Ministry of Education and Science of Ukraine
Lutsk National Technical University

ANALYTICAL CHEMISTRY

Methodological instructions for laboratory classes
for applicants for the first (bachelor's) level of higher education
of the educational and professional programme "Food Technologies"
areas of expertise 18 Production and technology
speciality 181 Food technology
full-time and part-time forms of study

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Analytical chemistry [Text]: methodical instructions for laboratory classes for applicants for the first (bachelor's) level of higher education of the educational and professional program "Food Technologies" of the field of knowledge 18 Production and Technologies, specialty 181 Food Technologies full-time and part-time forms of study / compiled by. I. A. Moroz - Lutsk: Lutsk NTU, 2023. 72 p.

The publication contains methodological instructions for performing laboratory work, questions for preparation for laboratory classes, exercises and tasks, and recommended reading.

It is intended for students majoring in 181 Food Technologies of full-time and part-time forms of study.

CONTENTS

INTRODUCTION

Analytical chemistry is the fundamental chemical science of methods for determining the chemical composition of compounds and their mixtures. It occupies a leading position in the system of theoretical and practical training of a specialist in food technology. According to its application, analytical chemistry is divided into qualitative, quantitative chemical analyses and instrumental methods of analysis. In the course of qualitative analysis, students must master the methods of detecting ions, elements and chemical compounds that are part of the substances under study and their mixtures. In the course of quantitative analysis, students must master the methods by which chemical compounds and their mixtures can be quantified.

Successful completion of the laboratory workshop allows students not only to effectively master the theoretical material of the course, but also to acquire the skills of conducting a chemical experiment, develops independent thinking, the ability to draw conclusions and predict research results.

The methodological instructions for laboratory work in analytical chemistry for each topic provide a detailed description of the methodology for performing the experiment, control questions, and questions for independent work.

Before starting the laboratory workshop, each student must have a good understanding of the rules of work and safety in the chemical laboratory, as well as how to provide first aid if necessary.

Students perform all laboratory work in analytical chemistry individually. At the beginning of the lesson, the teacher checks the degree of preparation of each student for the laboratory lesson. At the end of each lesson, the student defends the laboratory work, which is credited only if he or she has completed the prescribed amount of practical work, acquired practical skills on the relevant topic, answered theoretical questions on the topic of the lesson, and prepared a diary with the results of the work performed.

For theoretical and practical preparation for all classes, students are provided with literary sources.

WORK PROCEDURE AND SAFETY IN THE CHEMICAL LABORATORY

I. RULES OF WORK IN THE LABORATORY

The following rules must be observed when working in a chemical laboratory:

1. Work diligently and attentively, and be quiet.

2. The workplace should be free of clutter. Briefcases, hats, etc. must be kept in a specially designated place in the laboratory.

3. When performing experiments, follow the order and sequence of operations specified in the methodological recommendations.

4. Carefully observe the course of the experiment and note each of its features and changes (precipitation or dissolution of the sediment, changes in colour, temperature, gas emission, etc.)

5. Prepare the laboratory work at home (p.1-4) and complete it immediately after the experiment in the laboratory notebook according to the following scheme:

- ✓ Date, number and topic of the laboratory work.
- ✓ Number and name of the experiment.
- ✓ Summary or conditions of the experiment.
- ✓ A diagram or drawing of a device.
- ✓ Observations and results.
- ✓ Equations of reactions.
- ✓ Calculations.
- ✓ Conclusions.

6. Perform only those experiments specified in the instructions and discussed with the teacher.

7. Keep your workstation clean. Wipe up spilled water or reagent carefully. Dispose of broken glass, pieces of paper, residual solids, metals, etc. in a trash can or in a special container, but not down the drain.

8. After finishing work, tidy up your workplace, turn off the light, gas and water.

II. RULES FOR WORKING WITH REAGENTS

1. Each reagent beaker must be labelled with the name and concentration of the reagent (for solutions).

2. Use reagents sparingly. Only use a clean spatula or a special spoon to take dry reagents from the jars. When pouring liquid reagents, keep the beaker with the label facing you.

3. Reagents in common use, which are placed on special shelves or in fume hoods, must not be brought to their workstations.

4. After using the reagent, immediately close the beaker tightly with the same stopper and put it back. Do not keep reagents open and mix up the stoppers when closing them.

5. Do not pour or pour excess reagents back into the beaker - this may spoil all the reagents in the beaker.

6. Samples of liquid reagents should be taken with the same pipette.

7. Do not pour unused concentrated acids and alkalis, as well as reagents containing silver and mercury compounds into sinks - they should be poured into special glasses.

III. SAFETY RULES

1. All experiments involving the release of poisonous gases and vapours, as well as experiments with concentrated acids, shall be carried out in a fume hood with the draft switched off.

2. Pour the concentrated acids and alkalis into the test tubes carefully, making sure that the reagents do not get on your hands or clothing.

3. When diluting concentrated acids, especially sulphuric acid, it is necessary to pour small portions of the acid into the water, and not vice versa.

4. Do not smell the gases released by leaning close to the cookware. To detect the smell of a gas or liquid, gently inhale the air, gently directing the air stream from the cookware towards you with a wave of your hand.

5. Do not work with flammable substances near a lit burner.

6. Do not lean over the reagent vessel when pouring the reagent to avoid getting reagent on your face or clothing.

7. Do not lean over the dishes with hot liquids as they may splash out.

8. When heating the liquid in the test tube, hold it so that the opening of the test tube is directed away from yourself and from the people next to you.

9. Do not leave pieces of metallic sodium in the air, do not throw them down the sink or into the garbage can.

10. In the event of a fire of flammable liquids, immediately extinguish the fire by throwing a fire blanket or covering the flames with sand.

11. Take hot objects only with special tongs.

12. If a large amount of acid or alkali is spilled during the work, inform the laboratory assistant or teacher immediately.

13. Wash your hands thoroughly after working in the laboratory.

IV. FIRST AID

1. In case of acid contact with hands or face, rinse the affected area thoroughly with running water and then treat with 5% sodium bicarbonate (baking soda) solution.

2. If alkali gets on your hands or face, rinse the affected area thoroughly with running water until it feels soapy and then treat with a 2% boric acid solution.

3. In case of alkali or acid contact with the eyes, rinse the eyes well with water using a rinsing glass or a conventional chemical cup, then instil eye drops and consult a doctor.

4. In case of thermal burns, cool the burned area under running water, treat with dilute ethyl alcohol or 3-5% potassium permanganate solution and bandage. In case of severe burns, seek medical attention immediately.

5. In case of hand cuts, first of all, remove glass fragments from the wound, then wash off the blood with 2% potassium permanganate solution, 3% hydrogen peroxide solution, treat the area around the wound with 3% iodine alcohol solution, and then bandage it.

6. In case of poisoning, seek medical advice immediately.

Part 1. QUALITATIVE ANALYSIS

Analytical chemistry is the *science of methods for determining the composition and structure of chemical systems (individual substances, their mixtures or any material).* The composition of substances and materials has qualitative and quantitative characteristics that can be determined using analytical chemistry methods - qualitative and quantitative analysis.

Analytical chemistry is of great scientific importance; it was with the help of qualitative and quantitative analysis that the basic stoichiometric laws of chemistry were formulated, the atomic masses of elements and chemical formulas of substances and chemical compounds were established.

Qualitative analysis allows us to determine what chemical elements a substance consists of, which ions, groups of atoms, or molecules are part of it. Qualitative analysis is the first step in the study of any unknown or synthesised substance.

Quantitative analysis is a set of chemical and physical methods for determining the relative amount of elements, ions or chemical compounds in a substance under study.

For chemical analysis, larger or smaller amounts of the substances under investigation can be taken. Depending on this, a distinction is made between *macroanalysis* (macromethod) - used to analyse 0.1-1 g of a substance, such analysis is performed in test tubes; *semi-microanalysis* (semi-micro method) - 0.01-0.1 g of a substance is used, performed in ordinary or microtubes; *microanalysis* (micro method) - no more than 0.01 g of a substance is used. Sometimes it is necessary to investigate the qualitative and quantitative composition of a substance with a small amount of it. In such cases, *ultramicroanalysis is used,* when a very small amount of a substance is taken for analysis and the external effect of the reaction is observed under a microscope.

The chemical reactions used in qualitative chemical analysis must have characteristic external signs, i.e. have an analytical effect. Reactions that are accompanied by external signs are called *analytical* or *qualitative reactions*. Qualitative reactions that can be used to identify a particular ion or substance and to distinguish it from others are called *individual* or *characteristic reactions*.

There are reactions that do not interfere with foreign ions. Such reactions are called *specific reactions,* but there are very few of them.

Reactions that give the same analytical effect with several ions are called *selective* or *selective*. For example, Cl^- ions form a white precipitate with Ag^+ , Hg^{2+} , Pb^{2+} ions. Selective reactions include the so-called group reactions, which are designed to detect a specific group of ions.

There are many systems for separating cations into groups. The most common is the acid-base system. According to the acid-base classification, cations are divided into six analytical groups as shown in Table 1.

The classification of anions is based on the different solubilities of barium and argentum salts of the respective anions (Table 2).

Table 1

Acid-base classification of cations

Group number	Cations	Group reagent	Reaction products and their properties
I	Li^{+} , K^{+} , Na^{+} , NH_4^{+}	no	Sulphates, chlorides and hydroxides are soluble
II	Ag^{+} , Pb^{2+} , Hg_2^{2+}	HCl	Chloride precipitates are insoluble in dilute acids
III	Ba^{2+} , Sr^{2+} , Ca^{2+} , $(Pb\ )^{2+}$	$H_2\ SO_4$	Sulphate precipitates are insoluble in acids, alkalis, ammonia solution
IV	Al^{3+} , Cr^{3+} , Zn^{2+} , Sn^{2+} , Sn^{4+} , As^{3+}	NaOH (surplus)	Hydroxide precipitates dissolve in excess alkali
V	Fe^{3+} , Fe^{2+} , Mn^{2+} , Mg^{2+}, $(Bi\ )^{3+}$	NaOH	Hydroxide precipitates are insoluble in excess alkali and ammonia solution
VI	Cu^{2+} , Ni^{2+} , Co^{2+}	$NH_4\ OH$ (surplus)	Hydroxide precipitates dissolve in excess ammonia

Table 2

Classification of anions

Group number	Anions	Group reagent	Properties of reaction products
I	SO_4^{2-} - sulphate ion SO_3^{2-} - sulphite ion CO_3^{2-} - carbonate ion PO_4^{3-} - phosphate ion SiO_3^{2-} - silicate ion	$BaCl_2$	Barium salts are highly insoluble in water
II	Cl^{-} - chloride ion Br^{-} - bromide ion I^{-} - iodide ion S -sulfide-ion^{2-}	$AgNO_3$	Argentum salts are highly insoluble in water and dilute with HNO_3
III	NO_3^{-} -nitrate ion NO_2^{-} -nitrite ion	no	Barium and argentium salts are soluble in water

In anion analysis, group reagents are used to determine the respective groups. To simplify the analysis of anions, so-called group tests are performed to detect the presence of the respective anion groups:

- test for oxidising anions ($C_2O_7^{2-}$, AsO_4^{3-} , NO_3^-) - anions are determined by the action of KJ solution in an acidic medium in the presence of chloroform, which, if present, is coloured red-violet;

- reducing anions test ($C_2O_4^{2-}$, $S_2O_3^{2-}$, S^{2-} , SO_3^{2-} , AsO_3^{3-} , J^- , NO_2^-) - anions are determined by recording the discolouration of iodine solution in a slightly acidic environment, except for AsO_3^{3-} ions, which are determined in a slightly alkaline environment;

- the test for anions of unstable acids (H_2 SO_3 , H_2 S_2O_3, H_2CO_3 , etc.) is carried out by the action of HCl, which results in the formation of gaseous products (SO_2 , CO_2 , H_2S , etc.);

- anion test (Cl^- , Br^- , J^- , $C_2O_4^{2-}$, NO_3^- , SO_3^{2-} , $S_2O_3^{2-}$, etc.) is performed by exposing their salts to concentrated H SO_{24} , resulting in the formation of gaseous products (Cl_2 , J_2 , CO_2, etc.).

