied contains Mg^{2+} , Ni^{2+} , Hg^{2+} cations. What reagent allows to detect Ni^{2+} cations in the mixture?
- A. 1-Nitroso-2-naphthol
 - B. Ammonia solution
 - C. Dimethylglyoxime *
 - D. Alizarin
 - E. Magneson I (Azo violet)
5. A chemical analytical laboratory uses a reaction with dimethylglyoxime to identify nickel cations. What will be the color of the precipitate that forms as a result of this reaction?
- A. White
 - B. Green
 - C. Blue
 - D. Red *
 - E. Yellow

Anions

In a pharmaceutical analysis, a systematic analysis of anions mixtures is never performed using any classifications. The anions are detected by the fractional method using one or another particular analytical reaction to the corresponding anion.

Table 1
Classification of anions based on formation of slightly soluble barium and silver salts

| Group | Anions | Group reagent |
|-------|--|---|
| I | SO_4^{2-} , SO_3^{2-} , $\text{S}_2\text{O}_3^{2-}$, PO_4^{3-} , $\text{B}_4\text{O}_7^{2-}$, CO_3^{2-} , $\text{C}_2\text{O}_4^{2-}$, AsO_4^{3-} , AsO_3^{3-} , $\text{C}_4\text{H}_4\text{O}_6^{2-}$, $\text{C}_6\text{H}_5\text{O}_7^{3-}$, CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$, F^- etc. | BaCl_2 solution in a neutral or slightly alkaline medium |
| II | Cl^- , Br^- , I^- , S^{2-} , CN^- , SCN^- , $\text{C}_6\text{H}_5\text{COO}^-$ etc. | AgNO_3 solution in 2 M HNO_3 |
| III | NO_3^- , NO_2^- , BrO_3^- , CH_3COO^- , $\text{C}_6\text{H}_4\text{OHCOO}^-$, MnO_4^- etc. | absent |

Table 2
Classification of anions based on the redox properties

| Group | Anions | Group reagent |
|-----------------|--|--|
| Oxidizing agent | BrO_3^- , AsO_4^{3-} , $^*\text{NO}_2^-$, NO_3^- , MnO_4^- , CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$ | KI solution in sulfate medium |
| Reducing agent | S^{2-} , SO_3^{2-} , $\text{S}_2\text{O}_3^{2-}$, AsO_3^{3-} | I_2 solution in KI |
| | S^{2-} , SO_3^{2-} , $\text{S}_2\text{O}_3^{2-}$, AsO_3^{3-} , $^*\text{NO}_2^-$, $\text{C}_2\text{O}_4^{2-}$, Cl^- , Br^- , I^- , CN^- , SCN^- | KMnO_4 solution in sulfate medium |
| Indifferent | SO_4^{2-} , CO_3^{2-} , PO_4^{3-} , $\text{B}_4\text{O}_7^{2-}$, CH_3COO^- | absent |

$^*\text{NO}_2^-$ ions have redox-amphoteric properties. There is also a group of anions, which under the action of mineral acids decompose with the release of gaseous or volatile substances: SO_3^{2-} , $\text{S}_2\text{O}_3^{2-}$, CO_3^{2-} , NO_2^- , CH_3COO^- .

Chemistry of the I⁺ analytical group anions
(classification of anions based on formation of slightly soluble
barium and silver salts)

The first group includes anions which form slightly soluble salts in water (neutral or slightly alkaline medium) with barium cations Ba^{2+} . The group reagent is usually an aqueous solution of barium chloride BaCl_2 . Table 1 includes 14 anions of the first group: sulfate anion SO_4^{2-} , sulfite anion SO_3^{2-} , thiosulfate anion $\text{S}_2\text{O}_3^{2-}$, phosphate anion (orthophosphate anion) PO_4^{3-} , tetraborate anion $\text{B}_4\text{O}_7^{2-}$ (metaboric acid anions BO_2^- are also included here), carbonate anion CO_3^{2-} , oxalate anion $\text{C}_2\text{O}_4^{2-}$, arsenate anion AsO_4^{3-} , arsenite anion AsO_3^{3-} , tartrate anion $\text{C}_4\text{H}_4\text{O}_6^{2-}$, citrate anion $\text{C}_6\text{H}_5\text{O}_7^{3-}$, chromate anion CrO_4^{2-} , dichromate anion $\text{Cr}_2\text{O}_7^{2-}$, fluoride anion F^- .

1. Classification of anions is based on different solubility of their salts with Ba^{2+} and Ag^+ ions. Anions of the 1st analytical group form salts poorly soluble in water with the following ions:
 - A. Ag^+ (acid medium)
 - B. Ba^{2+} (alkaline or neutral medium) *
 - C. Ag^+ (alkaline medium)
 - D. Ag^+ (neutral medium)
 - E. Ag^+ (ammonia buffer medium)

2. Silver nitrate solution has been added to the solution containing anions of the first analytical group. It resulted in yellow precipitate. That means the following are present in the solution:
 - A. Bromide ions
 - B. Iodide ions
 - C. Sulphate ions
 - D. Arsenite ions *
 - E. Arsenate ions

3. Silver nitrate solution was added into a solution with anions of the first analytical group. A yellow precipitate was produced as the result, which indicates that this solution contained:
- A. Arsenate ions
 - B. Bromide ions
 - C. Arsenite ions *
 - D. Sulfate ions
 - E. Iodide ions
4. What reaction is the common reaction for detection of arsenic(III) and arsenic(V) compounds?
- A. Reaction of reduction to arsine*
 - B. Reaction with ammonium molybdate
 - C. Reaction with sodium nitrate
 - D. Reaction with iodine
 - E. Reaction with potassium iodide
5. Phosphate anions and arsenate anions form similar precipitates insoluble in an ammonia solution during their reaction with:
- A. Lead acetate solution
 - B. Cobalt sulfate solution
 - C. Sodium hydroxide solution
 - D. Nessler's reagent
 - E. Magnesia mixture (a solution containing MgCl_2 , NH_4Cl , NH_3)*

Chemistry of the IInd analytical group anions
(classification of anions based on formation of slightly soluble barium and silver salts)

The second group includes anions which form slightly soluble silver salts with silver cations Ag^+ in diluted aqueous solutions of nitric acid HNO_3 . The group reagent is an aqueous nitric acid solution of silver nitrate AgNO_3 . Table 1 includes 7 anions of this group: chloride anion Cl^- , bromide anion Br^- , iodide anion I^- , sulfide anion S^{2-} , cyanide anion CN^- , thiocyanate anion (thiocyanate anion) SCN^- , benzoic acid anion $\text{C}_6\text{H}_5\text{COO}^-$ and etc.

1. What anions form a precipitate soluble in 12% ammonium carbonate solution as a result of their interaction with a silver(I) nitrate solution?
 - A. Sulfide ions
 - B. Thiocyanate ions
 - C. Bromide ions
 - D. Chloride ions *
 - E. Iodide ions

2. What anion of the 2nd analytical group produces black precipitate with group reagent AgNO_3 ?
 - A. Br^-
 - B. NCS^-
 - C. Cl^-
 - D. S^{2-*}
 - E. I^-

3. A solution contains iodide and chloride ions. Choose the reagent to detect iodide ions:
 - A. Chlorine water*
 - B. Limewater
 - C. Hydrogen sulfide water
 - D. Gypsum water

E. Barium water

4. What solution can be used to determine the presence of chloride ions in the potable water?

A. Silver nitrate*

B. Potassium bromate

C. Iodine

D. Sodium hydroxide

E. Ammonia

Chemistry of the III^d analytical group anions
(classification of anions based on formation of slightly soluble barium and silver salts)

In the considered classification, the third analytical group includes anions that do not form barium or silver salts, which are slightly soluble in water. Only three of these anions are presented in table 1: nitrite anion NO_2^- , nitrate anion NO_3^- and acetate anion CH_3COO^- , although much more exist. For example, the third group sometimes includes sacylate anion $\text{HOC}_6\text{H}_4\text{COO}^-$, bromate anion BrO_3^- , perchlorate anion ClO_4^- . There is no group reagent for the third analytical group anions.

1. Explain to a pharmacy student, why group III anions have no group reagent:
 - A. They form water-soluble salts with most cations *
 - B. They belong to toxic elements
 - C. They have large ionic radii
 - D. They have close ionic radii
 - E. They can form soluble acids
2. What analytical effect is observed when a solution that contains acetate ions is heated with ethyl alcohol and concentrated sulfuric acid?
 - A. Formation of a black precipitate
 - B. Formation of a white precipitate
 - C. Release of a characteristic odor *
 - D. Formation of a yellow precipitate
 - E. Formation of a blue precipitate
3. Nitrite ions can be detected in the presence of nitrate ions using the following:
 - A. Dimethylglyoxime
 - B. Crystalline iron (III) sulfate
 - C. Crystalline antipyrine in the presence of diluted HCl *
 - D. Diphenylcarbazone
 - E. Crystalline sodium thiosulfate

4. What anions are present in the solution, if it colors violet when iron (III) chloride reagent is added into it?
- A. Acetate anions
 - B. Salicylate anions *
 - C. Carbonate anions
 - D. Benzoate anions
 - E. Nitrate anions

Anions are usually divided into three groups according to the analytical classification of anions *based on their redox properties* (see table 2): anions-oxidizing agents, anions-reducing agents and indifferent anions, i.e., those that do not have pronounced redox properties under ordinary conditions.

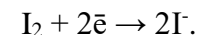
Chemistry of the I^t analytical group anions
(classification of anions based on the redox properties)

In this classification, the first group includes anions-oxidizing agents, which oxidize iodide ions I⁻ to molecular iodine I₂ *in a sulfuric acid medium*. Four of these anions are presented in table 2: bromate anion **BrO₃⁻**, arsenate anion **AsO₄³⁻**, nitrate anion **NO₃⁻** (although this anion practically does not react with iodide ions in a slightly acidic medium) and nitrite anion **NO₂⁻**. The latter anion sometimes is grouped with the second group of anions reducing agents, since the nitrite anion can react both as an oxidizing and reducing agent depending on the conditions. The group reagent for the anions-oxidizing agents of the first group is aqueous potassium iodide KI solution in a sulfuric acid medium.

**Chemistry of the II^d analytical group anions
(classification of anions based on the redox properties)**

The second group includes anions-reducing agents capable of reducing iodine I₂ to iodide ions I⁻ in aqueous solutions or discolor aqueous sulfat solution of potassium permanganate KMnO₄ by reducing manganese(VII) (the permanganate ion MnO₄⁻) to manganese(II) (Mn²⁺ cations). These 11 anions-reducing agents are listed in table 2: sulfide anion S²⁻, sulfite anion SO₃²⁻, thiosulfate anion S₂O₃²⁻, arsenite anion AsO₃³⁻, nitrite anion NO₂⁻ (sometimes it is included in the first group; see above), oxalate anion C₂O₄²⁻, chloride anion Cl⁻, bromide anion Br⁻, iodide anion I⁻, cyanide anion CN⁻, thiocyanate anion SCN⁻. The group reagent for all anions of this group is an aqueous sulfate solution of potassium permanganate KMnO₄. In the presence of anions-reducing agents, the pinkish-violet color of the potassium permanganate solution disappears (the solution is discolored), since permanganate ions are decomposed.

Iodine solution in aqueous potassium iodide solution is also recommended to use as a group reagent for the first four anions (sulfide, sulfite, thiosulfate and arsenite anions), which also discolors in the presence of these anions-reducing agents (the yellow color of iodine solution disappears) due to iodine reduction to iodide ions:



Potassium iodide is added to the iodine solution in order to increase iodine solubility: in the presence of iodide ions, the iodine solubility increases than its solubility in pure water due to the formation of highly soluble potassium triiodide KI₃:



1. Nitrate anions, unlike nitrite anions, do not interact with:
 - A. Potassium permanganate *
 - B. Diphenylamine
 - C. Sulfanilic acid
 - D. Iron(II) sulfate and sulfuric acid

E. Antipyrine

2. In qualitative analysis, a reaction with an iodine solution is used to detect arsenite ions. What is used to create the medium for this purpose?

A. Nitric acid solution

B. Acetic acid solution

C. Saturated solution of sodium hydrogen carbonate*

D. Sulfuric acid solution

E. Ammonia solution

Chemistry of the III^d analytical group anions
(classification of anions based on the redox properties)

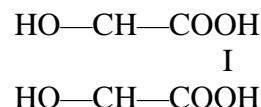
The third group includes anions, which are neither oxidizing nor reducing agents under ordinary conditions. Only 5 of these anions are listed in table 2: sulfate anion SO_4^{2-} , carbonate anion CO_3^{2-} , orthophosphate anion PO_4^{3-} , acetate anion CH_3COO^- and tetraborate anion $\text{B}_4\text{O}_7^{2-}$ (or BO_3^{3-} , BO_2^-). This group does not have a group reagent.

Analytical reactions of some organic anions: tartrate, citrate, benzoate and salicylate ions

In the Ukrainian Pharmacopoeia provides general identification reactions of some organic anions: tartrate ion $^-OOC-CH(OH)-CH(OH)-COO^-$, citrate ion $^-OOCCH_2-C(OH)(COO^-)-CH_2COO^-$, benzoate ion $C_6H_5COO^-$ and salicylate ion *ortho*- $HO-C_6H_4-COO^-$.

Reaction of tartrate-ions $C_4H_4O_6^{2-}$

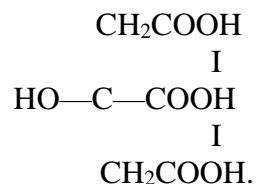
The tartrate ion is the anion of a weak dibasic ($pA_1 = 3.04$, $pK_2 = 4.37$) tartaric acid



which is highly soluble in water. In aqueous solutions, tartrate ions are colorless, undergo hydrolysis, participate in complexation reactions, forming stable tartrate complexes with many metal cations. Tartaric acid forms two number of salts: neutral tartrates containing a double charged tartrate ion $^-OOCCH(OH)CH(OH)COO^-$, and acidic tartrates (hydrogen tartrates) containing a single charged hydrogen tartrate ion $HOOCCH(OH)CH(OH)COO^-$. Potassium hydrogen tartrate («tartar») $HOOCCH(OH)CH(OH)COOK$ (or $KHC_4H_4O_6$) is practically insoluble in water, which is used to detect potassium cations. The neutral calcium salt $CaC_4H_4O_6$ is also slightly soluble in water. Neutral potassium salt $K_2C_4H_4O_6$ is highly soluble in water.

Reaction of citrate-ions $C_6H_5O_7^{3-}$

The citrate ion $^-OOCCH_2-C(OH)(COO^-)-CH_2COO^-$ is an anion of weak ($pK_1 = 3.13$, $pK_2 = 4.66$, $pK_3 = 6.4$) tribasic citric acid



The proton is practically not split off from the alcohol group in solutions under ordinary conditions ($pK_4 = 16.0$). The citric acid is highly soluble in water. In aqueous solutions, citrate ions are colorless, undergo hydrolysis, and are able to form stable citrate complexes with many metal cations.

Neutral sodium citrate is soluble in water.

The neutral calcium salt of citric acid is slightly soluble in hot water but highly soluble in cold water, which is used in practice.

Reaction of benzoate-ions $C_6H_5COO^-$

The benzoate ion is an anion of weak ($pK = 4.20$) monobasic benzoic acid C_6H_5COOH , which is slightly soluble in water (~ 0.3 at $20^\circ C$). The benzoate ion in aqueous solutions is colorless, undergoes hydrolysis, and is capable of forming benzoate metal complexes.

In contrast to benzoic acid, sodium benzoate is highly soluble in water.

1. Rapid analysis of benzoate ions by means of Pharmacopoeia reaction with iron(III) chloride produces:
 - A. Green precipitate
 - B. Pink-yellow precipitate *
 - C. Blue precipitate
 - D. Red precipitate
 - E. Black precipitate
2. A solution contains anions of organic acids. When a solution of iron(III) chloride was added, a pink-yellow precipitate formed. What anions are present in the solution?
 - A. Carbonate anions
 - B. Tetraborate anions
 - C. Benzoate anions *
 - D. Oxalate anions
 - E. Formate anions

Reaction of *ortho*- C₆H₄OHCOO⁻ salicylate-ions

The salicylate ion is an anion of weak monobasic salicylic (ortho- hydroxybenzoic) acid ortho-HO-C₆H₄-COOH. pK₁ =2.97 corresponds to carboxyl group dissociation, and a proton is split off from the phenolic group at pK₂ = 13.59, i.e., the proton practically does not split off from the phenolic group in solution under ordinary conditions (only in strongly alkaline media).

Salicylic acid is slightly soluble in water (~0.22% at 20 °C), therefore, when solutions of its salts (salicylates) are acidified, a white precipitate is formed. Salicylate ions in aqueous solutions are colorless, undergo hydrolysis, and able to participate in complexation reactions. Salicylate complexes of a number of metals are known.

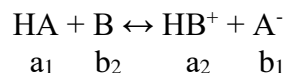
Salicylic acid forms two series of salts containing either single charged HOC₆H₄COO⁻ anions (HSal⁻ for short) or double charged anions -OC₆H₄COO²⁻ (Sal²⁻). Crystalline cobalt(II) Co(HSal)₂ · 4H₂O, nickel(II) Ni(HSal)₂ · 4H₂O, manganese(II) Mn(HSal)₂ · 4H₂O, zinc Zn(HSal)₂ · 2H₂O salicylates are typical complex compounds, which are colored according to the cations and soluble in water. White cadmium salicylate Cd(HSal)₂ · 2H₂O is slightly soluble in cold water. Anhydrous salicylates Co(HSal)₂, Ni(HSal)₂, Cd(HSal)₂ are slightly soluble in cold water; anhydrous Zn(HSal)₂ is soluble in water.

Sodium NaHSal and potassium KHSal salicylates are soluble in water. Known anhydrous ZnSal, CdSal and MnSal salicylates are slightly soluble in water.

QUANTITATIVE ANALYSIS

Acid-base titration

In acid-base titration is a method for determination of acids, bases, salts, based on the reaction between protoliths (acid HA and base B):



Depending on the titrant, a distinction is made between acidimetric and alkalimetric titration.

In the method of acidimetry, 0.01-1 M acid solutions (HCl, H₂SO₄, HNO₃, HClO₄) are used as titrants; in the method of alkalimetry – 0.01-1 M solutions of alkalies (NaOH, KOH, Ba(OH)₂).

These substances do not meet the requirements for standard substances; therefore, so their solutions are prepared by the method of the set titer. The exact concentration (molarity) of titrants is found against standard substances or by titration with solutions of the known concentration.

Standardization of acid solutions is carried out by:

- for standard substances: *sodium tetraborate decahydrate Na₂B₄O₇·10H₂O or sodium carbonate Na₂CO₃.*

- standard alkali solutions : NaOH та KOH.

Standardization of alkali solutions is carried out by:

- for standard substances : *oxalic acid dihydrate H₂C₂O₄·2H₂O, benzoic acid C₆H₅COOH, succinic acid C₄H₆O₆.*

- by standard acid solutions : HCl, H₂SO₄.

Acid-base indicators are weak organic acids or bases that change their structure and color when the pH of the medium changes.

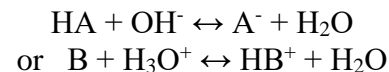
The pH interval in which the indicator changes its color is called the indicator color transition interval.

Indicators are often characterized by the titration indicator pT, the pH value at which the titration is completed, because at this moment there is a distinct change in the color of the indicator.

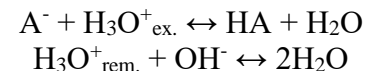
Types of titration used in titrimetric analysis

Direct titration, back titration, and indirect titration, or titration with substituent (substitution titration) are used in the titrimetric analysis.

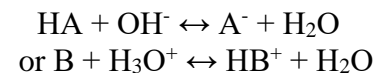
Direct titration is a type of titration during which the determined substance is directly titrated with standard titrant solution or vice versa.



Back titration (titration by residue) is titration of unreacted substance, which has been added as a standard solution in excess to the analyzed solution.



Indirect titration (substitution titration) is titration, during which a determined substance does not react directly with a titrant, and is determined indirectly by using a stoichiometrically proceeding reaction leading to the formation of another substance that reacts with the titrant.



During titration, either a predetermined mass of the analyzed substance or precisely measured volume of the analyzed solution can be taken. According to this, two methods are distinguished: *the method of individual weights* and *method of pipetting*.

1. What substance can be used to prepare primary standard solutions of titrants?
 - A. NaOH
 - B. I₂
 - C. K₂Cr₂O₇ *
 - D. KMnO₄
 - E. HCl

2. To determine the mass-volume fraction of ammonia in the solution, neutralization back titration was used. Specify the pair of titrants necessary in this case:
- A. HCl, NaOH *
 - B. HCl, AgNO₃
 - C. HCl, Hg₂(NO₃)₂
 - D. HCl, Hg(NO₃)₂
 - E. CH₃COOH, KOH
3. What method is used for the quantification of ammonia?
- A. Alkalimetry, direct titration
 - B. Acidimetry, back titration
 - C. Alkalimetry, back titration *
 - D. Acidimetry, direct titration
 - E. Complexonometry
4. What solution is used as a process solution (titrant) in alkalimetry?
- A. Potassium hydroxide *
 - B. Hydrochloric acid
 - C. Oxalic acid
 - D. Ammonium hydroxide
 - E. Sodium tetraborate
5. Non-aqueous acid-base titration is used for the substances that have low solubility in water and weak basic or weak acidic properties. Choose the titrant and medium for titration of substances with weak basic properties.
- A. HClO solution in anhydrous acetic acid
 - B. HCl solution in methanol
 - C. HClO₄ solution in anhydrous acetic acid *
 - D. HCl solution in dioxane
 - E. HCl solution in anhydrous acetic acid

6. In acidimetry, titrants are prepared using the method of determined titer. What substance is used for their standardization according to the State Pharmacopoeia of Ukraine?
- A. Potassium chloride
 - B. Sodium chloride
 - C. Metallic zinc
 - D. Metallic iron
 - E. Sodium carbonate *
7. What indicators are used to determine the titration endpoint in the acid-base titration method?
- A. pH indicators *
 - B. Adsorption indicators
 - C. Metal indicators
 - D. Redox indicators
 - E. Luminescent indicators
8. What indicator is used for the quantitative determination of sodium carbonate in a preparation by the method of acid-base titration?
- A. Ferroin
 - B. Murexide
 - C. Diphenylamine
 - D. Methylene blue
 - E. Methyl orange *
9. What characteristic is used to choose indicator for titration analysis?
- A. Titration curve jump
 - B. Equivalence point
 - C. Titration indicator
 - D. Indicator constant
 - E. Transition interval *

10. What characteristic is used in titrimetric methods of analysis, when choosing the indicator?
- A. Titration index
 - B. Neutralization point
 - C. Transition interval *
 - D. Titration jump
 - E. Indicator constant
11. To determine the end point of an acid-base titration the following indicators are used:
- A. Redox indicators
 - B. Metal indicators
 - C. Luminescent indicators
 - D. pH-indicators *
 - E. Adsorption indicators
12. Choose the indicator and titration method to determine hydrogen carbonate ions in a drug:
- A. Murexide, acidimetry
 - B. Phenolphthalein, acidimetry
 - C. Phenolphthalein, alkalimetry
 - D. Methyl-orange, acidimetry *
 - E. Methyl-orange, alkalimetry
13. What indicator should be chosen for standardization of a hydrochloric acid solution using Na_2CO_3 and $\text{Na}_2\text{B}_4\text{O}_7$ solutions?
- A. Thymol blue
 - B. Eosin
 - C. Methyl red *
 - D. Tropaeolin 00
 - E. Murexide
14. A standard alkali solution is used to determine substances of acidic nature. This method is called:
- A. Alkalimetry*

- B. Acidimetry
- C. Redoxymetry (Oxidimetry)
- D. Complexometry (Chelatometry)
- E. Gravimetry

15. To choose an indicator for acid-base titration, a titration curve needs to be built. This curve reflects the dependence of:

- A. Solution pH from the temperature
- B. Solution pH from the volume of the added titrant*
- C. Concentration of the analyzed compound from solution pH
- D. Solution pH from the volume of the solution being analyzed
- E. Solution pH from the concentration of the added titrant solution

16. The following is used to determine the titrant volume in the process of titrimetric analysis:

- A. Measuring flasks
- B. Measuring glasses
- C. Burettes*
- D. Cylinders
- E. Measuring tubes

17. What is used as an indicator in the back titration of an aqueous solution of acetic acid?

- A. Murexide
- B. Eriochrome black T
- C. Diphenylamine
- D. Diphenylcarbazone
- E. Phenolphthalein *

18. What solution is used to determine the mass-volume fraction of ammonia in a solution?

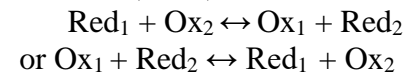
- A. Hydrochloric acid solution *
- B. Sulfuric acid solution
- C. Potassium permanganate solution
- D. Sodium hydroxide solution

E. Iodine solution

19. What indicator is used, when sodium carbonate is being quantified in the preparation by means of acid-base titration?
- A. Ferroin
 - B. Murexide
 - C. Diphenylamine
 - D. Methylene blue
 - E. Methyl orange *
20. What method of titration is used, when a precisely measured excess of the auxiliary titrant is added to the solution of the analyte substance?
- A. Non-aqueous titration
 - B. Residual titration *
 - C. Any titration
 - D. Direct titration
 - E. Substitution titration
21. What method can be used to determine the moisture content in thermally unstable preparations?
- A. Permanganatometric method
 - B. Nitritometric method
 - C. Iodometric method
 - D. Non-aqueous titration using the Fischer's method*
 - E. Bromatometric method
22. Moisture content of thermally unstable preparations can be determined by:
- A. Permanganatometry
 - B. Iodometry
 - C. Karl Fischer titration*
 - D. Nitritometry
 - E. Bromatometry

Oxidation-reduction titration

Methods of oxidation-reduction titration or *redox methods* are based on reactions associated with the transfer of electrons – oxidation-reduction reactions (ORR).