Labs 2-10 on qualitative analysis are presented in the form of a table:

Ion under study	Conditions for the reaction	Reagents	Observations	Reaction equation
Qualitative reactions of cations of analytical group I.				

Laboratory work 1
COPMLEX COMPOUNDS

THEORETICAL INFORMATION
The main provisions of the coordination theory

All inorganic compounds are conventionally divided into first-order and higher-order compounds. The first-order compounds include oxides, some acids, salts (CuO, HBr, NaCl, etc.) Higher-order compounds, *complex (coordination) compounds,* are products of the interaction of certain first-order compounds.

The basic principles of the formation of complex compounds were first outlined in 1893 by the Swiss chemist Werner in the form of the so-called coordination theory. Let us consider the main provisions of the coordination theory.

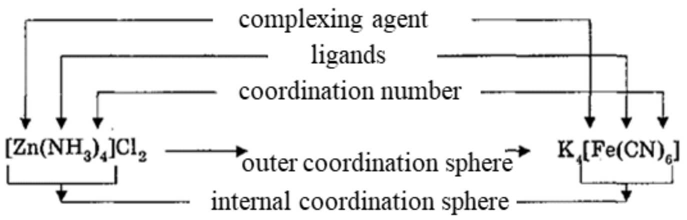
1. In the molecule of any complex compound, one of the ions occupies a central position and is called the *complexing agent,* or *central ion.*

2. A number of oppositely charged ions or neutral molecules, called *ligands* or *adends, are arranged* or concentrated around the central ion.

3. The central ion with ligands placed around it forms the so-called *internal coordination sphere of the* compound or complex ion.

4. The number that shows how many ligands are located around the complexing agent in the inner sphere is called the *coordination number.*

5. 5. Ions located further away from the central ion make up the *outer coordination sphere of the* complex compound.



Classification of complex compounds by charge and chemical nature of ligands

Depending on the charge of the inner sphere, all complex compounds can be divided into three categories.

1. Complex compounds of a cationic nature, in which the complex ion has a positive charge. The role of ligands in these cases is usually played by neutral molecules. For example, $[Cu(NH_3)_4]SO_4$; $[Ca(H_2O)_6]Cl_2$. They can be considered as a product of the interaction of such substances:

$CuSO_4 + 4NH_4OH = [Cu(NH_3)_4]SO_4 + 4H_2O$;

$CaCl_2 + 6H_2O = [Ca(H_2O)_6]Cl_2$.

In aqueous solutions, such complex compounds dissociate into complex cations and anions of acid residues:

$[Cu(NH_3)]SO_4 \leftrightarrow [Cu(NH_3)_4]^{2+} + SO_4^{2-}$;

$[Ca(H_2O)_6]C1_2 \leftrightarrow [Ca(H_2O)_6]^{2+} + 2C1^-$.

2. Complex compounds of an anionic nature, the complex ion of which has a negative charge due to the coordination of negative ligands around a positively charged complexing agent, the total charge of which exceeds the charge of the complexing agent by absolute value. For example, $K_2[CuCl_4]$; $Na_3[Co(NO_2)_6]$. They are obtained as follows:

$2KC1 + CuCl_2 = K_2[CuCl_4]$;

$6NaNO_2 + Co(NO_3)_3 = Na_3[Co(NO_2)_6] + 3NaNO_3$.

In aqueous solutions, such complex compounds dissociate into complex anions and cations of the outer sphere:

$K_2[CuCl_4] \leftrightarrow 2K^+ + [CuCl_4]^{2-}$;

$Na_3[Co(NO_2)_6] \leftrightarrow 3Na^+ + [Co(NO_2)_6]^{3-}$.

3. Molecular complex compounds in which the absolute charges of complexing agents and ligands are equal. Such complex compounds are neutral and their aqueous solutions are not electrolytes. For example, $[Cr(H_2O)_3C1_3]$, $[Pt(NH_3)_2Cl_2]$.

The ability to form complexes is most often exhibited by multicharged heavy metal ions with an 18-electron or transitional from 8- to 18-electron external configuration, which have free orbitals, as well as by ions of some nonmetals (Table 3).

Table 3

Coordination numbers of some complexing agents

Coordination number	Complexing agent	Examples of complex compounds
2	Ag^+	$[Ag(NH_3)_2]NO_3$
	Cu^+	$[Cu(NH_3)_2]Cl$
	Au^+	$Na[Au(CN)_2]$
4	Cu^{2+}	$[Cu(NH_3)_4]SO_4$
	Hg^{2+}	$[Hg(NH_3)_4](NO_3)_2$
	B^{3+}	$H[BF_4]$
	Pt^{2+}	$K_2[PtCl_4]$
	Co^{2+}	$(NH_4)_2[Co(SCN)_4]$
	Zn^{2+}	$Na_2[Zn(OH)_4]$
6	Cr^{3+}	$[Cr(H_2O)_6]Cl_3$
	Co^{3+}	$[Co(NH_3)_6]Br_3$
	AI^{3+}	$Na_3[AlF_6]$
	Pt^{4+}	$H_2[PtCl_6]$
	Si^{4+}	$Na_2[SiF_6]$
	Fe^{2+}	$K_4[Fe(CN)_6]$
	Fe^{3+}	$K_3[Fe(CN)_6]$

Nomenclature of complex compounds

The main provisions of the modern nomenclature of complex compounds are as follows.

1. In the name of any type of complex compound, the cation is first named, followed by the anion in the nominative case:

a) the name of anionic complexes begins with the characteristic of the outer sphere of the complex compound;

b) for cationic complexes, the names of the ions of the outer sphere are given after the composition of the inner sphere.

2. For all types of complex compounds (cationic, anionic, molecular), a complete description of the inner sphere is given. First of all, the names of the ligand anions are given in alphabetical order, adding the ending -o (F^- - fluoro, $C1^-$ - chloro, CN^- - ciano, OH^- - hydroxo, SO_3^{2-} - sulfito, SCN^- - thiocyanato, SO_4^{2-} - sulfato, $C_2O_4^{2-}$ - oxalato, $P_2O_7^{4-}$ - diphosphato, etc.). The number of ligands is indicated by Greek numeral prefixes: 1-mono, 2-di, 3-tri, 4-tetra, 5-penta, 6-hexa, etc. (the numeral mono is usually omitted).

Ligands are further referred to as neutral molecules: NH_3 - amine, H_2O - aqua, NO - nitrosyl, CO - carbonyl. Other ligands retain their usual names.

3. The latter is called the central atom (complexing agent): a) if the central atom is part of a cation or molecule, use the Latin name of this element and indicate the degree of its oxidation in parentheses after it with Roman numerals; b) if the central atom is part of an anion, use the Latin name of the element, adding the ending -at, and indicate the degree of its oxidation in parentheses after it with Roman numerals;

c) in the case of molecular complexes, the Latin name of the complexing agent is indicated, but its charge is not indicated.

Below are the formulas and names of complex compounds of various chemical natures.

With a complex cation:

$[Ag(NH_3)_2]NO_3$ – diaminargentum (I) nitrate;

$[Co(H_2O)_6]Br_3$ – hexaaccobalt (III) bromide.

With a complex anion:

$K_3[Fe(CN)_6]$ – potassium hexacyanoferrate (III);

$Na_2[SiF_6]$ – sodium hexafluorosilicate (IV).

A molecular complex:

$[Pt(NH_3)_2Cl_2]$ – dichlorodiamine platinum;

$[Co(H_2O)_4(NO_2)_2]$ – dinitrotetraaccobalt.

EXPERIMENTAL PART

Experiment 1: Formation of compounds with a complex cation.

a) Prepare a precipitate of copper hydroxide by the action of a solution of KOH on a solution of copper sulphate. Write the reaction equation, noting the colour of the precipitate.

Dissolve the precipitate by adding a concentrated ammonia solution to the test tube. Observe the intense colour of the solution due to the formation of complex ions $[Cu(NH_3)_4]^{2+}$. Write the reaction equation and name the complex compound formed. Keep the resulting solution for experiment 4.

б) Pour the argentium nitrate solution into the test tube so that the liquid only covers the bottom of the test tube and add a little NaCl solution. Write the equation of the reaction, noting the colour of the resulting precipitate.

Pour ammonia solution over the precipitate until it dissolves. Write an equation for the reaction, given that the coordination number of silver is 2. Name the resulting complex compound.

Experiment 2: Formation of compounds with a complex anion.

In a test tube with 1-2 ml of $Hg(NO_3)_2$, add KI solution slowly until HgI_2 precipitates. Write down the reaction equation, noting the colour of the precipitate. Add a little more KI solution until the precipitate dissolves. Write an equation for the formation of the complex compound Hg^{2+} , given that its coordination number is 4.

Experiment 3: Electrolytic dissociation of complex compounds.

Solutions of Fe^{3+} compounds are studied: the medium salt $FeCl_3$ and the salt with the complex anion $K_3[Fe(CN)_6]$.

а) Add an alkali solution to 1-2 ml of $FeCl_3$ solution . Write down the reaction equation for the formation of ferrous (III) hydroxide, its colour and appearance.

Repeat the experiment using $K_3[Fe(CN)_6]$ instead of $FeCl_3$. Why is no precipitate formed in this case?

б) Rhodanide ion SCN^- is a reagent for Fe^{3+} ion. In the presence of Fe^{3+} ion, the rhodanide ion turns the solution blood red.

Investigate solutions of $FeCl_3$ and $K_3[Fe(CN)_6]$ by reacting each with a solution of potassium rhodanide KSCN. In which solution are Fe^{3+} ions found? Why did the colour of the solution $K_3[Fe(CN)_6]$ not change?

Based on the experiments, write the equations for the electrolytic dissociation of the compounds $FeCl_3$ and K_3 [Fe(CN)].$_6$

Experiment 4. Destruction of complex ions.