To titrant properties, methods are divided into *oxidimetry* and *reductometry*.

In *oxidimetry*, the titrant is a standard solution of oxidizing agent: permanganometry (KMnO_4), dichromatometry ($\text{K}_2\text{Cr}_2\text{O}_7$), bromatometry (KBrO_3), cerimetry (solution of cerium(IV) salts), chloriodometry (ICl), iodatometry (KIO_3).

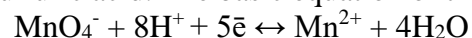
In *reductometry*, the titrant is a standard solution of reducing agent: titanometry (solution of titanium(III) salts), ferrometry (FeSO_4), ascorbinometry ($\text{C}_6\text{H}_8\text{O}_6$).

1. In redox titrimetry, the indicators that are added to the reaction system respond to the changes in the:
 - A. Ionic strength of the solution
 - B. Concentration of hydroxyl ions
 - C. Redox potential of the system *
 - D. Degree of ionization of the substance being analyzed
 - E. Concentration of hydrogen ions

PERMANGANOMETRY

Permanganometry or permanganometric titration is an method of oxidation-reduction titration in which KMnO_4 solution is used as a titrant.

The titration is usually carried out in strongly acidic medium in the presence of sulfuric acid. The basic equation of the method is:



$$E_{\text{MnO}_4^-, 8\text{H}^+/\text{Mn}^{2+}}^0 = 1,51\text{B};$$

$$f_e = 1/5.$$

Fixation of the titration end point in permanganometry is without an indicator. A single excess drop of permanganate colours the whole solution a pale pink.

The titrant of the method (a solution of potassium permanganate) is prepared by the technique of standardized titer. Crystalline KMnO_4 contains impurities of MnO_2 ; besides, aqueous solutions of KMnO_4 are unstable.

KMnO_4 solution is kept in a dark place or in a dark glass bottle for 7-10 days before the determination of exact concentration. During this time, oxidation of reducing agents (dust, traces of organic compounds, etc.) occurs. MnO_2 catalyzes KMnO_4 decomposition; therefore, solution of KMnO_4 is carefully decanted.

Many primary standards can be used for standartisation of KMnO_4 solutions: $\text{Na}_2\text{C}_2\text{O}_4$, $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, $(\text{NH})_2\text{C}_2\text{O}_4$, As_2O_3 , $\text{Fe}(\text{met.})$, $\text{K}_4[\text{Fe}(\text{CN})_6]$, Mohr's salt $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$.

The application of the method

The following substances can be determined:

1. *Reducing agents*: ions in lower oxidation states (Fe^{2+} , Cr^{2+} , Sn^{2+} , As^{III} , etc.), anions (Cl^- , Br^- , S^{2-} , SO_3^{2-} , SCN^- , NO_2^- , etc.), poly- and hydroxycarboxylic acids, aldehydes, sugars, etc., more often by direct titration;

2. *Oxidizing agents*: Fe^{3+} , Ce^{IV} , Cr^{VI} , BrO_3^- , $\text{S}_2\text{O}_8^{2-}$, etc. by back-titration;

3. *Substances that do not possess oxidation-reduction properties* (indifferent substances): Ba^{2+} , Ca^{2+} , Sr^{2+} , Zn^{2+} by back and displacement titration.

1. Permanganatometry is used in determination of many organic and inorganic compounds. What are the main advantages of permanganatometry over the other oxidimetric methods?
 - A. Various types of indicators can be used; in some cases catalysts are necessary to accelerate the reaction
 - B. High selectivity and sensitivity when determining compounds
 - C. Sufficiently high stability of potassium permanganate and its solutions
 - D. Pure potassium permanganate is easily available and obtainable
 - E. Sufficiently high redox potential; it is possible to determine titration end-point without indicator *

2. What titrimetric method of analysis is used for the quantification of calcium chloride?
 - A. Nitritometry, direct titration
 - B. Cerimetry, direct titration
 - C. Acidimetry, back titration
 - D. Permanganatometry, direct titration
 - E. Permanganatometry, back titration *

3. In permanganatometry, KMnO_4 is used as a titrant. What is the equivalence factor of this compound, if the titration is performed in an acidic medium?
 - A. 1/2
 - B. 1/5 *
 - C. 1/3
 - D. 1/4
 - E. 1

4. Quantitative content of oxalic acid can be determined by means of permanganometry. How to determine equivalence point for this kind of titration?
- A. With pH indicator
 - B. With redox indicator diphenylamine
 - C. With adsorption indicator
 - D. When titrate changes its color after another drop of process solution is added *
 - E. With specific indicator
5. Quantitative content of hydrogen peroxide can be determined by means of the following self-indicator method:
- A. Iodometry
 - B. Argentometry
 - C. Bromatometry
 - D. Nitritometry
 - E. Permanganometry *
6. What analytical method can be used to quantify hydrogen peroxide without any special indicators?
- A. Iodometry
 - B. Permanganometry *
 - C. Complexonometry
 - D. Nitritometry
 - E. Argentometry
7. Permanganometry is a titrimetric method for the determination of substances based on oxidation reactions involving permanganate ions. Which of the following are the standard solutions that are used according to this method for the quantitative determination of oxidants by reverse titration method?
- A. Potassium dichromate, sodium thiosulfate
 - B. Potassium bromate, sodium thiosulfate
 - C. Cerium (IV) sulfate, iron (II) sulfate

- D. Potassium iodate, sodium thiosulfate
- E. Potassium permanganate, iron (II) sulfate *

8. Specify the standard solutions that are used in permanganatometry to quantify the oxidants by the residual titration method:

- A. Potassium dichromate, sodium thiosulfate
- B. Potassium iodate, sodium thiosulfate
- C. Potassium permanganate, iron (II) sulfate*
- D. Cerium (IV) sulfate, iron (II) sulfate
- E. Potassium bromate, sodium thiosulfate

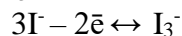
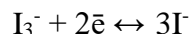
IODIMETRY AND IODOMETRY

Iodimetry or *iodimetric titration* is a method for the determination of substances based on the usage of oxidizing properties of standard iodine solution.

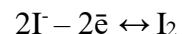
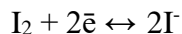
Iodometry or *iodometric titration* is a method for the determination of oxidizing agents based on the usage of reducing properties of iodide ions and a standard solution of sodium thiosulfate.

The iodometric method of volumetric analysis is based on oxidation-reduction processes associated with reduction of iodine to iodide ions and oxidation of iodide to iodine.

Methods of iodimetry and iodometry are based on the following half-reactions:



or:



The equivalence factor of iodine is $\frac{1}{2}$.

The end point of the titration is determined with an indicator and methods without an indicator. A 0.5-1.0% solution of starch as a sensitive reagent is used, which forms an intense blue adsorption compound with iodine. In titration in the presence of a starch solution the end point is determined from the appearance of a permanent blue colour on addition of one excess drop of iodine. It is also possible to titrate iodine solution with thiosulphate until one drop of the latter decolorizes the blue solution. In that case, the starch solution must be added at the very end of the titration, when very little iodine remains and the solution being titrated has a faint (straw-yellow) colour.

Without an indicator, the end point can be found by the yellow color of molecular iodine extracted with organic solvents (benzene, chloroform, carbon tetrachloride).

The titrant of the iodimetric method is iodine solution in potassium iodide. It is applied for the determination of reducing agents by direct titration. Two titrants, such as standard solutions of iodine and sodium thiosulfate, are used in case of the determination of reducing agents by back titration.

In iodometry, sodium thiosulfate solution is used as *a titrant* to determine oxidizing agents by displacement titration.

Standard iodine solution can be prepared in two ways: by prepared and standardized titers. More often, iodine solution is prepared by the method of standardized titer.

Iodine solution is standardized according to primary standards: arsenic(III) oxide and hydrazine sulfate.

Iodine solutions are stored in dark glass bottles with glass ground stoppers, in places protected from light, preferably in the cold.

Standard sodium thiosulfate solution is prepared from $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ by the method of standardized titer, because sodium thiosulfate does not conform to the requirements for primary standards (it may lose crystallization water).

Sodium thiosulfate solutions are unstable during storage. Thiosulfate ions in aqueous solutions are decomposed by the action of microorganisms (thiobacteria), which leads to a decrease in concentration. To prevent this decomposition, mercuric iodide may be added as an antiseptic.

Standardization is performed about 7-10 days after preparation. Numerous primary standards can be used for the standardization of sodium thiosulfate. They include potassium dichromate, potassium bromate, potassium iodate and potassium ferricyanide. Standardization can be also performed with standard iodine solution.

Conditions required for iodimetric and iodometric titration

1. Since iodine is volatile, the titration must be conducted in the cold. This is also necessary because the sensitivity of starch as indicator diminished with rise of temperature. If a starch solution

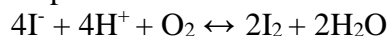
turned blue by a single drop of iodine is heated, the blue colour disappears; when the solution is cooled the colour returns.

2. Iodimetric determination cannot be performed in strongly alkaline solutions (at $\text{pH} > 9$), because iodine reacts with alkalies in accordance with the equation:



The presence of hypoiodide is inadmissible, because it is a stronger oxidant than pure iodine and partially oxidises thiosulphate to sulphate.

In strongly acidic medium, oxidation of iodide ions with atmospheric oxygen takes place:



Also in strongly acidic medium, sensitivity of indicator decreases.

3. In the iodometric titration of oxidizing agents, the determination is performed in glass bottles with a glass stopper, in acidic medium, and presence of an excess of potassium iodide solution. For quantitative proceeding of reaction, the mixture is kept in a dark place for 10-15 minutes. The indicator is added at the very end of the titration.

The application of the method

The standard oxidation potential of the $\text{I}_3^-/\text{3I}^-$ system has the relatively low value of +0.535 V. Low potential allows using I_2 as an oxidizing agent and I^- ions as a reducing agent.

Therefore, the iodimetry can be applied for the followed substances:

1. Reducing agents, the standard potential of which is less than 0.54 V (arsenic(III) oxide, sodium thiosulfate, hydrazine sulfate, etc.) by direct titration. Reducing agents such as formaldehyde, sodium sulfite and sodium sulfide are determined by back titration.

2. Oxidizing agents, the standard potential of which is greater than 0.54 V (hydrogen peroxide, potassium dichromate, sodium arsenate, etc.) by displacement titration.

3. Aromatic and heterocyclic compounds with which iodine goes into chemical displacement reactions (antipyrine), unsaturated organic compounds by addition reactions.

1. What titrimetry method allows to determine quantitative content of ascorbic acid using starch as an indicator?

- A. Permanganatometry
- B. Ferrometry
- C. Iodimetry *
- D. Nitritometry
- E. Titanometry

2. Specify what method of redox titration requires the use of specific indicator - starch - to fix the end point:

- A. Cerimetry
- B. Bromatometry
- C. Nitritometry
- D. Iodometry *
- E. Permanganatometry

3. A specialist of the analytical laboratory performs direct iodometric determination of ascorbic acid. What indicator is used in this case?

- A. Diphenylamine
- B. Starch *
- C. Phenolphthalein
- D. Methyl orange
- E. Methyl red

4. Iodimetry involves use of standard solutions of iodine and $\text{Na}_2\text{S}_2\text{O}_3$. What substance is used to standardize the sodium thiosulfate solution?

- A. NaCl
- B. $\text{N}_2\text{B}_4\text{O}_7$
- C. As_2O_3

D. $\text{K}_2\text{Cr}_2\text{O}_7$ *

E. K_2CO_3

5. Specify the standard solution (titrant) for the iodometric determination of oxidants:

A. KBrO_3

B. I_2

C. $\text{K}_2\text{Cr}_2\text{O}_7$

D. KMnO_4

E. $\text{Na}_2\text{S}_2\text{O}_3$ *

6. When determining oxidizing agents by means of iodometry in the presence of starch the following phenomenon can be observed at the titration endpoint:

A. Red coloring appears

B. Blue coloring disappears *

C. White precipitate forms

D. Green coloring of precipitate appears

E. Green coloring of solution disappears

7. A laboratory has received a sample of copper(II) sulfate pentahydrate. Choose the method for quantification of copper(II) in copper sulfate.