Add sulphuric acid to the intense solution of the ammonium complex of copper (II) obtained in Experiment 1(a) until the colour of the solution changes. Compare the colour with that of the CuSO solution$_4$. Explain the change in colour and write the reaction equation.

QUESTIONS FOR PREPARATION

1. How are complex compounds formed?
2. Types of complex compounds.
3. What is a complexing agent and what is its role in complex formation?
4. Types of ligands. Method of forming a bond between ligands and complexing agents.
5. Coordination number: what factors determine what value it takes?
6. Nomenclature of complex compounds.
7. Electrolytic dissociation of complex compounds.
8. The instability constant of a complex: how is it expressed, what determines it?

TASKS AND EXERCISES

1. Find the magnitude and sign of the charge of the complex ion and the complexing ion in the following compounds: $K_3[Co(CN_6)]$; $K_3[Pt(NH_3)Cl_5]$; $[Pt(NH_3)_2]Cl_2$. What is the coordination number of the complexing agent in these compounds?
2. Write expressions for the instability constant of complexes:

$[Cd(NH_3)_4]^{2+}$; $[Cu(CN)_4]^{2-}$; $[Ag(NH_3)_2]^{+}$; $[HgI_4]^{2-}$.

Using the table of instability constants of complex compounds, arrange these ions in order of increasing stability.

3. It is known that silver nitrate precipitates all chlorine from a solution of the complex salt $CoCl_3 \cdot 6NH_3$, and only $^2/_3$ from a solution of $CoCl_3 \cdot 5NH_3$. Write the coordination formulas of these salts and their dissociation equations. Determine the coordination number of cobalt in these salts.
4. If an alkaline solution is applied to a solution of the salts $KCrCl_4$ and $CrCl_3$ $6NH_3$, then a precipitate of chromium hydroxide will form only in the first case. Indicate which of these salts is a complex salt and which is a double salt. Write the equation for the electrolytic dissociation of both salts.
5. Determine the magnitude and sign of the charge of the complex ions $[Ag(CN)_2]$, $[Co(NH_3)_5Cl]$, $[Cr(NH_3)_2SO_4]$, knowing that the complexing ions are Ag^{+}, Co^{3+}, Cr^{3+}.
6. Write down the reaction of dissolution of copper (II) and nickel (II) hydroxide precipitates with ammonia. Name the compounds obtained.
7. Write the formulas for potassium hexacyanoferrate (II) and hexacyanoferrate (III). Write the ligands, complexing agent, coordination number.
8. Write an equation for the interaction of amphoteric aluminium and zinc hydroxides with an alkali. Write the dissociation equation for the resulting complex compounds.
9. Give an example of a plane, tetrahedral, octahedral complex.
10. Which base is stronger – $Cu(OH)_2$ or $[Cu(NH_3)_4](OH)_2$? Justify your answer.

Laboratory work 2
QUALITATIVE REACTIONS CATIONS OF THE I ANALYTICAL GROUP

THEORETICAL INFORMATION

The first analytical group includes alkali metal cations and NH_4^+ . The structure of the electron shells of K^+ and Na^+ is similar to that of the electron shells of the atoms of the noble gases Ar and He, respectively. The polarisation properties of these cations are small because they have large radii. All cations of this analytical group form compounds with ionic chemical bonding and most of them are highly soluble in water. Therefore, cations of the I analytical group do not have a group reagent. The K^+ and Na^+ ions are resistant to oxidants and reducing agents.

The hydrated ions K^+ , Na^+ and NH_4^+ are colourless. Salts of these ions have a colour if they contain coloured anions. For example, Na_2CrO_4 is yellow, $KMnO_4$ is purple.

Cations of other analytical groups interfere with the detection of K^+ and Na^+ . Therefore, during systematic analysis, these ions are detected only after all other cations have been completely removed from the solution.

EXPERIMENTAL PART

Experiment 1: Detection of Na^+ cations .

Flame colouring reaction. Volatile Na^+ ions colour the flame bright yellow.

Moisten a nichrome or platinum wire that has been pre-treated with hydrochloric acid, calcined in the torch flame and re-treated with hydrochloric acid, and place it in the torch flame. The flame will turn bright yellow.

Experiment 2: Detection of K^+ cations.

Flame colouring reaction. Volatile K^+ ions turn the flame purple.

Moisten a nichrome or platinum wire that has been pre-treated with hydrochloric acid, calcined in the torch flame, and re-treated with hydrochloric acid, and place it in the torch flame. The flame will turn purple.

Sodium hexanitrocobaltate $Na_3[Co(NO_2)_6]$ with K^+ ions forms a yellow crystalline precipitate $K_2Na[Co(NO_2)_6]$.

$$Na_3[Co(NO_2)_6] + 2K^+ = K_2Na[Co(NO_2)_6]\downarrow + 2Na^+$$

The precipitate is insoluble in weak acids. In an alkaline environment, the reagent $Na_3[Co(NO_2)_6]$ decomposes to form a brown precipitate $Co(OH)_3\downarrow$. Detection is interfered by NH_4^+ ions, which also form a yellow precipitate. Therefore, the reaction should be carried out in the absence of NH_4^+ ions.

Pour 3-4 drops of potassium salt solution into the test tube and add 2-3 drops of sodium hexanitrocobaltate solution. Observe the formation of a yellow precipitate.

Experiment 3. Detection of NH_4^+ cations.

Alkalis release ammonia gas from ammonium salt solutions when heated, which can be detected by smell or with a test paper:

$$NaOH + NH_4^+ \xrightarrow{t} Na^+ + NH_3\uparrow + H_2O.$$

This is a specific reaction that can be used to detect the NH_4^+ ion in the presence of cations of all analytical groups.

The reaction can be carried out in a test tube or in a gas chamber. In the latter case, place 1-2 drops of ammonium salt solution and 3-4 drops of alkali solution on a watch glass, cover the glass with another glass of the same type, and attach a piece of damp phenolphthalein paper to the middle of its concave surface. The ammonia released turns the phenolphthalein paper crimson.

Nessler's reagent (solution of $K_2[HgJ_4]$ in KOH) forms a characteristic red-brown precipitate with solutions of ammonium salts.

$$NH_4^+ + 2[HgJ_4]^{2-} + 4OH^- = [NH_2Hg_2O]J\downarrow + 7J^- + 3H_2O.$$

At a low concentration of NH_4^+ ions, no precipitate may form, but only a yellow colouration of the solution. This is a very sensitive reaction.

Pour 3-4 drops of potassium salt solution into the test tube and add 2-3 drops of Nessler's reagent solution. Observe the formation of a red-brown precipitate.

QUESTIONS FOR PREPARATION

1. What is the essence of systematic and fractional analysis?
2. What reactions are called specific reactions?
3. What reactions are called group reactions?
4. Classification of cations into groups, action of group reagents.
5. Qualitative reactions of group I cations.
6. What cations colour the flame?
7. Why is there no group reagent for cations of the first group?

Laboratory work 3
QUALITATIVE REACTIONS OF CATIONS OF THE II ANALYTICAL GROUP

THEORETICAL INFORMATION

Analytical group II includes cations of d-elements Ag^{+}, Hg_2^{2+} ($-Hg^{+1} – Hg^{+1}-$), and *p-elements* Pb^{2+}.

Cations of the analytical group II form insoluble halides (except for argentium fluoride), sulfates, sulfides, chromates, phosphates, arsenates, hydroxides (oxides) and carbonates due to their high polarising effect.

Group reagent for cations of analytical group II is a 2 M HCl solution with which these cations form white precipitates of AgCl, Hg_2Cl_2 (calomel) and $PbCl_2$. The group reagent allows selective separation of these cations during systematic analysis.

Cations of this group are characterised by complexation reactions, while Hg ions$_2^{2+}$ are characterised by oxidation-reduction reactions.

The salts of cations in this group are colourless, but if they contain coloured anions, they acquire a certain colour.

EXPERIMENTAL PART

Experiment 1: Action of a group reagent.

Dilute hydrochloric acid with group II cations forms white chloride precipitates, of which plumbum (II) chloride is crystalline and argentum chloride is amorphous (syrupy):

$Ag^{+} + HCl = AgCl\downarrow + H^{+}$,

$Pb^{2+} + 2HCl = PbCl_2\downarrow + 2H^{+}$.

Pour 2-3 drops of the solutions of group II cations into test tubes and add 2-3 drops of 2N HCl solution to each tube. Investigate the properties of the resulting chlorides:

a) $PbCl_2$ precipitate dissolves in hot water (test). This is used to separate it from AgCl. $PbCl_2$ is also quite soluble in cold water. Because of this, hydrochloric acid does not completely precipitate the plumbum ions;

b) the AgCl precipitate is insoluble in dilute acids (HNO_3 , H_2SO_4), but readily dissolves in NH_4OH to form the complex salt $[Ag(NH_3)_2]Cl$ (test):

$AgCl + 2NH_4OH = [Ag(NH_3)_2]Cl + 2H_2O$.

Experiment 2. Effect of alkalis on cations of group II.

Alkalis form precipitates with cations of group II. Thus, Ag^{+} ions form a brown precipitate Ag_2O:

$2Ag^{+} + 2OH^{-} = 2AgOH\downarrow$,

$2AgOH = Ag_2O\downarrow + H_2O$.

The precipitate Ag_2O dissolves in NH_4OH to form an ammonium argentum complex:

$Ag_2O + 4NH_4OH = 2[Ag(NH_3)_2]^{+} + 2OH^{-} + 3H_2O$.

With Pb^{2+} ions, alkalis form a white hydroxide precipitate:

$Pb^{2+} + 2OH^{-} = Pb(OH)_2\downarrow$.

The precipitate has amphoteric properties, i.e. it is soluble in both acid and alkaline solutions. When dissolved in alkaline solutions, plumbites are formed.

$Pb(OH)_2 + 2OH^- = [Pb(OH)_4]^{2-}$.

Pour 3-4 drops of argentum salt solution into the test tube and add 1-2 drops of alkali solution. After a precipitate forms, add ammonium hydroxide solution dropwise until the precipitate dissolves.

Pour 3-4 drops of the plumbum salt solution into the test tube and add 1-2 drops of the alkali solution. After a precipitate has formed, divide the contents of the test tube into two parts. Add the nitric acid solution to the first part and the excess alkali solution to the second part.

Experiment 3: Detection of Ag^+ cations .

Solutions of chlorides, bromides and iodides with Ag^+ ions form precipitates:

$Ag^+ + Cl^- = AgCl\downarrow$ (white),

$Ag^+ + Br^- = AgBr\downarrow$ (yellowish),

$Ag^+ + I^- = AgJ\downarrow$ (yellow).

Pour 1-2 drops of AgNO solution into three test tubes$_3$, add 2-3 drops of KCl solution to the first, KBr solution to the second, and KJ solution to the third. Precipitates of AgCl (white), AgBr (yellowish), and AgJ (yellow) will form.

Experiment 4. Detection of Pb cations^{2+} .