A. Argentometry

B. Acidimetry

C. Iodometry *

D. Alkalimetry

E. Permanganatometry

8. What two working solutions are used in determination of hydrogen sulfide in mineral waters by means of iodometry (back titration)?

A. NaOH , HCl

B. AgNO_3 , H_2SO_4

C. Na_2CO_3 , HCl

- D. I_2 , $Na_2S_2O_3$ *
- E. $H_2C_2O_4$, $KMnO_4$

9. What reaction occurs when ascorbic acid is being determined by means of iodometry?

- A. Complex formation
- B. Redox*
- C. Acylation
- D. Neutralization
- E. Precipitation

10. In iodometry, titrimetric quantitative analysis is used to measure the amount of iodine utilized for the oxidation of a reducing agent or released as a result of iodide oxidation. What salt is used to make an iodide solution for iodometry?

- A. Lithium iodide
- B. Calcium iodide
- C. Magnesium iodide
- D. Potassium iodide*
- E. Sodium iodide

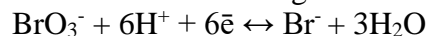
11. What substance is used as a primary standard in permanganometry, bromatometry, dichromatometry, iodometry, and cerimetry?

- A. Sodium carbonate
- B. Arsenic(III) oxide*
- C. Sodium chloride
- D. Potassium hydroxide
- E. Ammonium acetate

BROMATOMETRY

Bromatometry or bromatometric titration is a method for the determination of reducing agents using a titrant, standard solution of potassium bromate.

The method is based on the following half-reaction:



$$E_{\text{BrO}_3^-, 6\text{H}^+/\text{Br}^-}^0 = 1.44 \text{ V};$$

$$f_e = 1/6.$$

Standard OR potential of the $\text{BrO}_3^-, 6\text{H}^+/\text{Br}^-$ redox pair is rather high; therefore, KBrO_3 is a strong oxidizing agent in acidic medium.

Titrant of the method. The standard solution in bromatometry is KBrO_3 solution, which can be prepared by accurate weighing of the recrystallised salt, dried at $150\text{-}180^\circ\text{C}$. But if KBrO_3 solution is prepared as a secondary standard (by a standardized titer method), then standardization is performed with respect to arsenic(III) oxide, sodium oxalate, ammonium oxalate, oxalic acid and hydrazine sulfate. Standardization can also be performed by the iodometric method.

Fixation of end point of the titration. During titration, bromate ions are reduced to bromide ions, which, after reaching the equivalence point (EP), react with an excess of bromate ions to form free bromine:



Resulting bromine colors the solution pale yellow. However, coloring is too weak and insufficient for EPT fixation. Therefore, bromatometric titration is more often performed in the presence of pH indicators, for example, methyl orange, methyl red and neutral red, which colour the titrated solution red in acidic medium. After reaching EP, these azo indicators are non-reversible bromated with bromine. As a result, a whole solution is decolorised. The titration is carried out slowly to avoid the local formation of bromine up to EP (at that, coloring may disappear). At the end of titration, a few more

drops of the indicator should be added. In repeated titrations, the indicator is introduced before the end of titration.

Also, the following redox indicators are used for the determination of EPT: α -naphthoflavone, hydrochloric p-ethoxychrysoidin and quinoline yellow, which react reversibly with bromine.

Conditions for bromatometric titration

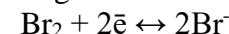
To increase the reaction rate, titration is carried out in a strongly acidic solution, heated up to 70°C. The pH is created by hydrochloric acid with a concentration of around 1-2 mol/l. Sometimes mercury(II) salts are used as catalysts.

The application of the method

The method is used to determine reducing agents by direct titration: As(III), Sb(III), Fe(II), H₂O₂, N₂H₄, as well as some pharmaceuticals. An analyzed solution is added with an excess of arsenite, which is titrated with potassium bromate (back titration) in case of determining oxidizing agents (permanganate, hypochlorites, etc.).

BROMOMETRY

Bromometry or bromometric titration is a method for the determination of substances using Br₂ solution as a reagent:



$$E^0_{\text{Br}_2/2\text{Br}^-} = 1.09 \text{ V.}$$

Bromine is a weaker oxidizing agent than potassium bromate. Bromine solutions are unstable and very toxic; therefore, they are not used as a titrant. Bromine source is a bromate-bromide mixture KBrO₃ + KBr in acidic medium:



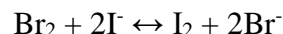
Bromine being liberated reacts with the analyzed substance. Bromometric titration is successfully applied for the determination of organic compounds, which can be bromated.

In direct titration, the excess of potassium bromide and an indicator are added to the acidified analyzed solution. This mixture

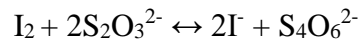
is titrated with potassium bromate solution until the colour of the indicator disappears.

At the same time, the analyzed substance must be bromated first. After the EP, the indicator is bromated.

Back and displacement titrations with iodometric fixation of EPT are performed more often. In back titration, the exact volume of potassium bromate solution and the excess of potassium bromide solution are added to the acidified analyzed solution. The mixture is left for a while (5-10 min). The bromine being liberated bromates the analyzed substance. Then, the excess of potassium iodide solution is added, and the mixture is left again for 5-10 minutes. The excess of bromine, which has not reacted with the substance, reacts with iodide ions:



Free iodine is titrated with a standard sodium thiosulfate solution, more often with starch indicator.



The determination is performed in glass bottles with ground stoppers.

The application of the method

The method is used to determine organic compounds, which can be bromated, including medicines, for example, mesatonum, phenol, resorcinol, thymol, streptocide, and other sulfanilamides, salicylates, isoniazid, etc. The method is also applicable for the analysis of metal cations precipitated by 8-oxyquinoline or anthranilic acid, such as Mg^{2+} , Al^{3+} , Cd^{2+} .

1. Bromatometric determination of streptocide (Sulfanilamide) is performed by means of direct titration with a standard solution of potassium bromate. What is used as an indicator in this method of titration?
 - A. Murexide
 - B. Eriochrome black T
 - C. Iron(III) thiocyanate
 - D. Phenolphthalein

E. Methyl orange *

2. What titrant is used in bromatometric titration?

- A. Br₂
- B. KBrO₄ + KCl
- C. KBrO₃ *
- D. KBr
- E. KBrO₄

3. What method of titrimetric analysis is used to quantify streptocide (sulfanilamide) with a KBrO₃ solution in the presence of KBr?

- A. Dichromatometry
- B. Bromatometry *
- C. Permanganometry
- D. Iodometry
- E. Vanadatometry

4. Name the titrimetric method for quantitative determination of phenol and its derivatives:

- A. Nitritometry
- B. Cerimetry
- C. Bromatometry *
- D. Ascorbinometry
- E. Permanganatometry

5. What method of redox titration uses specific pH indicators for fixation of the titration endpoint?

- A. Nitritometry
- B. Permanganatometry
- C. Cerimetry
- D. Bromatometry*
- E. Iodometry

NITRITOMETRY

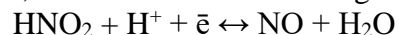
Nitritometry or nitritometric titration is a method for the quantitative determination of substances using sodium nitrite solution (NaNO_2) as a titrant.

The method is based on reactions of oxidation-reduction, diazotization, nitrosation, and azation. Sodium nitrite can exhibit properties of oxidizing and reducing agent.

The titrant of the method is usually applied in the form of an aqueous solution with concentration of 0.1 or 0.5 M. The solution is prepared by technique of standardized titer, since sodium nitrite is unstable during storage and can be oxidized to nitrate.

The standardization of sodium nitrite solution is performed with the reaction, which will be used for the determination. If NaNO_2 is used as *an oxidizing agent*, then its standardization is performed with iron(II), arsenic(III) and hydrazine. If NaNO_2 is used as *a reducing agent*, then with potassium permanganate (a secondary standard) and potassium dichromate. If NaNO_2 takes part in *diazotization* reactions, then with sulfanilic acid, p-aminobenzoic acid, p-aminoethyl benzoate.

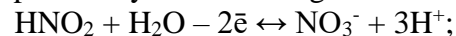
As *an oxidizing agent*, sodium nitrite is used to determine reducing agents, for instance, Sn^{2+} , Fe^{2+} , As_2O_3 , hydrazine and other compounds. In this case, nitrite is reduced to nitrogen oxide:



$$E_{\text{HNO}_2, \text{H}^+ / \text{NO}}^0 = 0.98 \text{ V};$$

$$f_e = 1.$$

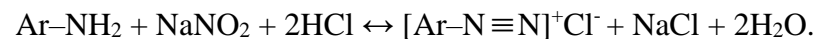
As *a reducing agent*, sodium nitrite is used to find out the concentration of potassium permanganate, chlorine, potassium iodate and other compounds by the following reaction:



$$E_{\text{NO}_3^-, 3\text{H}^+ / \text{HNO}_2}^0 = 0.94 \text{ V};$$

$$f_e = 1/2.$$

More often than others, *diazotization* reaction is used, which proceeds with primary aromatic amines in acidic medium:



Conditions required for nitritometric titration

1. The titration is performed at a temperature of 18–20°C, sometimes solution is cooled to 0–5°C to avoid decomposition of diazonium salts.

2. The titration is carried out in the presence of twofold excess of hydrochloric acid (one part – for converting sodium nitrite into nitrous acid, the second part – for protonation of nitrous acid, in addition to it, chloride anion stabilizes diazonium cation).

3. To speed up the reaction, crystalline KBr is added as a catalyst.

4. The titration is performed slowly, constantly stirring of the solution. At the beginning of the titration, sodium nitrite solution is added at a rate of 2 ml per minute, and at the end of the titration at a rate of 0.05 ml per minute.

Fixation of the end point of the titration. External and internal indicators are used in nitritometry.

As an external indicator, starch-iodide paper (potassium iodide-starch paper) is used. This is some filter paper soaked in a starch solution and potassium iodide and then dried.

As internal indicators, redox indicators are used, such as tropaeolin 00 (in the EPT colouring turns from red to yellow), its mixture with methylene blue (colouring turns from raspberry to blue), neutral red (colouring turns from red-violet to blue), as well as safranin G, metanil yellow, acid blue 2K.

The application of nitritometry

Nitritometry is applied for the determination of inorganic substances (reducing and oxidizing agents). It is also can be used for quantitative analysis of organic compounds containing a primary or secondary aromatic amino group, aromatic nitro derivatives (after preliminary reduction of a nitro group to an amino group), heterocyclic compounds, hydrazides, including pharmaceutical drugs, such as anesthesin, dicaine, novocaine, novocainamide,

norsulfazole, streptocide, sulfacyl sodium, sulfadimezinum, and others.

1. Nitritometry is used to determine primary aromatic amines. What indicator is used in the process?
 - A. Methyl orange
 - B. Eosin
 - C. Potassium chromate
 - D. Tropaeolin 00 *
 - E. Phenolphthalein

2. Most often, the quantitative content of primary and secondary aromatic amines in drugs is determined using the following method:
 - A. Nitritometry *
 - B. Permanganatometry
 - C. Ascorbinometry
 - D. Cerimetry
 - E. Titanometry
 - F.

3. What indicator is used in determination of primary aromatic amines using the nitritometric method?
 - A. Tropeolin 00 *
 - B. Phenolphthalein
 - C. Methyl orange
 - D. Eosin
 - E. Potassium chromate

4. Mass fraction of pharmaceutical preparations that contain aromatic amino groups is defined through nitrite titration. What external indicator is used in this case?
 - A. Phenolphthalein
 - B. Eosin
 - C. Starch-iodide paper *
 - D. Methylene red

E. Eriochrome Black T

5. In nitritometry, titrant is a 0.1 M solution of sodium nitrite that is prepared as a secondary standard solution. What acid is used to determine the exact concentration of sodium nitrite?

- A. Acetic
- B. Oxalic
- C. Sulfuric
- D. Hydrochloric
- E. Sulfanilic *

6. What method of titrimetric analysis requires the use of both external and internal indicators?

- A. Nitrite titration *
- B. Permanganatometry
- C. Alkalimetry
- D. Argentometry
- E. Complexometric titration

7. Sulfanilamides contain a primary aromatic amino group in their structure. What method is used for quantitative determination of these compounds?

- A. Iodometry
- B. Nitritometry *
- C. Dichromatometry
- D. Permanganatometry
- E. Cerimetry

8. What titrimetric method of analysis requires the use of both external and internal indicators?

- A. Nitritometry*
- B. Permanganatometry
- C. Argentometry
- D. Complexometric titration
- E. Alkalimetry

PRECIPITATION TITRATION

Precipitation titration is a method of titrimetric analysis based on the use of titrants that form slightly soluble compounds with the analyzed substance. The essence of methods is in that the equivalent quantity of the precipitant in the form of the standard solution is added to the solution of a certain substance.

Determination the equivalent point in precipitation titration method

The following types of indicators are used to determine the equivalent point in precipitation titration method: *precipitating, metalochromic, adsorption* ones.

Precipitation indicators – such indicators that escape from solution as a precipitate in the easy-to-see- form in EP or near it. A small number of precipitation indicators is known.

An example of precipitation indicators would be potassium chromate K_2CrO_4 proposed by Mohr for argentometric titration of chloride ions by means of silver nitrate.

Metalochrome indicators in precipitation titration – indicators forming with titrant colored complexes near EP.

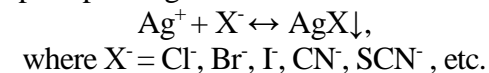
Ammonium iron alum is most often used as a metalochromic indicator $FeNH_4(SO_4)_2 \cdot 12H_2O$.

Adsorption indicators are indicators whose adsorption or desorption by the precipitate during precipitation titration is accompanied by the change in color at EP or close to it.

Typical adsorption indicators – fluoresceine and eosin (tetrabromofluorescein). The generally accepted action mechanism of the considered adsorption indicators is as follows.

ARGENTOMETRY

The essence of the method. Argentometry, or argentometric titration, - the method of precipitation titration based on the use of standard silver nitrate solution AgNO_3 as a precipitating agent. The method is based on precipitating reactions:



Titration of the method. Standard solution of AgNO_3 most often with concentration 0.1 and 0.05 mol/L is used as the main titrant of the method. Silver nitrate in water solution is unstable due to the behavior of redox processes in the presence of silver(I) cations that oxidate possible organic impurities in water. So first a silver nitrate solution with approximate concentration must be prepared and then standardized according to the standard solution of sodium chloride in the presence of potassium dichromate K_2CrO_4 as an indicator.

Standardized silver nitrate solution is stored in stoppered vessels made horn amber glass, in a dark place.

Types of argentometry. Depending on the titration method and indicator used, 4 methods of argentometric titration are distinguished: Gay-Lussac's method, Mohr's method, Fajans-Fisher-Khodakov method, and Volhard's method.

Gay-Lussac's method is a direct titration of halide ions with standard silver nitrate solution without indicators. Completion of titration is visually determined by the termination of formation of silver salt precipitation and clarification of the solution. The method gives very accurate results; it was used for original determination of the atomic masses of halogens and silver. Requires specific skill, comparatively time-consuming. Rarely used presently.

The **Mohr method** – determining halides ions by means of direct titration with silver nitrate solution in the presence of indicator – potassium chromate solution. Used for determining Cl^- , Br^- . However, the method does not allow to determine I^- and SCN^- , because, during titration, co-precipitation of potassium chromate with precipitations of AgI or AgSCN takes place.

Determination is hindered by Ba^{2+} , Pb^{2+} , Bi^{3+} cations forming precipitates of chromates as well as anions of PO_4^{3-} , CO_3^{2-} , $\text{C}_2\text{O}_4^{2-}$, AsO_4^{3-} and others forming precipitates of silver salts.

The *method of Fajans-Fisher-Kchodakov* – determining halides ions by means of direct titration with silver nitrate solution in the presence of adsorption indicators – fluoresceine, eosin, etc., (see above).

The method allows determining chlorides, bromides, iodides, cyanides, sulphocyanates.

Volhard's method – back titration of silver cations excess with a solution of ammonium sulphocyanate NH_4SCN^- or potassium sulphocyanate KSCN^- in the presence of indicator – iron(III) salt, usually as was mentioned above, – Mohr's salt $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$.

It is used to determine halide ions, CN^- , SCN^- , S^{2-} , CO_3^{2-} , CrO_4^{2-} , $\text{C}_2\text{O}_4^{2-}$, ASO_4^{3-} and in some other cases.

In order to perform the analysis, in a typical experiment, diluted nitric acid.

1. Select from the list an adsorption indicator:
 - A. Methyl-orange
 - B. Eosin *
 - C. Phenolphthalein
 - D. Sulfosalicylic acid
 - E. Eriochrome black T
2. What indicator is used in the Fajans-Khodakov method to determine sodium iodide (NaI)?
 - A. Methyl orange
 - B. Ammonium iron(III) sulfate
 - C. Diphenylcarbazone
 - D. Potassium chromate
 - E. Eosin *

3. The Fajans-Khodakov method is used to determine the mass fraction of sodium chloride (NaCl) in a drug. What indicator is used in this titration method?
- A. Ammonium iron(III) sulfate
 - B. Potassium chromate
 - C. Fluorescein *
 - D. Phenolphthalein
 - E. Methyl red
4. What solution is used to standardize the silver(I) nitrate titrant solution in Mohr's method?
- A. Sodium carbonate solution
 - B. Potassium dichromate solution
 - C. Sodium chloride solution *
 - D. Sodium oxalate solution
 - E. Sodium tetraborate solution
5. Quantitative determination of iodides by Fajans method is performed with adsorption indicators. The following can be used as an adsorption indicator:
- A. Murexide
 - B. Phenolphthalein
 - C. Diphenylamine
 - D. Eosin *
 - E. Methyl orange
6. What medium is necessary for determining the halide ions argentometrically using the Volhard method?
- A. Acetic acid medium
 - B. Weak alkaline medium
 - C. Neutral medium
 - D. Nitric acid medium *
 - E. Strong alkaline medium
7. Ammonium iron(III) sulfate can be used as an indicator in:

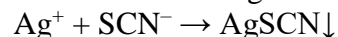
- A. Acidimetry
 - B. Argentometry, Mohr method
 - C. Alkalimetry
 - D. Argentometry, Volhard method *
 - E. Complexometric titration
8. What anions interfere with the determination of halide ions by means of the Volhard method, because they form a strong colorless complex with iron(III) ions?
- A. MnO_4^-
 - B. F^- *
 - C. NO_3^-
 - D. NO_2^-
 - E. SO_3^{2-}
9. What working solutions (titrants) are used in the method of precipitation titration - Volhard method?
- A. KMnO_4 and KBrO_3
 - B. HClO_4 and KOH
 - C. AgNO_3 and NH_4SCN *
 - D. $\text{Na}_2\text{S}_2\text{O}_3$ and $\text{K(I}_3)$
 - E. H_2SO_4 and NaOH
10. What analytical effect is observed during fixation of the end point in the Volhard titration?
- A. A red precipitate is produced
 - B. A yellow precipitate is produced
 - C. The solution colors yellow
 - D. A brown precipitate is produced
 - E. The solution colors red *
11. What titrimetric method of analysis can be used to determine the total content of CaCl_2 and NaBr in solution?
- A. Iodometry
 - B. Argentometry*

- C. Acidimetry
- D. Alkalimetry
- E. Permanganometry

THIOCYANATOMETRY

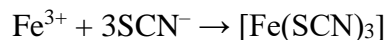
Thiocyanatometry, or thiocyanatometric titration (rhodanometry, rhodanometric titration), is a method of titrimetric analysis based on the use of standard ammonium thiocyanate NH_4SCN (or potassium thiocyanate KSCN) solution as a reagent that reacts with the determined substance, usually with Ag^+ silver cations.

The method is based on the following reaction:



During titration of the analyzed solution containing the determined silver cations with ammonium or potassium thiocyanate solution, the titrated solution turns red near EP due to the formation of intense red thiocyanate iron(III) complexes (refer to the description of Volhard's method in the previous sections).

As mentioned above, the method allows performing titration in acidic medium, since iron(III) thiocyanate complexes are stable in acidic solutions, while silver thiocyanate precipitated during titration is insoluble in acidic medium.



Titration can be performed in the presence of such cations as Ba^{2+} , Pb^{2+} , Bi^{3+} , etc., which do not form precipitates with thiocyanate ions in *acidic medium*.

Titrant of the method. Aqueous solutions of ammonium NH_4SCN or potassium KSCN thiocyanates, usually with a concentration of 0.1 mol/L, are used as indicators of the method.

Initially, titrant solution with approximate concentration is prepared, and then it is standardized using a standard silver nitrate solution.

1. Thiocyanatometric titration method requires secondary standard solution of potassium thiocyanate that is standardized with standard solution of:

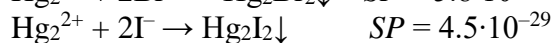
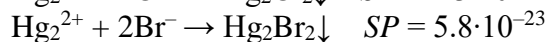
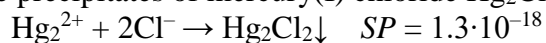
- A. Iron(II) sulfate
- B. Hydrochloric acid

- C. Silver nitrate*
- D. Sulfuric acid
- E. Copper(II) nitrate

MERCUROMETRY

Mercurometry or mercurometric titration is determination of chlorides and iodides based on the use of mercury(I) nitrate $\text{Hg}_2(\text{NO}_3)_2$ solution as a titrant in the presence of indicators.

The method is based on reactions leading to very slightly soluble precipitates of mercury(I) chloride Hg_2Cl_2 and iodide Hg_2I_2 :



Titrant of the method. Aqueous mercury(I) nitrate $\text{Hg}_2(\text{NO}_3)_2$ solution, usually with a molar concentration of 0.05 mol/L (molar equivalent concentration is 0.1 mol/L), is used as titrant of the method. Initially, the titrant solution with approximate concentration is prepared by dissolving a sample weight of $\text{Hg}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ in 0.2 mol/L nitric acid solution. Since mercury(I) salts may contain mercury(II) impurities, then mercury(II) is transformed to mercury(I) by adding a small amount of metallic mercury to the solution with stirring, after which the mixture is left to stand for about 24 hours. In this case, mercury(II) is transformed into mercury(I):



The resulting mercury(I) nitrate solution is standardized using standard sodium chloride solution in the presence of indicators.

Indicators of the method. Iron(III) thiocyanate complexes or diphenylcarbazone are used as indicators of the method.

Iron(III) thiocyanate complexes are formed directly in titrated solution when ammonium thiocyanate NH_4SCN and iron(III) nitrate $\text{Fe}(\text{NO}_3)_3$ are added to it. Thiocyanate complexes are colored red, and as a result, the analyzed solution also turns red and remains this color until the end of the titration.

Diphenylcarbazone is an adsorption indicator. It is added to a titrated solution before the end of the titration. Near EP, the indicator colors precipitate intense blue.

1. Mercurimetry is used for quantification of halide ions in their interaction with solutions of mercury salts (Hg_2^{2+}). What indicator allows analytical visualization of complete precipitation of halide ions?
- A. Potassium dichromate
 - B. Methyl orange
 - C. Diphenylcarbazone *
 - D. Eosin
 - E. Fluorescein

COMPLEXIMETRIC TITRATION

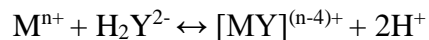
Compleximetry, or *compleximetric titration* is a method of titrimetric analysis based on the use of complexation reactions between a determined component of analyzed solution and titrant.

The method is commonly used to determine cations of metal complexing agents.

Complexonometry

During complexometric titration, the reaction between the metal cation and complexone leads to the formation of metal complexonate.

Complexones are commonly polybasic aminopolycarboxylic acids and their salts, whose anions, acting as polydentate chelating ligands, are able to form stable soluble complexes (complexonates) with various metal cations. Complexone III (trilon B, disodium edetate dihydrate $\text{Na}_2\text{H}_2\text{Y}_2 \cdot 2\text{H}_2\text{O}$, EDTA). EDTA manifests itself as a six-dentate ligand and forms complexes mainly with the composition $\text{MY}^{(n-4)+}$:



Complexonometry titrants

Standard water solutions of EDTA usually with molar concentration 0.1, 0.05, 0.025 and 0.01 mol/L as well as standard solutions of magnesium or zinc sulphate are used as titrants used in the method.

Titration solution - Trilon B - is prepared according to the precisely weighed quantity of $\text{Na}_2\text{H}_2\text{Y} \cdot 2\text{H}_2\text{O}$ and then is normalized according to a standard solution of magnesium or zinc sulphate.

Complexometry indicators

For visual determination of EPT, two types of indicators are used.

The first type of indicators includes colorless organic substances that form colored complexes with cations of the metals being determined. Such indicators include salicylic acid, sulfosalicylic acid, tyrosine, hydroxamic acids, thiocarbamide and

some others. Indicators of this type are used relatively rarely in complexometry.

The second type of indicators which are most often used in complexometry includes *metalchromic indicators* (sometimes called *metal indicators*) which are organic dyes with their own chromophore groups that can reversibly change color when complexes with metal cations are formed. In other words, metalchromic indicators are weak protoliths that reversibly form intensely colored complexes with cations of the metals being determined, and the *color of the complexes differs from the color of the free indicator*.