Potassium iodide with Pb^{2+} ions forms a yellow precipitate of plumbum diiodide PbJ_2. The precipitate can be obtained in the form of golden crystals characteristic of PbJ_2 , so this reaction is specific for Pb^{2+} ions.

$Pb^{2+} + 2J^- = PbJ_2\downarrow$

Pour 2-3 drops of plumbum salt solution into a test tube and add 2-3 drops of KJ solution - a yellow precipitate of PbJ will precipitate$_2$. Add 4-5 drops of water and 2-3 drops of 2N acetic acid solution to the solution with the precipitate and heat. The precipitate will dissolve. After further slow cooling, the precipitate PbJ_2 will precipitate again in the form of shiny gold crystals characteristic of plumbum diiodide.

Sulphuric acid and soluble sulphates form a white crystalline precipitate of plumbum (II) sulphate with Pb^{2+} ions. The precipitate is soluble when heated in caustic alkalis to form plumbites.

$Pb^{2+} + SO_4^{2-} = PbSO_4\downarrow$

$PbSO_4 + 4KOH = K_2[Pb(OH)_4] + K_2SO_4$

Pour 2-3 drops of the plumbum salt solution into a test tube and add 2-3 drops of 2N sulfuric acid solution. Check the solubility of the precipitate in the alkali solution. To do this, add 5-6 drops of alkaline solution to the test tube (after the formation of plumbum (II) sulphate precipitate) and heat. Write the equations for all the reactions.

QUESTIONS FOR PREPARATION

1. Group reagent for cationic analytical group II?
2. Features of the use of the group reagent for the II analytical group of cations. Effect of excess group reagent.
3. Why can't nitric acid be used as a group reagent for cation group II?
4. Qualitative reactions of analytical group II ions?
5. Amphotericity of plumbum compounds and its influence on the analysis results.

Laboratory work 4
QUALITATIVE REACTIONS OF CATIONS OF ANALYTICAL GROUP III

THEORETICAL INFORMATION

Cations of the third analytical group include cations of alkaline earth metals. The electronic structure of these ions is similar to that of inert gases. The rather high polarising effect of cations of analytical group III leads to the fact that most salts of these cations are poorly soluble: sulfates, carbonates, chromates, oxalates, phosphates.

However, only *dilute sulfuric acid* forms precipitates with cations of analytical group III without interacting with cations of other analytical groups, so H_2SO_4 *is a group reagent* that allows the systematic separation of cations of analytical group III from cations of other analytical groups.

Ba^{2+} (Sr^{2+} , Ca^{2+}) + H_2 SO_4 = $BaSO_4$↓ + $2H^+$ ($SrSO_4$↓ , $CaSO_4$↓).

These are white crystalline precipitates, insoluble in alkalis, acids and water.

EXPERIMENTAL PART

Experiment 1: Action of a group reagent.

During the interaction of SO_4^{2-} ions with Ba^{2+} cations, almost complete precipitation of barium ions is achieved. Ca^{2+} cations mostly do not precipitate in the form of $CaSO_4$, but remain in solution. $K_{sp(BaSO4)}$= 1.1 · 10^{-10} ; $K_{sp(CaSO4)}$ = 2.5 · 10^{-5} . In the presence of alcohol or acetone, the solubility of $CaSO_4$ decreases significantly. Therefore, if the precipitation of Ca^{2+} cations is carried out with sulfuric acid in a solution to which a 50-60% solution of alcohol or acetone is added, the Ca^{2+} ions will almost completely precipitate as $CaSO_4$. This property is used in the analysis to separate and detect Ca^{2+} cations.

Place 3-4 drops of Ba^{2+} salt solution in one test tube and Ca^{2+} salt in the other, and then add a few drops of 2N solution of H_2SO_4 to each. Add alcohol or acetone to the test tube with the calcium salt. Observe what happens. Test the sensitivity of sulphates to strong acids and alkalis.

Experiment 2: Colour of the flame.

Volatile Ca^{2+} ions colour the flame brick red. Volatile Sr^{2+} ions colour the flame carmine red. Volatile Ba ions^{2+} colour the flame yellow-green.

Moisten a nickel or platinum wire that has been pretreated with concentrated hydrochloric acid, calcined in the torch flame, and re-treated with hydrochloric acid, and place it in the torch flame. Observe the colour of the flame.

Perform the same tests with solutions of salts of other cations of analytical group III.

Experiment 3: Detection of Ba cations^{2+} .

Potassium bichromate $K_2Cr_2O_7$ forms a yellow precipitate $BaCrO_4$ with Ba^{2+} ions, but not $BaCr_2O_7$. This is due to the fact that $K_{sp(BaCrO4)}$ < $K_{sp(BaCr2O7)}$.

$Cr_2O_7^{2-}$ + H_2O ↔ $2CrO_4^{2-}$ + $2H^+$;

$2CrO_4^{2-}$ + $2Ba^{2+}$ = $2BaCrO_4$↓ .

The $BaCrO_4$ precipitate is soluble in strong acids but insoluble in acetic acid. Ca^{2+} ions with $K_2Cr_2O_7$ do not form a precipitate and therefore do not interfere with the detection of Ba^{2+} ions. The reaction under consideration is used not only to detect Ba^{2+} cations but also to separate it from Ca^{2+} ions. The precipitate $BaCrO_4$ is also formed when potassium chromate is exposed to solutions of barium salts.

Pour 2-3 drops of barium salt solution, 4-5 drops of distilled water into a test tube and add 1-2 drops of potassium bichromate solution. After a precipitate has formed, divide the contents of the test tube into two parts. Add strong acid to the first part and weak acetic acid to the second.

Write down the relevant reaction equations and observations.

Experiment 4. Detection of Ca^{2+} cations.

Ammonium oxalate $(NH_4)_2C_2O_4$ with Ca^{2+} ions forms a white crystalline precipitate CaC_2O_4: $Ca^{2+} + C_2O_4^{2-} = CaC_2O_4 \downarrow$.

Heating the solution and alkalising it with ammonia promotes the precipitation of calcium. Calcium oxalate is insoluble in acetic acid, but soluble in strong acids.

The detection of Ca^{2+} is interfered with by Ba^{2+} ions, which form a white crystalline precipitate from $(NH_4)_2C_2O_4$, which is also soluble in mineral acids and acetic acid when boiled.

Pour 2-3 drops of calcium salt solution, 4-5 drops of distilled water into a test tube and add 1-2 drops of $(NH_4)_2C_2O_4$. After the precipitate has formed, divide the contents of the test tube into two parts. Add strong acid to the first part and weak acetic acid to the second part. Record the reactions and observations.

Microcrystalloscopic reaction. In the presence of Ca^{2+} ions, $CaSO_4 \cdot 2H_2O$ crystals precipitate from dilute sulfuric acid solutions in the form of long needles that form bundles (rosettes), and in more concentrated solutions, in the form of diamond-shaped plates.

Place a drop of calcium chloride solution on a thoroughly washed and dried slide, then add a drop of 2N H_2SO_4.

Look at the crystals under a microscope.

If crystals do not fall out, the mixture should be evaporated on a glass slide until crystallisation begins.

QUESTIONS FOR PREPARATION

1. Dependence of the properties of cations of the third analytical group on the structure of their electronic shells, ionic radii, ionisation potentials and position in the periodic table of D.I. Mendeleev?
2. Qualitative reactions of group III cations.
3. Group reagent used for precipitation of cations of the third analytical group, solubility of sulphates of the third group.
4. What is the most characteristic reagent for the detection of Ba^{2+} cation and why?
5. What is the best reagent for the discovery of Ca ion $?^{2+}$
6. What cations of the third analytical group colour the flame?

Laboratory work 5
QUALITATIVE REACTIONS OF CATIONS OF IV ANALYTICAL GROUP

THEORETICAL INFORMATION

Analytical group IV includes cations of *p-elements*: Al^{3+}, Sn^{2+}, Sn(IV), As(III), As(V) and *d-elements* Cr^{3+} , Zn^{2+} .

The cations of *p-* and *d-elements* have a pronounced polarising effect, which leads to the formation of poorly soluble compounds (sulfides, phosphates, carbonates, hydroxides, etc.).

The ions of *p-elements* (Sn, As) and *d-elements* (Cr) with an incomplete 18-electron shell easily undergo redox reactions, which are used in the analysis for the detection and separation of these ions.

The hydroxides of cations of the analytical group IV are amphoteric, so the action of an excess of NaOH solution leads to the transition to the corresponding hydroxoanions.

The group reagent of this group is a 6 M NaOH solution in the presence of a 3% solution of H_2O_2 . During the action of the group reagent, hydroxide precipitates are first formed, which dissolve in excess NaOH. The presence of H_2O_2 causes the formation of hydroxo- and oxoanions of these elements in higher oxidation states. The solubility of hydroxide precipitates of cations of analytical group IV in an excess of group reagent allows for the systematic separation of cations of group IV from cations of analytical groups V and VI, since cations of analytical groups V and VI precipitate as hydroxides.

EXPERIMENTAL PART

Experiment 1: Action of a group reagent.

Alkalis with all cations of group IV (except As^{3+}) form hydroxide precipitates, which in excess of alkali are easily dissolved to form the corresponding salts: aluminates, chromites, zincates, stannates, and stannates.

$Cr^{3+} + 3NaOH = Cr(OH)_3\downarrow + 3Na^+$;

$Cr(OH)_3 + 3NaOH = Na_3[Cr(OH)_6]$.

These reactions indicate the amphotericity of group IV cation hydroxides.

Pour 2-3 drops of group IV cation salts into test tubes. Add 1-2 drops of 2N NaOH. Then add a few more drops of alkali. Observe the precipitation and subsequent dissolution of the precipitate. Write the equations for the reactions.

Experiment 2: Detection of Al^{3+} cations.

Dry ammonium chloride releases a hydroxide precipitate from the aluminium hydroxide:

$[Al(OH)_4]^- + NH_4Cl = Al(OH)_3\downarrow + Cl^- + NH_3\uparrow + H_2O$.

Add an excess of alkali solution to 2 drops of Al^{3+} solution until the hydroxide precipitate that precipitates first dissolves. Add dry ammonium chloride to the resulting solution. The test tube is shaken several times, heated in a water bath, and the precipitate is observed.

Alizarin forms a water- and acetate-insoluble compound called aluminium varnish with Al^{3+} cations, which has a characteristic bright red colour. This is one of the most sensitive reactions to the Al^{3+} ion. Cr^{3+} and Zn^{2+} ions interfere with this reaction.

Perform the reaction using the drop method. Put a drop of the Al^{3+} salt solution on a piece of filter paper and wait until the liquid is absorbed. Then hold the paper for 1-2 minutes over the neck of a beaker of concentrated ammonia solution. This will form $Al(OH)_3$ on the paper . Moisten the stain with an alizarin solution and treat it again with ammonia vapour. This produces a bright red colour - a sign of the presence of Al^{3+} ions in the solution to be analysed.

Experiment 3. Detection of Cr cations^{+3} .

Hydrogen peroxide in the presence of an alkali oxidises Cr^{3+} to CrO_4^{2-} .