1. What compound is added along with the murexide indicator to reach $\text{pH} > 12$, when detecting calcium cations?
 - A. Acetate buffer
 - B. Ammonium hydroxide
 - C. Urotropin
 - D. Ammoniac buffer
 - E. Sodium hydroxide *
2. Complexonometry is a titrimetric method of analysis based on the interaction of polydentate ligand complexes with cations of alkaline earth and heavy metals, which results in formation of strong, easily water-soluble compounds. Solution of what substance is used in complexonometry as a titrant?
 - A. Potassium dichromate
 - B. Sulfuric acid
 - C. Silver(I) nitrate
 - D. Trilon B (ethylenediaminetetraacetic acid tetrasodium salt) *
 - E. Sodium thiosulfate
3. The following method can be used to quantitatively determine magnesium sulfate in the solution:
 - A. Thiocyanate titration
 - B. Nitrite titration

- C. Complexometric titration *
- D. Acidimetry
- E. Argentometry

4. Metallochromic indicators are used in complexometric titration, when determining total water hardness. For this purpose, the following can be used as an indicator:

- A. Eriochrome black T *
- B. Methyl red
- C. Potassium chromate
- D. Fluorescein
- E. Phenolphthalein

5. What method is used for the quantification of bismuth in a preparation?

- A. Complexonometry *
- B. Mercurimetry
- C. Iodometry
- D. Permanganatometry
- E. Argentometry

6. What method is used for the quantification of magnesium sulfate solution for injections?

- A. Cerimetry
- B. Acid-base titration
- C. Complexonometry*
- D. Nitritometry
- E. Iodine monochloride titration

7. Laboratories of various specialization use the following method to determine general water hardness of potable water:

- A. Oxidimetry
- B. Acidimetry
- C. Alkalimetry
- D. Complexometric titration*

E. Precipitation

8. What method is used for quantification of bismuth in a preparation?

- A. Iodometry
- B. Argentometry
- C. Mercurimetry
- D. Complexonometry *
- E. Permanganatometry

9. Select a metallochromic indicator from the list below.

- A. Starch
- B. Methyl orange
- C. Litmus
- D. Eosin
- E. Murexide*

10. A solution containing calcium and magnesium cations is titrated with Trilon B solution. Complexometric titration of these cations requires the following medium:

- A. Acidic solution
- B. Acetate buffer solution
- C. Neutral medium
- D. Formate buffer solution
- E. Ammonium buffer solution*

11. Direct complexometric titration is used to determine the concentration of:

- A. Strong acid anions
- B. Weak acid anions
- C. Hydrogen ions
- D. Hydroxide ions
- E. Metal cations*

Mercurimetry

Mercurimetry, or mercurimetric titration, is a titrimetric analysis method based on the use of reactions of the formation of stable, weakly dissociating, soluble mercury compounds(II) – HgCl_2 , $\text{Hg}(\text{CN})_2$, $\text{Hg}(\text{SCN})_2$ which are present in solutions in the form of complex compounds.

The essence of the method. The method is used to determine anions Cl^- , Br^- , I^- , CN^- , SCN^- as well as mercury(II) Hg^{2+} .

Titrant of the method. Standard solutions of mercury nitrate $\text{Hg}(\text{NO}_3)_2$ or mercury chlorate $\text{Hg}(\text{ClO}_4)_2$ are used as titrant usually with molar concentration 0.05 mol/L. Mercury(II) nitrate and perchlorate are strong electrolytes and dissociate into ions in aqueous solution.

Initially, the titrant solution with approximate concentration is prepared, and then it is standardized using standard NaCl or NH_4SCN solution in the presence of indicator.

Indicators of the method. Sodium nitroprusside $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$, diphenyl carbazone, diphenyl carbazide and some others are used as indicators in mercury measurements.

Application of mercurimetry. The method is most often used for the determination of chlorides; less commonly determined are bromides, iodides, cyanides.

1. When determining substances by means of mercurimetric titration, the following solution is used as a titrant:
 - A. Mercury(II) nitrate *
 - B. Ammonium thiocyanate
 - C. Mercury(I) nitrate
 - D. Potassium iodide
 - E. Silver(I) nitrate
2. The titrant of mercurimetry method is:
 - A. 0,1mol solution of AgNO_3
 - B. 0,1mol solution of NH_4SCN

- C. 0,1mol solution of $\text{Hg}_2(\text{NO}_3)_2^*$
- D. 0,1mol solution of NaNO_2
- E. 0,1mol solution of KSCN

GRAVIMETRIC METHOD OF ANALYSIS

Gravimetric (weight) analysis, or gravimetry, is one quantitative analytical methods based on determining the mass of desirable component of an analyzed sample by measuring (accurate weighing) the mass of known stable end substance to which this determined component is fully transferred.

Main steps of gravimetric determination

Main stages of gravimetric analysis in the precipitation method, in general, include the following:

- a) calculation of the mass of the weighed quantity of analyzed sample and the volume (or mass) of precipitant;
- b) weighing (taking) the weighed quantity of analyzed sample;
- c) dissolution of the weighed quantity of analyzed sample;
- d) precipitation, i.e., preparation of *the precipitation form* of analyte;
- e) filtration (separation of precipitate from the supernatant liquid);
- f) washing of precipitate;
- g) drying and (if necessary) ignition of precipitate to constant mass, i.e., preparation of the *gravimetric form*; weighing of the gravimetric form;
- h) calculation of analysis results, statistical processing of them and presentation.

Let us briefly consider each of these procedures.

The precipitated form is a compound in the form of which the analyte is precipitated from solution.

Requirements for precipitation form

- 1) The determined component must be quantitatively precipitated. Precipitate must be negligibly soluble: a mass of dissolved precipitate should not exceed the weighing error of an analytical balance, i.e., 0.0002 g.
- 2) The precipitate should not be soluble in excess precipitant with the formation of soluble coordination complexes.

- 3) The precipitate should not contain impurities.
- 4) The precipitate must be resistant to external effects, i.e., not be oxidized, reduced, etc.
- 5) During drying or ignition, the precipitated form must completely transform into a gravimetric form without loss of determined component.
- 6) The precipitate structure shall provide optimal precipitate filtrating and washing from impurities.

The gravimetric form is a compound that is weighed to obtain the final result.

Gravimetric form requirements

1. Composition of the gravimetric form must exactly corresponds to its stoichiometry (for example, CaSO_4 , BaSO_4 , BiPO_3 , Al_2O_3 , Fe_2O_3 , CaO , etc).
2. Gravimetric form must be stable with access to air, not decomposed, not subjected to redox processes, etc.
3. Gravimetric factor F must have the lowest possible value since this condition reduces the relative error of gravimetric determination.

Weighing of gravimetric form. Gravimetric form is adjusted to constant mass during precipitate ignition. For this purpose, after the first ignition for a time mentioned in the analytical procedure (often about 1 – 1.5 hours), the crucible with precipitate is quickly transferred from a muffle furnace to a desiccator, cooled to room temperature for about 30 minutes, and weighed using an analytical balance.

Use of gravimetric analysis

Indirect distillation methods are widely used to determine the content of volatile substances, especially in drug products (most often inactive substances), and also to determine dry residue in tinctures and extracts. Gravimetric determination of loss on drying drug products is a multifunctional compendial method used in the quality control of numerous medications.

Gravimetric methods are used in the quality control of drug products and herbal raw materials to determine such parameters as

total ash content (ash residue after igniting and calcinating the analyzed sample), sulfate ash, and ash insoluble in hydrochloric acid.

Electrogravimetry is used in the analysis of metals and alloys.

1. What conditions are necessary for the formation of crystalline precipitates?
 - A. Rapid precipitation in hot dilute solutions
 - B. Slow precipitation in cold concentrated solutions
 - C. Slow precipitation in cold dilute solutions
 - D. Slow precipitation in hot dilute solutions *
 - E. Rapid precipitation in hot concentrated solutions
2. Gravimetry was used to analyze sodium sulfate crystalline hydrate by precipitating sulfate ions with a barium chloride solution. After its maturation, the barium sulfate precipitate must be washed using decantation. What is used as a washing liquid for this purpose?
 - A. Ammonium sulfate solution
 - B. Barium chloride solution
 - C. Dilute solution of sulfuric acid*
 - D. Sodium sulfate solution
 - E. Distilled water
3. Gravimetric titration was used to determine aluminium mass fraction in a medicinal preparation. Ammonium hydroxide solution was used as a precipitant. In this case the gravimetric form will be:
 - A. Ammonium chloride
 - B. Aluminium oxide*
 - C. Aluminium hydroxide
 - D. Aluminium carbonate
 - E. Ammonium nitrate

INSTRUMENTAL METHODS OF ANALYSIS

OPTICAL METHODS OF ANALYSIS

Optical methods of analysis are based on the measuring the optical properties of a substance (emission, absorption, scattering, reflection, refraction, light polarization), which occur as a result of interaction between electromagnetic radiation and substance.

The first law of light absorption (the first law of photometry – *Bouguer-Lambert law*) can be formulated as follows:

each thin layer of constant thickness in a homogeneous medium absorbs an equal fraction of incident light flux.

The second law of light absorption (the second law of photometry – *Bouguer-Beer law* or just *Beer law*) can be expressed as follows:

a fraction of light flux absorbed by a given thin layer in a homogeneous medium is proportional to the number of light-absorbing particles per volume unit, i.e., concentration.

Both laws of light absorption are combined into *Bouguer-Lambert-Beer consolidated principal law of light absorption*, which characterize the dependence of *monochromatic* (at a constant wavelength) radiation absorption on the absorbing layer thickness and concentration of light-absorbing particles.

The law can be presented in the logarithmic form:

$$A = k \cdot C \cdot l.$$

If concentration C is expressed in units of mol/L, then k is called the *molar absorption coefficient* and designated ϵ . Then

$$A = \epsilon \cdot C \cdot l.$$

If concentration C is expressed in grams of the dissolved substance per 100 ml of the solution and designated $A_{1cm}^{1\%}$. Then k is called the *specific absorption coefficient*.

$$A = A_{1cm}^{1\%} \cdot C \cdot l.$$

It is easy to show that molar and specific absorption coefficients are related by equations:

$$\epsilon = \frac{A_{1cm}^{1\%} \cdot M}{10} \quad \text{and} \quad A_{1cm}^{1\%} = \frac{\epsilon \cdot 10}{M},$$

where M is the molar mass of the dissolved substance.

Optical methods of analysis

| Methods | Measured parameters |
|---------------------------------------|---|
| Spectrophotometry Photocolorimetry | Absorption |
| Refractometry | Refractive index |
| Polarimetry | Rotation angle of the polarization plane of optically active substances |

1. Molar attenuation coefficient is the optical density of a solution with absorbent layer 1 cm thick and concentration that equals:
 - A. 1 mol/L *
 - B. 1 g/mL
 - C. 1%
 - D. 1 g/L
 - E. 0.1 mol/L
2. Molecular absorption analysis is based on the Beer–Lambert–Bouguer law. According to this law, optical density of a solution is:
 - A. Inversely proportional to the layer thickness and concentration of the substance
 - B. Directly proportional to the layer thickness and concentration of the substance *
 - C. Directly proportional to the layer thickness and monochromatic light absorption index
 - D. Directly proportional to the concentration and inversely proportional to the layer thickness
 - E. Directly proportional to the concentration and inversely proportional to the monochromatic light absorption index

PHOTOELECTROCOLORIMETRY

It is applied for measuring absorption or transmission of the light by coloured solutions using the light with the narrow wavelength range instead of the monochromatic radiation. With this purpose devices called the photoelectrocolorimeters are used.

Photoelectric methods of measuring the intensity of colour are related to the use of photoelectric cells. The latter transforms the light energy into the electric one. Measurement of the light flows with the help of photoelectric photometry is more accurate and does not depend on the peculiarities of the observer's eye.

The application of photoelectric cells allows to automate determination of the substances concentration in chemical control of technological processes. Therefore, photoelectric colorimetry is widely used in practice.