To 2-3 drops of Cr^{3+} salt solution, add 2 n. NaOH solution dropwise until a precipitate is formed and further dissolved to form green chromite. Add 3-4 drops of a 6% solution of H O_{22} to the solution of chromite formed and heat in a water bath until the colour changes from green to yellow due to the formation of chromate ions:

$2Cr^{3+} + 3H_2O_2 + 10OH^- = 2\ CrO_4^{2-} + 8H_2O.$

To confirm the presence of chromate ions in the solution, a specific reaction to CrO_4^{2-} is required, which is the formation of suprachromic acid (H_2CrO_6).

Add 3 drops of dilute H_2SO_4 , 2 drops of H_2O_2 solution and 1 ml of ether to a clean test tube. Shake the mixture well. Then add 2-3 drops of the resulting chromate solution (yellow) and shake again. Observe the blue colouration of the ether layer.

Experiment 4. Detection of Sn cations^{2+} .

Reduction of bismuth salts with *sodium stannate*. To 2 drops of $SnCl_2$ solution add 8-10 drops of 2N NaOH or KOH solution to dissolve the precipitate that initially fell out to form a stannate:

$Sn(OH)_2 + 2OH^- = SnO_2^{2-} + 2H_2O.$

Add a drop of Bi^{3+} salt solution to the solution. Sodium stannate reduces the Bi^{3+} ion to metallic bismuth and the precipitate turns black:

$3SnO_2^{2-} + 2Bi(OH)_3 = 2Bi\downarrow + 3SnO_3^{2-} + 3H_2O.$

Detection of Sn^{2+} using *ammonium phosphorus molybdate*. Add 5-6 drops of ammonium phosphorus molybdate to 1-2 drops of Sn^{2+} salt solution and dilute with 5-10 drops of water. The solution will turn blue because Sn^{2+} reduces colourless hexavalent molybdenum to molybdenum blue (Mo^{5+}). This reaction is very sensitive.

Experiment 5. Detection of Zn cations^{2+} .

Potassium hexacyanoferrate (III) (red blood salt) with Zn salts^{2+} gives a yellow precipitate of zinc hexacyanoferrate (III):

$3Zn^{2+} + 2K_3[Fe(CN)_6] = Zn_3[Fe(CN)_6]_2\downarrow + 6K^+.$

To 2 drops of Zn^{2+} salt solutionadd 2 drops of red blood salt solution. The resulting precipitate is dissolved in HCl and ammonia solution.

Potassium hexacyanoferrate (II) (yellow blood salt) reacts with zinc salts to form a white precipitate of zinc-potassium hexacyanoferrate (II):

$2Zn^{2+} + 2K_4[Fe(CN)_6] = Zn_3K_2[Fe(CN)_6]_2\downarrow + 6K^+$.

To 2 drops of Zn^{2+} solution add 2 drops of yellow blood salt solution.

QUESTIONS FOR PREPARATION

1. Qualitative reactions of group IV cations.
2. A group reagent used for the precipitation of cations of the fourth analytical group.
3. Can ammonium hydroxide be used to separate cations of the fourth analytical group?
4. Amphoteric compounds. The use of amphotericity in the analysis of cations of the fourth analytical group.
5. What is the best reagent for the discovery of Al^{3+}ion ?
6. What is the best reagent for the discovery of Cr^{3+}ion ?

Laboratory work 6
QUALITATIVE REACTIONS OF CATIONS OF THE V ANALYTICAL GROUP

THEORETICAL INFORMATION

The V analytical group includes cations of s-elements - Mg^{2+} , p-elements - Sb(III), Sb(V), Vi^{3+} and d-elements - Fe^{2+} , Fe^{3+} , Mn^{2+} . Due to the strong polarising effect of cations of the V analytical group, most of their compounds (hydroxides, sulfides, phosphates) are insoluble in water, but chlorides, bromides, nitrites, nitrates, acetates, sulfates are soluble in water.

The grouping reagent is a concentrated ammonia solution that precipitates cations of the V analytical group as hydroxides, which are insoluble in excess reagent.

The further analysis of cations of the V analytical group is based on the different solubility of hydroxides of these cations in concentrated solutions of ammonia salts, acids, as well as on the use of redox reactions and precipitation reactions of these cations.

Fe^{3+} compounds are yellow-brown, Fe^{2+} – light green; solutions of all other cations are colourless.

EXPERIMENTAL PART

Experiment 1. General reactions of group V cations.

The action of alkalis. Under the action of an alkali solution on solutions of cation salts of group V, amorphous hydroxide precipitates are formed.

Pour 2-3 drops of solutions of salts of cations of group V into test tubes. Add 1-2 drops of 2N alkali solution to each test tube. Mix the contents of the tubes and observe what happens. Describe the properties of the precipitates: colour, solubility in water, excess alkali and ammonia solutions, acids.

Properties of individual hydroxides: Ferric (II) hydroxide $Fe(OH)_2$ (greenish precipitate) in air and especially when heated rapidly oxidises to $Fe(OH)_3$, which changes its colour to red-brown. Manganese (II) hydroxide $Mn(OH)_2$ (white precipitate) changes colour to brown in air due to oxidation to the tetravalent state. Write the corresponding equations for the oxidation reactions of these hydroxides.

The action of ammonium hydroxide. The action of ammonium hydroxide solution on cations of group V, as well as on alkali solutions, produces hydroxide precipitates, but they are relatively easily soluble in ammonium salts. Therefore, these cations are not completely precipitated from solutions of their salts by ammonium hydroxide solution.

Experiment 2: Detection of Fe^{3+} cations.

Potassium hexacyanoferrate (II) (yellow blood salt) with Fe^{3+} ionsforms a precipitate of ferrous hexacyanoferrate (II).

$$4Fe^{3+} + 3[Fe(CN)_6]^{4-} = Fe_4[Fe(CN)_6]\downarrow$$

(Berlin blue).

Pour 3-4 drops of trivalent ferric salt solution into a test tube and add 2-3 drops of solution $K_4[Fe(CN)_6]$. The reaction must be carried out in a slightly acidic or neutral environment, because in an alkaline environment the precipitate is destroyed with the release of $Fe(OH)_3$. A very large excess of $K_4[Fe(CN)_6]$ or a strongly acidic environment can cause the precipitate to dissolve. Other cations of group V do not interfere with the detection of the Fe^{3+} ion.

Ammonium thiocyanate NH_4CNS forms blood-red thiocyanate with Fe^{3+} ions, which is highly soluble in water.

$Fe^{3+} + 3CNS^- = Fe(CNS)_3$.

Dilute a few drops of iron (III) salt solution with 5-8 drops of distilled water and add 5-8 drops of ammonium thiocyanate solution. The solution will turn a blood-red colour. An excess of reagent intensifies the colour. The reaction should be carried out in a neutral or acidic solution. This reaction can be used to detect Fe^{3+} ions in the presence of other cations.

The reaction can be carried out by the drop method. To do this, apply a drop of the test solution, 1 drop of dilute (1:1) HCl solution and 2-3 drops of ammonium rhodanide solution to a filter paper. In the presence of Fe^{3+} ions, a red spot will form.

Oxidising properties of Fe^{3+} *ions. The* Fe^{3+} ion is a relatively weak oxidant φ_0 (Fe^{2+} /Fe^{3+}) = 0.77 V, so it is capable of oxidising only relatively strong reducing agents, such as the iodide ion J^- :

$2J^- + 2 Fe^{3+} = J_2 + 2Fe^{2+}$.

To a few drops of KJ solution, add 1-2 drops of hydrochloric acid solution and then 3-4 drops of ferric (III) salt solution. The solution turns brown due to the formation of iodine. If you add a few drops of benzene to the solution, the iodine will be converted to benzene and the benzene layer will turn purple, which is characteristic of iodine.

Experiment 3: Detection of Fe^{2+} cations.

Potassium hexacyanoferrate (III) (red blood salt) forms a dark blue precipitate (Turnbull blue) with Fe^{2+} ions. This is the most characteristic reaction for Fe^{2+} ions.

$3 Fe^{2+} + 2[Fe(CN)_6]^{3-} = Fe_3[Fe(CN)_6]_2\downarrow$.

Pour 2-3 drops of Fe^{2+} solution into a test tube, add 1-2 drops of hydrochloric acid solution and 2-3 drops of $K_3[Fe(CN)_6]$ solution. A dark blue precipitate will form. The precipitate is insoluble in acids, but decomposes with alkalis. Group V cations do not interfere with this reaction, but at a high concentration of Mn^{2+} the precipitate may turn dark green.

Brown ring reaction. The Fe^{2+} ionis a strong reducing agent, so it is oxidised by both weak and strong oxidising agents, e.g. J_2, HNO_3, H_2O_2, $KMnO_4$.

Pour 2-3 drops of Fe^{2+} solution into a test-tube, add 2 drops of 2N sulfuric acid solution and 2 drops of 6N nitric acid solution. Heat the mixture gently until the brown colour disappears, which is due to the formation of an unstable intermediate complex compound[$Fe(NO)] SO_4$. After cooling, add 2 drops of ammonium thiocyanate solution. The solution turns a blood red colour due to the presence of Fe^{3+} ions formed during the oxidation of Fe^{2+} ions.

$3 Fe^{2+} + 4H^+ + NO_3^- = 3 Fe^{3+} + NO\uparrow + 2 H_2O$.

$Fe^{2+} + NO + H_2SO_4 = [Fe(NO)]SO_4 + 2H^+$.

The reaction with phenanthroline is also used to detect Fe^{2+} ions.

Experiment 4. Detection of Mn^{2+} cations.

Ammonium persulfate $(NH_4)_2S_2O_8$ in the presence of $AgNO_3$ (catalyst) oxidises the Mn^{2+} ion to MnO_4^- , the solution turns purple, and at low concentrations of Mn^{2+} pink.

$$2Mn^{2+} + 5S_2O_8^{2-} + 8H_2O = 2\,MnO_4^- + 10SO_4^{2-} + 16\,H^+.$$

Place several crystals of ammonium persulfate in a test tube, add 5-6 drops of a 2N solution of sulfuric acid and 2-3 drops of a 0.1N solution of argentum nitrate. Heat the mixture to 60-70° C, add 1 drop of the solution to be analysed with a glass rod, and continue heating for another minute. In the presence of Mn^{2+} ions, the solution turns purple or pink. When performing this reaction, add a very small amount of the solution to be analysed, as excess Mn^{2+} ion reduces the MnO_4^- ion and a brown precipitate is formed. The solution should be free of reducing agents, as they will be oxidised by the resulting permanganate ion MnO_4^-.

Sodium bismuthate $NaBiO_3$ in a solution of nitric acid oxidises the Mn^{2+} ion to MnO_4^- .

$$2Mn^{2+} + 5BiO_3^- + 16\,H^+ = 2MnO_4^- + 5Bi^{3+} + 7\,H_2O.$$

Put a small amount of sodium bismuthate powder into a test tube with a glass rod, add 5-6 drops of 2N nitric acid solution and 1-2 drops of a solution containing Mn^{2+} ion, mix and let stand for 1-2 minutes. The solution above the precipitate will turn purple-pink.

When performing a reaction, it is important to follow the order of the reaction.

To separate the excess sodium bismuthate (which can mask the colour), centrifugation of the solution can be used.

Experiment 5. Detection of Mg^{2+} cations.

Sodium hydrophosphate Na_2HPO_4 in the presence of NH_4OH and NH_4Cl with ammonium salts forms a white crystalline precipitate of the double salt of ammonium-magnesium phosphate $MgNH_4PO_4$

$$Mg^{2+} + HPO_4^- + NH_4OH = MgNH_4PO_4\downarrow + H_2O.$$

Ammonium salt is necessary to prevent the formation of magnesium hydroxide precipitate when exposed to ammonium hydroxide.

Place 2-3 drops of magnesium salt solution in a test tube, add 2-3 drops of 2N hydrochloric acid solution and 3-4 drops of sodium hydrogen phosphate solution, then add a few drops (with stirring) of 2 nm ammonium hydroxide solution until the solution is slightly alkaline.

If other cations of analytical group V are present, this reaction should be carried out after separating them with sodium hydrogen phosphate. Take the test solution, add the Na_2HPO_4 solution and centrifuge. Then check the completeness of the precipitation (add another 1-2 drops of sodium hydrogen phosphate solution, no precipitate should form) and add ammonium hydroxide solution.

QUESTIONS FOR PREPARATION

1. Qualitative reactions of group V cations.
2. A group reagent used for the precipitation of cations of the V analytical group.
3. Can sodium hydroxide be used as a group reagent for cations of the V analytical group?
4. To identify which cations of the fifth analytical group are redox reactions used?
5. Write reactions that allow you to distinguish between cations of the fifth analytical group with different degrees of oxidation.
6. What is the best reagent for the discovery of Fe^{3+} ion ?

Laboratory work 7
QUALITATIVE REACTIONS OF CATIONS OF THE VI ANALYTICAL GROUP

THEORETICAL INFORMATION

The VI analytical group includes cations of the *d-elements* Cu^{2+} , Hg^{2+} , Co^{2+} , Ni^{2+} , whose electronic shell has vacant *d-orbitals*. Therefore, cations of this group are characterised by complexation reactions.

Most compounds (sulphates, chlorides, nitrates, acetates, etc.) are highly soluble in water, while hydroxides, carbonates, and phosphates are insoluble in water.

The group reagent for analytical group VI is a concentrated ammonia solution, which forms soluble ammonia complex compounds with its cations. The further analysis is based on the destruction of these complexes by the action of a 6 M sulfuric acid solution, the precipitation of Cu(I) and Hg sulfides^{2+} by the action of crystalline sodium thiosulfate and the different solubilities of these sulfides in nitric acid and bromine water.

The determination of cations of analytical group VI is based on the use of complexation and oxidation-reduction reactions. All cations of analytical group VI (except Hg^{2+}) are coloured and form coloured compounds.

EXPERIMENTAL PART

Experiment 1. General reactions of group VI cations.

The action of the group reagent is NH_4OH. When ammonium hydroxide acts on cations of the VI analytical group, precipitates of hydroxides or basic salts are formed:

$Ni^{2+} + 2NH_4OH = Ni(OH)_2\downarrow + 2NH_4^+$;

$Cu^{2+} + 2NH_4OH = Cu(OH)_2\downarrow + 2NH_4^+$;

$Co^{2+} + 2NH_4OH = Co(OH)_2\downarrow + 2NH_4^+$.

Precipitates are soluble in mineral acids, ammonia and ammonium salts. When they dissolve in ammonia and ammonium salts, complex salts are formed.

$Cu(OH)_2 + 2NH_4OH + 2NH_4^+ = [Cu(NH_3)_4]^{2+} + 4H_2O$.

Pour 4-5 drops of soluble salts of group VI cations into separate test tubes and add 2-3 drops of 2N solution of NH_4OH to each tube. Observe the formation of precipitates and the variety of their colours. Add an excess of concentrated solution of NH_4OH to each test tube with the resulting precipitate, while the precipitates dissolve and form complex compounds - ammonia. Write the reaction equations. What is the colour of the resulting solutions?

Alkalis with all cations of group VI form amphoteric hydroxide precipitates, and with cobalt cations - basic salts.

$Cu^{2+} + 2OH^- = Cu(OH)_2\downarrow$.

$Ni^{2+} + 2OH^- = Ni(OH)_2\downarrow$.

$Co^{2+} + 2OH^- = Co(OH)_2\downarrow$.

All of these precipitates are soluble in acids and ammonia solution.

Experiment 2: Detection of Cu^{2+} cations.

Solutions of copper salts are coloured blue or green.

Ammonium hydroxide NH_4OH with Cu^{2+} salts forms a cornflower-coloured complex compound:

$Cu^{2+} + 4NH_4OH = [Cu(NH_3)_4]^{2+} + 4H_2O$.

Take 3-4 drops of a solution of copper salt into a test tube, add 2N solution of NH_4OH. First, a precipitate will form, which will dissolve in excess ammonia to form a cornflower-coloured complex compound.

Potassium iodide. A solution of potassium iodide with Cu^{2+} ions forms an ivory-coloured precipitate of copper (I) iodide. This releases brown iodine, and in the presence of starch (as an indicator) the colour of the solution turns blue.

$2Cu^{2+} + 4J^- = 2CuJ\downarrow + J_2$.

Experiment 3: Detection of Ni^{2+} cations.

Nicol salts have a light green colour.

Alkali metal carbonates form a green precipitate, nicol carbonate $NiCO_3$, which is soluble in acids, ammonia and ammonium carbonate solutions.

Reaction with *dimethyl glyoxime* (Chugaev's reagent). Nicotine salts in the presence of ammonia form a red complex compound with dimethyl glyoxime solution. At first, the solution turns pink, then a bright red precipitate of nicotine dimethylglyoxymate precipitates.

The reaction is very sensitive. It can also be carried out using the droplet method on filter paper.

If Fe^{2+} ions are present in the solution (which interfere with the detection of nicotine ions), a hydrogen peroxide solution is added to the solution first, which oxidises Fe^{2+} to Fe^{3+}.

Sodium hydrogen phosphate Na_2HPO_4 forms a green precipitate $Ni_3(PO_4)_2\downarrow$, soluble in acids, including acetate acid. The precipitate is also soluble in ammonia, but insoluble in alkalis.

Take 2-3 drops of nicotine salt solution into a test tube, add 5-6 drops of distilled water, and add 2-3 drops of sodium hydrogen phosphate solution. Divide the contents of the test tube into three parts and test the solubility of the precipitate in acid, ammonia and alkali solutions. Write the corresponding reaction equations.

Experiment 4. Detection of Co^{2+} cations.

Anhydrous cobalt salts are blue. Crystalline hydrates and dilute solutions of cobalt salts are pink in colour.

The reaction with -nitroso-$\alpha\beta$ -naphthol (Ilyinsky's reagent). αNitroso-β -naphthol oxidises Co^{2+} ions to Co^{3+} to form a bulky red-brown precipitate of the complex salt $[C_{10}H_6(NO)O]_3Co$.

Add 2-3 drops of cobalt salt solution Co^{2+} (the reaction of the solution should be neutral or slightly acidic, if the reaction of the solution is strongly acidic, add sodium acetate) to a test tube and heat.

The detection of the Co^{2+} ion is hampered by the presence of the Fe^{3+} ion, which gives a brownish-black precipitate with the reagent.

Sodium hydrogen phosphate Na_2HPO_4 forms a purple precipitate $Co_3(PO_4)_2$, soluble in acids, including acetate acid. When exposed to alkalis, it is converted to $Co(OH)_2$, and when exposed to ammonia, it dissolves to form a dirty yellow complex salt.

Take 1-2 ml of cobalt salt solution into a test tube, add 3-4 drops of distilled water and 2-3 drops of sodium hydrogen phosphate solution. Divide the contents of the test tube into three parts. Test the solubility of the precipitate in acid solution and ammonia solution. Investigate the effect of alkali on the $Co_3(PO_4)_2$ precipitate. Write the corresponding reaction equations.

QUESTIONS FOR PREPARATION

1. Qualitative reactions of cations of the VI analytical group.
2. A group reagent used for the detection of cations of the VI analytical group.
3. Peculiarities of the action of a group reagent on a mixture of cations of the sixth analytical group.
4. Use of complexation reactions in the analysis of a mixture of cations of the sixth analytical group.
5. Conditions of destruction of complex compounds.
6. Why do hydroxides of cations of the fourth group dissolve in excess alkali, and those of the sixth group in excess ammonia?

Laboratory work 8
QUALITATIVE REACTIONS OF ANIONS OF THE I ANALYTICAL GROUP

THEORETICAL INFORMATION

The anions of the following acids belong to analytical group I: carbonate, metabolic, sulfate, sulfite, thiosulfate, orthophosphoric, silicate and others. Solutions of sodium or potassium salts are used to study the reactions of Group I anions. The *group reagent* for anions of the first analytical group is a solution of barium salt in a neutral or slightly alkaline medium. Under these conditions, the anions form salts with Ba^{2+} ions that are insoluble in water but soluble in dilute hydrochloric acid, with the exception of $BaSO_4$.

The first group of anions, in turn, can be divided into three subgroups. The first subgroup includes anions whose barium salts are poorly soluble in mineral acids and water. Only the sulphate ion SO_4^{2-} belongs to this subgroup.

The second subgroup of group I anions is characterised by the fact that their barium salts are poorly soluble in acetic acid and water, but well soluble in mineral acids. These include SO_3^{2-} , CrO_4^{2-} , $C_2O_4^{2-}$, F^- .

The third subgroup includes the remaining anions. The barium salts of these anions are poorly soluble in water, but well soluble in acetic and mineral acids.

EXPERIMENTAL PART

Experiment 1: Action of a group reagent.

Put 2 drops of the salt solutions into different test tubes: Na_2SO_4, Na_2SO_3, Na_2CO_3, Na_2HPO_4 . Add 2-3 drops of $BaCl_2$ solution to each test tube. Observe the formation of precipitates. Add 3-4 drops of 2N HCl solution to the same test tubes. Write down your observations and the equations for the reactions.

Experiment 2. Detection of sulfate anion SO_4^{2-} .

Action of *barium chloride*. Add 3 drops of $BaCl_2$ solution to 2-3 drops of the test solution acidified with 2-3 drops of 2N HCl solution. In the presence of SO_4^{2-} ion, a crystalline precipitate of $BaSO_4$ will instantly form:

$SO_4^{2-} + Ba^{2+} = BaSO_4\downarrow$.

Experiment 3. Detection of sulfite anion SO_3^{2-} .

Most sulphites are insoluble in water. Only sulphites of alkali metals, magnesium and ammonium, are water-soluble. They have an alkaline reaction in aqueous solutions due to hydrolysis.

Action of oxidants. Sulfite ion is a reducing anion. It readily reduces free iodine to iodine ions J^- , permanganate ions MnO_4^- to manganese (II) ions Mn^{2+} .