1. By means of photoelectrocolorimetric analysis the concentration of the following can be determined:
 - A. Any type of solution
 - B. Colored solution *
 - C. Colorless solution
 - D. Optically active substance
 - E. Turbid solution
2. To quantitatively determine Fe^{3+} ions, a photometric reaction with sulfosalicylic acid was conducted. Photometric determination of the obtained solution requires measuring of the following:
 - A. Optical density *
 - B. Specific rotation
 - C. Half-wave potential
 - D. Refractive index
 - E. Wavelength

3. What solution can be determined by the photolorimetric method measuring self-absorbance?
- A. Potassium chloride
 - B. Potassium nitrate
 - C. Potassium sulphate
 - D. Potassium phosphate
 - E. Potassium chromate *
4. What method is used for simultaneous elimination of the effect of foreign substances, concentration, and determination of concentration?
- A. Fluorimetry
 - B. Differential spectrophotometry
 - C. Extraction-photometric analysis *
 - D. Refractometry
 - E. Polarimetry
5. Photometry is one of the most common instrumental methods of analysis. It is based on the measurement of:
- A. Fluorescence intensity
 - B. Refractive index
 - C. Optical density *
 - D. Wavelength
 - E. Rotation angle

SPECTROPHOTOMETRY

Spectrophotometry is a technique used to measure how much light a substance absorbs at different wavelengths. When light passes through a sample, the molecules in the sample absorb some of it, and the rest passes through. By analyzing how much light is absorbed at specific wavelengths, we can learn important information about the substance, such as its concentration or chemical composition.

Principle

Spectrophotometry is built on the principle of light and its interaction with matter. Light is a form of electromagnetic radiation that travels in waves.

When light encounters a material, several things can happen. The light can be reflected off the surface, transmitted through the material, or absorbed by the material. Absorption occurs when the energy of the light matches the energy needed to move electrons within the molecules of the material to a higher energy level. Different substances absorb light at different wavelengths, depending on their molecular structure.

In spectrophotometry, we focus on measuring the absorption of light by a substance. The amount of light absorbed at a particular wavelength can tell us a lot about the substance's concentration and its identity. This measurement is based on the Bouguer-Lambert-Beer Law .

1. Potassium dichromate solution is to be analyzed. What physicochemical method of analysis will be used to determine its concentration?
 - A. Conductometric titration
 - B. Spectrophotometry*
 - C. Polarimetry
 - D. Fluorimetry
 - E. Coulometry

2. A dispensing chemist performs identification of pharmaceutical substance using ultraviolet spectrophotometry. The specialist obtains the graph of optical density to wavelength ratio, which is called:
- A. Logarithmic curve
 - B. Calibration curve
 - C. Light absorption curve *
 - D. Emission spectrum
 - E. Titration curve

REFRACTOMETRY

The refractometric method of analysis is based on measuring light refraction index (refractive index) of liquids or crystals.

Methods for determining the concentration

1. The method of the calibrated curve.

Refraction indices n must be measured for several reference solutions with precisely known content X of determinate and according to obtained data plot the calibration curve in $n - X$ coordinates. Then, under strictly the same conditions, measure the refraction index of an analyzed solution.

2. According to the tables.

For many substances designed tables, which are the refractive indices of solutions with known concentrations.

3. By refractometric factor.

POLARIMETRY

The basis of the polarimetric method of analysis is the measurement of the angle of rotation of the plane of polarization of polarized light that has passed through the optically active medium.

The deviation of the plane of polarization from the initial position, expressed in angular degrees, is called the angle of rotation and is denoted by the Greek letter α .

The deviation of the plane of polarization from the initial position, expressed in angular degrees, is called the angle of rotation and is denoted by the Greek letter α .

The optical activity of the substance is characterized by the value of specific rotation, which is determined by calculation as the angle of rotation of the plane of polarization when passing polarized light through a layer of solution 1 dm thick, with a concentration of 1 g/cm³.

1. Optical activity of monosaccharides can be explained by their:
 - A. Number of hydroxyl groups in a molecule
 - B. Aldehyde or ketone group
 - C. Asymmetric carbon atoms in a molecule *
 - D. Asymmetric crystal
 - E. Complicated rotation around sigma-bond

ELECTROCHEMICAL METHODS OF ANALYSIS

The application of electrochemical methods in quantitative analysis is based on the use of the dependences of the measured parameters of electrochemical processes on the content of the analyte in the analyzed solution.

Classification of electrochemical methods of analysis.

Classification based on considering the type of system electric power source. There exist two groups of methods.

- a) *Methods without application of external (supporting) potential.* The electrochemical system itself, consisting of a galvanic cell, serves as the electric power source (galvanic circuit). Such methods include *potentiometric methods*. The electromotive force - EMF - and electrode potentials in such a system depend on the content of determinate in solution.
- b) *Methods with an application of external (supporting) potential.*

Such a method includes:

- *conductometric analysis* is based on measuring the electrical conductivity of solutions as a function of their concentration;
- *voltammetric analysis* is based on measuring the current as a function of the applied known potential difference and solution concentration;
- *coulometric analysis* is based on measuring the quantity of electricity passed through solution as a function of its concentration;
- *electro-gravimetric analysis* is based on measuring the mass of electrochemical reaction product.

Classification of electrochemical methods by means of application.

A distinction is made between direct and indirect methods.

- a) *Direct methods.* An electrochemical parameter is measured as a known function of solution concentration, and the content of determinate in solution is found by the reading of the appropriate measuring device.

b) *Indirect methods* are titration methods in which the end of titration is determined based on measuring electrical parameters of the system.

According to this classification, a distinction is made between, for example, *direct conductometry and conductometric titration*, *direct potentiometry and potentiometric titration* and so on.

POTENTIOMETRY

Potentiometric measurement system consists of two electrodes called reference and indicator electrode, potentiometer and a solution of analyte.

By appointment potentiometric method of analysis is divided into *direct potentiometry and potentiometric titration.*

Use of direct potentiometry. The method is used for determination of hydrogen ion (pH of solutions), anions, metal ions (ionometry) concentrations.

Advantages of direct potentiometry include measuring simplicity and rapidity; small solution volumes are required for measurements.

Potentiometric titration is a method of determining the volume of titrant used for titration of determinate in analyzed solution by measuring EMF (during titration) by means of the galvanic circuit composed of the indicating electrode and reference electrode.

In the case of potentiometric titration, using indicators changing color near EP is not required.

Electrodes used in potentiometry

An indicator electrode has a potential that varies with variations in the concentration of an analyte. Most indicator electrodes used in potentiometry are selective in their responses. Metallic indicator electrode and membrane electrodes are types of indicator electrodes.

A reference electrode is a half-cell having a known potential that remains constant at constant temperature and independent of the composition of the analyte solution. The reference electrode is always treated as the left-hand electrode in potentiometric measurements. Calomel electrodes and silver/silver chloride electrodes are types of reference electrodes.

The following types of electrodes are used in potentiometry: electrodes of the first kind, the second kind, redox and membrane electrodes.

Electrode systems for potentiometric titration

Electrodes of the first kind are electrodes reversible by cation (same as electrode material). There are three types of electrodes of the first kind.

a) **Metal *M*** submerged in a solution of the salt of the same metal.

b) **Gas electrodes** (for example - hydrogen electrode, including the standard hydrogen electrode.) Potential of the reversible hydrogen gas electrode is defined by the activity of hydrogen ions

c) **Amalgam electrodes**, consisting of a metal amalgam submerged in a solution containing cations of the same metal.

Electrodes of the second kind are reversible by anion. The following types of electrodes of the second kind are distinguished.

a) Metal whose surface is covered with a slightly soluble salt of the same metal, submerged in a solution containing anions that are a part of this slightly soluble salt. An example would be the silver-silver chloride electrode $\text{Ag}|\text{AgCl}, \text{KCl}$ or the calomel electrode $\text{Hg}|\text{Hg}_2\text{Cl}_2, \text{KCl}$.

b) Gas electrodes of the second kind, for example, chlorine electrode $\text{Pt}, \text{Cl}_2|\text{KCl}$.

Oxidation-reduction electrodes consist of inert material (platinum, gold, tungsten, titanium, graphite, etc.) submerged and a solution containing oxidized Ox and reduced Red forms of the given substance. There are two kinds of redox electrodes:

a) electrodes whose potential is independent of hydrogen ion activity, for example: $\text{Pt}|\text{FeCl}_3, \text{FeCl}$; $\text{Pt}|\text{K}_3[\text{Fe}(\text{CN})_6], \text{K}_4[\text{Fe}(\text{CN})_6]$, etc.;

b) electrodes, whose potential depends on hydrogen ion activity, for example, quinhydrone electrode.

Membrane, or ion-selective, electrodes - electrodes reversible by certain ions (cations or anions) sorbed by a solid or liquid membrane. The real potential of such electrodes depends on the activity of the ions which are sorbed by the membrane.

| Type of analytical reaction | Indicator electrodes | Reference electrodes | Application |
|-----------------------------|-------------------------|---------------------------------|--|
| Acid-base | Glass | Silver chloride, Calomel | Titration of acids, bases and salts |
| Precipitation | Silver, silver sulphide | Silver chloride, Calomel, Glass | Titration of halogenides, rhodanides, cyanides, sulphides |
| Complexometric | Mercury, ion-selective | Silver chloride, Calomel, Glass | Titration of cations that form strong complexations |
| Oxidation-reduction | Platinum | Silver chloride, Calomel, Glass | Titration of reducing agents with different oxidants and vice versa. |

1. What reference electrode can be used in potentiometric analysis of a medicinal substance?
 - A. Silver chloride *
 - B. Glass
 - C. Zinc
 - D. Quinhydrone
 - E. Antimony

2. What pair of electrodes is used in potentiometric redox titration?
 - A. Silver sulfide electrode and silver chloride electrode
 - B. Silver electrode and platinum electrode
 - C. Platinum electrode and silver chloride electrode *

- D. Copper electrode and zinc electrode
 - E. Glass electrode and silver chloride electrode
3. Potentiometry is widely used in the analysis of medicinal products. What type of galvanic cell has the electromotive force that does not depend on the value of the standard electrode potential?
- A. Chemical galvanic cell
 - B. Galvanic cell without ion transfer
 - C. Reversible galvanic cell
 - D. Concentration galvanic cell *
 - E. Galvanic cell with ion transfer
4. What should be used as an indicator electrode in potentiometric titration aimed at quantifying iron(II) sulfate?
- A. Glass
 - B. Antimony
 - C. Platinum *
 - D. Quinhydrone
 - E. Silver chloride
5. Potentiometry is an analytical method widely used in pharmaceutical analysis. In what galvanic cell its electromotive force (EMF) does not depend on the value of standard electrode potentials?
- A. Galvanic cell without ionic transport
 - B. Reversible galvanic cell
 - C. Chemical galvanic cell
 - D. Galvanic cell with ionic transport
 - E. Concentration galvanic cell *
6. What potential forms at the interface between two solutions?
- A. Diffusion potential *
 - B. Electrokinetic potential
 - C. Contact potential

- D. Electrode potential
- E. Surface potential

7. Potentiometry is one of the electrochemical methods of analysis.

This method is based on measuring (determination) of:

- A. Indicator electrode potential*
- B. Diffuse layer potential
- C. Systemic redox potential
- D. Reference electrode potential
- E. Zeta-potential

8. How according to the Pharmacopoeia is pH determined?

- A. Polarography
- B. Potentiometry*
- C. Conductometry
- D. Spectrophotometry
- E. Indicator

9. In potentiometric titration the following indicator electrode is used for chloride and borate acids quantitative determination in their mixture:

- A. Silver
- B. Silver-chlorine
- C. Calomel
- D. Platinum
- E. Glass*

10. Acetic acid concentration in a solution being analyzed can be determined by means of potentiometric titration. Specify the indicator electrode:

- A. Silver chloride
- B. Mercury
- C. Calomel
- D. Glass *
- E. Zinc

11. What reference electrode can be used in the potentiometric analysis of a medicinal substance?
- A. Antimony electrode
 - B. Glass electrode
 - C. Zinc electrode
 - D. Silver chloride electrode *
 - E. Quinhydrone electrode
12. What physico-chemical method is used to determine the pH of solutions for injections?
- A. Amperometry
 - B. Potentiometry *
 - C. Electrolysis
 - D. Conductometry
 - E. Polarography
13. What value determines the degree to which extraneous ions have an effect on the potential of the ion-selective electrode?
- A. Activity coefficient
 - B. Osmotic coefficient
 - C. Diffusion coefficient
 - D. Selectivity coefficient *
 - E. Electrical conductivity coefficient

CONDUCTOMETRIC ANALYSIS (CONDUCTOMETRY)

Conductometric analysis (conductometry) is based on the use of dependence between electrical conductivity (electrical conductance) of electrolyte solutions and their concentration.

The electrical conductivity of electrolyte solutions - the second-class conductors - is estimated based on measuring their electrical resistance in the electrochemical cell, which is a glass vessel (beaker) with two brazed-in electrodes and analyzed electrolyte solution between them.

Direct conductometry

In direct conductometry, the concentration of a substance in an analyzed solution is determined by measurement results of specific electrical conductivity of this solution. On the treatment of measurement data, two methods are used: calculation method and calibration curve method.

Conductometric titration

When performing conductometric titrating, follow the course of titration by the change in electrical conductivity of analyzed solution placed in the conductometric cell between two inert electrodes (usually from platinized platinum). According to obtained data, plot the conductometric titration curve representing the dependence of electrical conductivity of titrated solution on the volume of added titrant. The end point of titration is most often determined by extrapolation of curved titration lines in a range of the change in the curve slope. In addition, the use of indicators that change color near the EP is not required.