Add 1-2 drops of iodine solution to 2-3 drops of the solution to be tested for SO_3^{2-} ion. This oxidises sulphites into sulphates, the reaction of the medium becomes acidic and the brown iodine solution becomes discoloured:

$SO_3^{2-} + I_2 + H_2O = SO_4^{2-} + 2I^- + 2H^+$.

The oxidation reaction of sulphites with iodine should be carried out in a neutral or acidic environment, because in an alkaline environment, I_2 discolours due to self-oxidation - self-repair.

Permanganate can also be reduced with sulphites. The reaction can be carried out in an acidic or alkaline environment. The presence of stronger reducing agents (e.g. S^{2-} anions) interferes with the detection of SO_3^{2-} anions by these reactions.

Experiment 4. Detection of phosphate anion PO_4^{3-} .

Of the phosphoric acid salts, only alkali metal and ammonium phosphates are soluble in water. Phosphates and hydrophosphates in aqueous solutions have an alkaline reaction due to hydrolysis.

Effect of *magnesia mixture* (mixture of $MgCl_2$ with NH_4OH and NH_4Cl).

Add 2-3 drops of the magnesium mixture to 3-4 drops of the test solution. A white crystalline precipitate will form. (This reaction was discussed in more detail in the study of Mg^{2+}).

$Mg^{2+} + HPO_4^{2-} + NH_4OH = MgNH_4PO_4 + H_2O$.

Reaction with *ammonium molybdate.* Ammonium molybdate in nitric acid forms a yellow crystalline precipitate of ammonium phosphorus molybdate with the phosphate anion.

$PO_4^{3-} + 3NH_4Cl + 12(NH_4)_2MoO_4 + 24\ HNO_3 =$

$= (NH_4)_3H_4[P(Mo_2O_7)_6] + 10H_2O + 24NH_4NO_3 + 3Cl^-$.

The detection of phosphate ions is interfered with by sulfite and sulfide ions, which reduce ammonium molybdate. To remove them, the test solution is pre-boiled with concentrated nitric acid.

Pour 2-3 drops of sodium phosphate into the test tube, add 2-3 drops of ammonium chloride, nitric acid and ammonium molybdate.

Experiment 5. Detection of carbonate anion CO_3^{2-} .

Most carbonates are practically insoluble in water. Only alkali metal and ammonium carbonates are soluble. They have an alkaline reaction in aqueous solutions due to hydrolysis.

Action of *acids.* Add 5-6 drops of 2N HCl solution to the Na_2CO_3 salt solution and observe the release of carbon dioxide bubbles.

$CO_3^{2-} + 2H^+ = H_2CO_3$.

$H_2CO_3 = H_2O + CO_2\uparrow$.

QUESTIONS FOR PREPARATION

1. How many analytical groups are anions divided into and on what grounds?
2. A group reagent for the first group of anions.
3. What subgroups are distinguished in the first group of anions?
4. Features of sulphite anion SO_3^{2-}.
5. Features of detection of phosphate anion PO_4^{3-} .
6. Features of the detection of sulfite anion CO_3^{2-}.

Laboratory work 9
QUALITATIVE REACTIONS OF ANIONS OF THE II – III ANALYTICAL GROUPS

THEORETICAL INFORMATION

Analytical group II includes anions of the following acids: chloride, bromide, iodide, and hydrogen sulphide. Solutions of NaCl or KCl, NaBr or KBr, NaJ or KJ, Na_2S or K_2S (or hydrogen sulphide water) are used to study the reactions of anions of this group. *A group reagent* for anions of the second analytical group is a solution of argentium nitrate in the presence of a 2 M HNO_3 solution . The anions of this group form precipitates with Ag cations$^+$ that are insoluble in dilute HNO_3 . Barium salts with group II anions are soluble in water.

Group III includes the anions of nitric acid HNO_3 , nitrite acid HNO_2 and acetic acid CH_3COOH. The anions of this group form salts with most cations that are highly soluble in water, so they do not have a group reagent.

EXPERIMENTAL PART

Experiment. 1. Action of the group reagent on anions of analytical group II.

Put 2 drops of the following salt solutions into different test tubes: NaCl, KBr, KJ. Add 2-3 drops of $AgNO_3$ solution to each test tube. Cheese-like precipitates are formed: AgCl (white), AgBr (yellowish), AgJ (yellow). On each of the precipitates, add a few drops of a 2n solution of nitric acid. The precipitates do not dissolve.

When exposed to an ammonia solution, the AgCl precipitate dissolves, the AgBr precipitate dissolves only slightly, and the AgJ precipitate does not dissolve.

Experiment. 2. Detection of the chloride anion Cl^-.

When a solution containing Cl^- ions is exposed to a solution of *argentum nitrate, a* white, cheesy (amorphous) precipitate forms. When the precipitate is exposed to a 2N solution of ammonium hydroxide, the precipitate dissolves due to the formation of a complex compound. When the solution is acidified, the complex decomposes and a precipitate of argentum chloride is formed again.

Experiment 2. Detection of the bromide anion Br^- .

To 1-2 drops of a solution containing Br^- add a few drops of a 2N solution of sulfuric acid and 2-3 drops of a solution of *hydrogen peroxide*. The solution turns brown due to the formation of bromine. To increase the sensitivity and selectivity of the reaction, add an organic solvent (benzene or toluene), and the organic layer turns pink.

Experiment 3. Detection of iodide anion J^- .

To 1-2 drops of the solution containing J^- , add a few drops of 2N sulfuric acid solution and 2-3 drops of *potassium nitrite* solution. The solution turns brown due to the formation of iodine or a dark grey iodine precipitate falls out.

$2J^- + 2NO_2^- + 4H^+ = J_2 + 2H_2O + 2NO\uparrow$.

When starch solution is added, the solution turns blue (dark brown).

The salts of copper (II) react with iodide ion to form iodine and an ivory-coloured precipitate of copper (I) iodide.

$2Cu^{2+} + 4J^{-} = 2CuJ\downarrow + J_2$.

When starch solution is added, the solution turns blue (dark brown).

Experiment 4. Detection of sulphide anion S^{2-} .

Action of *sodium nitroprusside* $Na_2[Fe(CN)_5NO]$. Add sodium nitroprusside to 2-3 drops of the solution to be analysed. In an alkaline environment, a characteristic red-purple colour appears. (SO ions$_3^{2-}$ colour the nitroprusside solution pinkish-red).

$[[Fe(CN)_5NO]^{2-} + S^{2-} = [Fe(CN)_5NOS]^{4-}$.

With Fe^{3+} sulphide ions, the ion forms a black precipitate Fe_2S_3.

$3S^{2-} + 2Fe^{3+} = Fe_2S_3\downarrow$.

Experiment 5. Detection of nitrate and nitrite ions. Reaction with diphenylamine $(C_6H_5)NH_2$.

Place 3-4 drops of diphenylamine solution and a drop of the solution to be analysed on a thoroughly washed and wiped glass. In the presence of nitrate and nitrite ions, an intense blue colour appears due to the oxidation of diphenylamine.

The nitrite anion in an acidic medium with iodide ion in the presence of starch gives a blue colour. Nitrate anion in an acidic medium with iodide ion in the presence of starch does not form a blue colour and therefore this test can be used to determine which anion (nitrate or nitrite) is present in the solution.

QUESTIONS FOR PREPARATION

1. A group reagent for the second group of anions.
2. Features of the detection of anions of the third analytical group.
3. What are the peculiarities of determining chloride ion?
4. How can prove that the white precipitate obtained after adding $AgNO_3$ is AgCl precipitate?
5. Features of bromide anion detection
6. Peculiarities of determining nitrite and nitrate ions in the combined presence.

Laboratory work 10
QUALITATIVE SALT ANALYSIS

THEORETICAL INFORMATION

An important step in both qualitative and quantitative analysis is taking a sample of a substance for analysis.

There are several types of samples: *primary* or *master* sample, which is taken at the first stage from a large mass of material; *laboratory* or *passport* sample, which is obtained after reducing the master sample to the mass required for the entire analysis; *analytical* sample, which is taken from the laboratory sample for a single determination.

Before taking the primary sample, its *representativeness* must be determined, and the laboratory sample must be of a mass (volume) that will allow for the entire analysis. Representativeness means that the sample corresponds to the average composition of the material being analysed. The methods of taking a *representative* sample depend on the nature of the material: the type, shape and total amount of the analysed material, and the uniformity of distribution of the components to be determined.

Sampling of solid materials may involve operations such as crushing (rocks, minerals), grinding (ores), pulverising (soil), sawing or drilling (metals, alloys), sieving, mixing, separating, etc. However, regardless of the sampling method, it is important that no possible changes in the composition of the substance occur during processing.

After taking a representative sample, the dry sample is reduced to the size of a laboratory sample by quarting. In quarting, the crushed sample is poured onto a flat surface, mixed, levelled into a square and divided diagonally into four parts. Two opposite parts are taken, and then the rest of the sample is quarted again until the required laboratory sample is obtained. The weight of the laboratory sample depends on the content of the substance to be determined and the sensitivity of the analytical method used.

After preparing the laboratory sample, analytical samples are taken from it for individual analyses, weighed on an analytical balance and subjected to further analytical processing.

Before analysis, the solid sample must be dried (completely or to a constant level) or the water content determined. Otherwise, it will not be possible to accurately calculate the content of the components.

For gases and liquids, the heterogeneity of the composition can almost always be neglected. Therefore, sampling operations are usually simpler and the sample size is smaller.

When analysing industrial gases or solutions, it is preferable to take samples directly from the process streams, either continuously or intermittently. Some modern analytical methods make it possible to perform sampling and analysis automatically in real time and thus to monitor and control the process.

Water sampling

From a surface source of centralised water supply (rivers, lakes, reservoirs), sampling is carried out at a distance of 1 km upstream from the water intake point, and in non-flowing water bodies and reservoirs at a distance of 1 km in both directions from the water intake point. Sampling is carried out from at least two horizons: near the surface and near the bottom (0.5 m from the bottom). From taps - after 10 minutes of open tap. The total sample volume is at least 1 dm^3 . At least 2-3 samples should be taken for analysis from each investigated water supply source. If necessary, preserve the samples.

Soil and snow cover sampling

When taking soil samples, a test site is allocated, the size of which depends on the type and homogeneity of the soil cover and the terrain. If the soil composition is homogeneous, one combined sample is taken from an area of 3 to 5 hectares, which is especially typical for forest-steppe and steppe areas. In the forest zone, one combined sample is taken from an area of 1-3 hectares. In mountainous areas, a combined sample is taken from an area of 0.5-1 ha. To compile the combined sample, the soil is taken using a scoop or shovel to make 30 diagonal holes 10 × 10 cm in area and up to 5 cm deep. All of this is mixed and an average sample (1 kg) is taken using the quarting method.

Food sampling

Food is divided into two main groups based on its physical properties: liquid and solid. Solid foods can be divided into dense (bread, meat, fish, etc.), loose (grain, salt, sugar, etc.) and porous (pasta, crackers).