Different types of reactions are used in conductometric titration: acid-base, redox, precipitating, complex formation processes.

1. In the process of conductometric titration of HCl and CH₃COOH acids mixture 0,1 M solution of NaOH is used to measure:

A. Rotation angle of polarized light plane

- B. Electrical conduction in solution*
- C. pH of medium
- D. Refractive index
- E. Potential difference

POLAROGRAPHIC ANALYSIS (POLAROGRAPHY, DIRECT VOLTAMMETRY)

Polarographic analysis (polarography) is based on the use of the following dependencies between electrical parameters of the electrochemical (in this case - polarographic) cell to which external potential is applied and properties of analyzed solution contained in the cell.

The qualitative polarographic analysis uses dependence between the value of applied to a micro-electrode external electrical potential at which reduction (or oxidation) of determinate on micro-electrode is observed under given conditions and the nature of a reducible (or oxidable) substance.

The quantitative polarographic analysis uses dependence between the value of diffusion current set in the polarographic cell after an achievement of the certain value of electrical potential applied to micro-electrode and concentration of determinate (reducible or oxidable) in analyzed solution.

Electrical parameters - electrical potential value and diffusion current value - are determined during an analysis of obtained polarizable, or voltampere, curves presenting graphically dependence of electrical current in the polarographic cell of the value of potential applied to the micro-electrode. For this reason, polarography is sometimes called *direct voltammetry*.

1. Polarography is one of the electrochemical methods of analysis.
What parameter is used in polarographic analysis to identify the substance being analyzed?
 - A. Height of a polarographic wave
 - B. Magnitude of the electromotive force
 - C. Half-wave potential *
 - D. Position of a polarographic wave
 - E. Width of a polarographic wave

AMPEROMETRIC (POLAROGRAPHIC) TITRATION

Amperometric titration (potentiostatic polarizing titration) is a variant of the voltammetric method (along with polarography). Amperometric titration is based on determination of the equivalence point by the sharp change of the limit diffusion current. Amperometric titration can be carried out on the common polarograph using both the indicator electrode and the dropping mercury microelectrode. However, the device can be more simple than the polarograph, and solid electrodes from platinum, gold, titanium, tungsten, graphite, etc., are used as indicator electrodes. Electrodes from solid materials should obligatory rotate with the rates of 300 - 600 revolutions per minute because unlike the dropping mercury electrode the surface of these electrodes is not renewed and it is contaminated with electrolysis products. While rotating the electrodes the latter are partially removed by mechanical means. Besides, when rotating the electrodes due to mixing the solution the thickness of the diffusion layer decreases, and it leads to increase of their sensitivity in 50 - 100 times comparing to the dropping mercury electrode.

When carrying out the amperometric titration the potential, which corresponds to the plateau of the limit diffusion current, is passed to the indicator electrode. Therefore, before beginning the titration the polarogram of the solution to be analysed is previously obtained and the plateau potential of the diffusion current is determined. The titration is carried out using the same polarographic background as the one used for obtaining the polarogram.

1. Amperometric titration is used in analysis of some pharmaceutical preparations. The amperometric titration method is based on the following:
 - A. Measuring the potential difference of the electrodes during the titration process
 - B. Ion exchange between the analyte solution and cationite
 - C. Measuring the cell voltage during the titration

- D. Determining the equivalence point by a sharp change in the diffusion current during the titration process*
- E. Ion exchange between the anionite and analyte solution

COULOMETRIC ANALYSIS (COULOMETRY)

Coulometric analysis (coulometry) is based on the use of dependence between the mass m of substance reacted during electrolysis in the electrochemical cell and the quantity of electricity passed through the electrochemical cell during electrolysis of this substance only.

Coulometric titration is carried out in ampere static (galvanostatic) or potentiostatic mode. More often coulometric titration is carried out in ampere static mode maintaining a constant electrical current during the entire time of electrolysis.

1. Coulometry is based on measuring the amount of electricity needed for an electrode reaction. What law is the basis for coulometric determination of substances?
 - A. Beer-Bouguer-Lambert law
 - B. Faraday law*
 - C. Coulomb law
 - D. Stokes law
 - E. Newton law
2. What electrochemical method of quantitative analysis is based on measuring the amount of electric current that has been used for electrochemical reduction or oxidation of ions or elements that are being determined in the process of electrolysis?
 - A. Polarography
 - B. Conductometry
 - C. Potentiometry
 - D. Coulometry *
 - E. Amperometry

CHROMATOGRAPHY

Chromatography is an area of science that studies the processes based on the movement of the zone of substance along the sorbent layer in the flow of the mobile phase and associated with repeated sorption and desorption acts.

In any variant of chromatographic methods, a combination of *fixed (stationary) phase* (FP) and *a mobile phase* (MP) is used. The mobile phase (gas, liquid) in the process of chromatography continuously moves along the stationary phase (solid, liquid), so that the particles of chromatographed substances, transported together with MP, can repeatedly convert from the mobile phase to the stationary phase and back. The separation of substances by chromatography is based on different affinities of the separated substances to the mobile and stationary phases. The variety in affinity leads to a difference in the speed of the particles of the movement of the separated substances together with mobile phase and eventually to their separation.

Thin-layer chromatography

One of the most common methods of adsorption chromatography is thin-layer chromatography (TLC) a type of plane chromatography, in which the adsorbent used is a thin layer on a plate.

As sorbents, silicon dioxide – silica gel SiO_2 and aluminum oxide Al_2O_3 are most often used, as well as some other materials (activated carbon, sucrose, calcium carbonate, cellulose, talc, polyamide resins, etc.).

The choice of solvent in the TLC method is determined by the nature of the sorbent and the properties of the analyzed mixture. Mixture of several solvents are often prepared as the MP.

As an example of solvent mixtures used in TLC, it is possible to specify, for example (in parentheses, the volume ratio of the components of the mixture is indicated):

- butanol + acetic acid + water (4:1:5);
- isopropanol + aqueous ammonia (7:3);

- 15% aqueous solution of acetic acid;
- 30% solution of acetonitrile.

1. Chromatographic analysis methods differ in their mechanism of sorbent-sorbate interaction. What partition mechanism is used in ion-exchange chromatography?
 - A. Solutes and sorbent producing precipitates of different solubility
 - B. Different solubility of the solutes in the stationary phase
 - C. Different ion-exchange capacity of the substances *
 - D. Different adsorption capacity of the solid sorbent towards different substances
 - E. Production of coordination compounds of different stability in the phase or on the sorbent surface

2. Chromatographic methods can be classified by the mechanism of the separation process. What type of chromatography is gas-liquid chromatography?
 - A. Distribution chromatography *
 - B. Adsorption chromatography
 - C. Ion-exchange chromatography
 - D. Gel-filtration chromatography
 - E. Affinity chromatography

3. Separation of substances in gas-liquid chromatography occurs due to the different speed of movement of substances through the column. What is the mobile phase in this method of analysis?
 - A. Organic solvent
 - B. Solid carrier
 - C. Water
 - D. Liquid phases
 - E. Carrier gas *

4. Ion-exchange adsorption is widely used for water softening and demineralization. Through what ionite columns should the water be passed for its demineralization?

- A. Through the cationite in the RH-form, and then through the cationite in the RK-form
 - B. Through the cationite in the RH-form, and then through the anionite in the ROH-form *
 - C. Through the cationite in the RK-form, and then through the anionite in the ROH-form
 - D. Through the anionite in the ROH-form, and then through the cationite in the R_2Ca -form
 - E. Through the anionite in the R_2SO_4 -form, and then through the cationite in the ROH-form
5. What type of chromatography does the gas-liquid chromatography method belong to?
- A. Distribution chromatography *
 - B. Ion exchange chromatography
 - C. Gel chromatography
 - D. Adsorption chromatography
 - E. Affinity chromatography
6. To identify a drug by thin-layer chromatography the following parameter is used:
- A. K_p
 - B. n
 - C. E, mV
 - D. R_f *
 - E. I, A
7. Extraction is often used in analysis of medicinal substances. In this method, the degree of extraction of the substance that is being determined depends on the following:
- A. The mass of the substance being extracted
 - B. pH of the solution
 - C. The amount of the substance being extracted
 - D. Distribution coefficient*
 - E. Temperature

Recommended literature

General literature

1. Освітній модуль для підготовки здобувачів до складання іспитів КРОК. Режим доступу: <https://test.testcentr.org.ua/>
2. Priti Malhotra. Analytical chemistry. Basic Techniques and Methods. Springer International Publishing, 2023. 339 p.
3. Alana Wood. Chemical Analysis. Modern Methods and Techniques. Willford Press, 2023. 247 p.
4. Christian Gary D., Purnendu K. Dasgupta, Kevin A. Schug. Analytical chemistry. 7 E. Wiley, 2020. 960 p.
5. Fundamentals of analytical chemistry / Scoog D., West D., Holler F. J., Crouch S. P. 10 E. Cengage, 2022. 1072 p.
6. Qualitative analysis. Acid-basic titration. Section 1. Theory and analysis of cations of I-III analytical groups. Basic topic 1. Theory and analysis of cations of IV-VI analytical groups. Basic topic 2. Theory and analysis of anions and compounds of unknown composition. Basic topic 3. Manual for students of the 2-nd course of the Pharmaceutical Faculty speciality 226 «Pharmacy, Industrial Pharmacy». – S. O. Vasyuk, A. S. Korzhova, A. O. Donchenko. – Zaporizhzhia, 2021 – 131 p.
7. Qualitative analysis. Acid-basic titration. Section 1. Acid-base titration and its application in chemical and pharmaceutical analysis. Basic topic 4. Manual for students of the 2-nd course of the Pharmaceutical Faculty speciality 226 «Pharmacy, Industrial Pharmacy». – S. O. Vasyuk, A. S. Korzhova, N. O. Nagorna, K. P. Miedviedieva. – Zaporizhzhia, 2021 – 110 p.
8. Quantitative analysis. Instrumental methods of analysis. Section 2. Oxidation-reduction titration and its application in the analysis of chemical compounds and medicines. Basic topic 1. Manual for students of the 2-st course of the Pharmaceutical Faculty specialty 226 «Pharmacy, Industrial Pharmacy». – S. O. Vasyuk, A. S. Korzhova, K. P. Miedviedieva. – Zaporizhzhia, 2021 – 66 p.
9. Quantitative analysis. Instrumental methods of analysis. Section 2. Precipitation titration, compleximetric titration.

Gravimetric analysis. Application of methods in the analysis of chemical compounds and medicines. Basic topic 2. Manual for students of the 2-st course of the Pharmaceutical Faculty specialty 226 «Pharmacy, Industrial Pharmacy». – S. O. Vasyuk, A. S. Korzhova, N. O. Nahorna. – Zaporizhzhia, 2021 – 75 p.

10. Physical methods of analysis. Manual for students of the 1-st course of the Pharmaceutical Faculty speciality 226 «Pharmacy, Industrial Pharmacy». – S. O. Vasyuk, A. S. Korzhova, O. R. Maletska. – Zaporizhzhia, 2021 – 46 p.

Additional literature

1. Modern analytical laboratory practice: manual for students of the 2-nd course speciality 226 «Pharmacy, Industrial pharmacy», qualifications of the professional «Pharmacist» / S.O. Vasyuk, A.S. Korzhova, N. O. Nagorna, K.P.Medvedeva, Y.M. Zhuk, A.O. Donchenko. - Zaporizhzhia: ZSMPU, 2023. - 97 p.

2. Fundamentals of chemical metrology: study guide for students of the 2nd year of the specialty «Pharmacy, industrial pharmacy» / Vasyuk S. A., Korzhova A. S., Nagorna N. O., Miedviedieva K.P., Zhuk Y. M., Donchenko A.O. Zaporizhzhia: ZDMU, 2023. 94 p.

3. United States Pharmacopeia 36. – USP Convention Inc. – Rockville, 2013. – 5640.

4. Державна Фармакопея України : в 3 т. / ДП «Український науковий фармакопейний центр якості лікарських засобів». 2-е вид. X. : ДП «Український науковий фармакопейний центр якості лікарських засобів», 2015. Т. 1. 1128 с.

5. Державна Фармакопея України: в 3 т. / ДП «Український науковий фармакопейний центр якості лікарських засобів». 2-е вид. X. : ДП «Український науковий фармакопейний центр якості лікарських засобів», 2014. Т. 2. 724 с.

6. Державна Фармакопея України: в 3 т. / ДП «Український науковий фармакопейний центр якості лікарських засобів». 2-е вид. X. : ДП «Український науковий фармакопейний центр якості лікарських засобів», 2014. Т. 3. 732 с.