The volume of the liquid sample is at least 1 dm^3; the weight of the solid sample is 2kg, including vegetables and fruits.

For a reliable determination, the collected samples must be analysed within 24 hours!

When preparing food for analysis, only edible parts are selected. Samples of liquid products are mixed in bottles by inverting them at least 10-20 times. Samples of bulk products are taken from different parts of the package, trying to capture the outer and inner layers of the material, which may differ in composition due to weathering, moistening or drying. Samples of viscous materials are taken after careful handling.

EXPERIMENTAL PART

1. Appearance of the salt.

Pay attention to the appearance of the salt: colour, state (crystalline or amorphous), smell. Draw preliminary conclusions about the possible composition of the salt.

2. Solubility test.

The salt you have received for analysis must be converted into a solution. Therefore, the analysis begins with tests for the solubility of the salt in water and in acids.

Treat 2-3 salt crystals with 10-12 drops of distilled water (stirring with a glass rod), first at room temperature and then (if necessary) with heating.

If the salt does not dissolve in water, check its solubility in hydrochloric acid solution. To do this, treat 2-3 crystals of salt with 10-12 drops of 2N nitric acid solution (stirring with a glass rod), first at room temperature and then (if necessary) under heating.

If the salt does not dissolve in the hydrochloric acid solution, the solubility of the salt is similarly tested (in sequence) in a 2N nitric acid solution, a concentrated nitric acid solution, and a concentrated hydrochloric acid solution.

If gases are released when a salt is dissolved in acids, determine their composition (CO_2, SO_2, H_2S) using the reactions you know.

After selecting the solvent, divide the salt for analysis into three parts. Use the first part for cation determination, the second for anion determination, and the third for repeat and control tests.

3. Detection of cations.

Dissolve 0.1-0.2 g of salt in 40-50 drops of the chosen solvent and use preliminary tests and group reagents to start detecting cations.

Pay attention to the colour of the solution. If the solution is colourless, then it does not contain Cr^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+} , and possibly Fe^{3+} ions. If the solution is coloured, it contains cations that are coloured.

Preliminarily determine the presence of Fe^{2+}, Fe^{3+} and NH_4^+ ions in the salt.

Next, use group reagents to determine which cation group the cation of the salt you are analysing belongs to. After determining the cation group, perform qualitative reactions on the individual cations of this group and determine which cation is part of the salt. Write the equations for the reactions.

4. Detection of anions.

Dissolve 0.1-0.2 g of salt in 40-50 drops of the chosen solvent. If chloride acid was chosen as the solvent, prepare a few drops of salt solution in nitric acid separately to detect the Cl^- ion. If nitric acid was chosen as the solvent, prepare a few drops of aqueous salt solution (all nitrates are water-soluble) or salt solution in hydrochloric acid to detect the NO_3^- ion .

The presence or absence of certain anions can be inferred from the solubility of the salt and from previous tests.

Determine the pH of the solution under test. Use a universal indicator paper to determine the pH of the salt solution (if it is soluble in water). If the medium of the solution under test is acidic, then it cannot contain the anions CO_3^{2-}, SO_3^{2-}, S^{2-} .

Test for anions of group 1 and detection of SO_4^{2-} anion. Pour 3-4 drops of the test solution into a test tube and add 3-4 drops of barium chloride solution. The formation of a precipitate indicates the presence of an anion belonging to the first group. Add a few drops of 2N nitric acid solution to the precipitate. If the precipitate does not dissolve in the acid, then the solution contains a sulphate anion.

Test for anions of group II. Pour 3-4 drops of the solution to be tested into a test tube and add 3-4 drops of argentum nitrate solution. (This reaction cannot be used if the salt was dissolved in HCl). If a precipitate forms, add a few drops of nitric acid. If the precipitate does not dissolve in the acid, then the solution contains group II anions.

Test for the presence of reducing anions. Pour 3-4 drops of the solution to be tested, 3-4 drops of 2N sulfuric acid solution and dropwise iodine solution into the test tube. Discolouration of the solution indicates the presence of reducing anions S^{2-} or SO_3^{2-} .

Carry out qualitative reactions on the individual anions of the identified group and determine which anion is part of the salt.

Based on the results of the determination of the cation and anion, write a formula for the salt, perform control tests and, after confirming the qualitative reactions, report your findings to the teacher.

Present the results of the group reagent tests in a table:

№ of experiment	Group reagent	The result of the interaction	Conclusion on the presence of ions
1.	HCl		
2.	H_2SO_4		
3.	NaOH		
4.	Excess NaOH		
5.	Excess NH_4OH		
6.	$BaCl_2$		
7.	$AgNO_3$		

QUESTIONS FOR PREPARATION

1. What are the different types of samples for analysis?
2. What is sample representativeness?
3. Peculiarities of taking a representative sample of solid materials?
4. Peculiarities of taking a representative sample of heterogeneous liquid substances?
5. How is a representative sample reduced to the size of a laboratory sample?
6. General principles of sample preparation for analysis.

Part 2. Quantitative analysis
Laboratory work 11
DETERMINATION OF CRYSTALLIZATION WATER IN BARIUM CHLORIDE

The composition of crystalline hydrates is expressed by the formula of the substance and the number of crystallization water molecules corresponding to one molecule of the substance. For example, $Na_2SO_4 \cdot 10H_2O$, $Fe_2(SO_4)_3 \cdot 9H_2O$, etc.

The content of crystallization water in different salts is determined by the loss of salt mass during heating. For each crystalline hydrate, the temperature at which the salt does not decompose and the crystallization water completely evaporates is selected. Barium chloride completely loses its crystallization water when heated to a temperature of 120÷125 °C.

EXPERIMENTAL PART

The thoroughly cleaned bullion is dried in an oven at 120-125 °C for 20-25 minutes (the lid of the bullion should be open and the edge should be placed on it). After that, the büx is placed in a desiccator to cool. After 20 to 30 minutes, the büx with the lid is weighed on an analytical balance and the weighing result is recorded in a workbook. Pour 1 to 1.6 g $BaCl_2$ into the bullion bin prepared in this way, close the lid, and weigh it on an analytical balance. Then the büx with salt is placed in a drying oven, where it is kept for 2 hours at a temperature of 120 ÷ 125 °C. During the drying of the salt, the lid of the büx should be open (water vapor should evaporate freely from the salt). After drying, the büx is placed in a desiccator to cool for 20÷25 minutes, and then weighed again on an analytical balance. The drying procedure is repeated until the weight of the bullion with salt differs from the previous weighing by no more than 0.0002 g. The removal of crystallization water is considered complete if the mass of the bullion with salt remains unchanged after two consecutive weighings.

All results are recorded in a table:

1.	Bux weight without substance, g	m_b =
2.	Weight of bux with salt, g	m_{b+s} =
3.	Weight of the substance sample, g	m_{weight} =
4.	Weight of bux with salt after roasting, g	
	- first weighing	$m_{1(b+s)}$ =
	- second weighing	$m_{2(b+s)}$ =
	- third weighing	$m_{3(b+s)}$ =
5.	Average value of weighing results after roasting, g	$m_{av.} = \frac{m_{2(b+s)} + m_{3(b+s)}}{2}$
6.	Mass of crystallization water, g	$m_{(cryst.\ water)} = m_{b+s} - m_{av.}$
7.	Crystallization water content in salt, %.	$\omega_{(water)} = m_{(cryst.\ water)} \cdot 100 / m_{weight}$

QUESTIONS FOR PREPARATION

1. What is the essence of the gravimetric method of analysis?

3. What are the stages of gravimetric analysis?

4. What are the requirements for the deposited and gravimetric molds?

5. What formula is used to calculate the gravimetric factor?

6. Under what conditions are crystalline and amorphous precipitates formed?

7. What formulas are used to calculate the mass of the analyzed substance in the gravimetric method?

8. How can the gravimetric method be used to determine the content of crystallization species in crystallohydrates? Give examples.

Laboratory work 12
NEUTRALIZATION METHOD. PREPARATION OF WORKING SOLUTIONS

THEORETICAL INFORMATION

When performing volumetric analyses, special chemical glassware is used: pipettes and burettes (see Figs. 1, 2).

Fig. 1. Burettes.

Fig. 2. Pipettes.

Fig. 3. Measuring flasks.

Measuring flasks are used to prepare solutions of the exact volume (Fig. 3).

A solution of the exact concentration can only be made from substances that meet these requirements:

- have a known molecular formula;
- do not contain any impurities;
- do not change their composition during weighing and storage.

Such substances are called *reference materials*, and their solutions are called *primary standards*. Solutions of substances that do not meet these requirements are called *working* or *secondary standards*. Their exact concentration is determined using solutions of the original substances.

The neutralization method is based on the interaction of hydrogen and hydroxyl ions to form water: $H^+ + OH^- \leftrightarrow H_2O$

The working solutions of the neutralization method are solutions of acids and bases. The most commonly used solutions are hydrochloric and sulfuric acids, as well as solutions of sodium and potassium hydroxides.

The best method for preparing titrated working solutions is to dissolve an exact weight of the respective pure substance in a certain volume of water. However, this method cannot be used to prepare acid and alkali solutions of precise concentration, because concentrated hypochlorous acid easily loses hydrogen as a gas, and concentrated sulfuric acid absorbs moisture from the air, and thus their concentration changes. Alkalis are difficult to obtain in pure form: during their manufacture (and especially during storage), a certain amount of sodium carbonate is always formed as a result of absorbing CO_2 from the air. Consequently, it is impossible to prepare titrated acid or alkali solutions based on an exact weight. Therefore, in the neutralization method, working solutions are prepared at an approximate concentration and then the exact concentration is established using the starting materials.

Sodium tetraborate is most commonly used to determine the titre and normality of strong acid solutions, and oxalic acid is used to determine the normality and titre of alkaline solutions.

Sodium tetraborate $Na_2B_4O_7 \cdot 10\ H_2O$ (borax) is obtained by recrystallization at 60°C and is chemically pure and meets the requirements for starting materials.

When dissolved in water, sodium tetraborate hydrolyzes according to the equation:

$$Na_2B_4O_7 + 7H_2O \leftrightarrow 2NaOH + 4H_3BO_3 .$$

The orthoboric acid H_3BO_3 , which is formed in this process, is a weak acid, and NaOH is a strong alkali, so the borax solution has a strongly alkaline reaction and can be titrated quite accurately with acids:

$$2NaOH + 2HCl = 2NaCl + 2H_2O.$$

Summing both equations, we get the general equation:

$$Na_2B_4O_7 + 2HCl + 5H_2O = 2NaCl + 4H_3BO_3 .$$

The equation shows that the solution at the equivalence point consists of a mixture of NaCl and free H_3BO_3 , and therefore the pH of the solution is determined by the presence of H_3BO_3 .

Therefore, at the equivalence point, the solution should contain only NaCl and H_3BO_3, which causes a slightly acidic reaction of the solution. The pH value of the solution at the equivalence point is determined based on the value of the dissociation constant H_3BO_3 .

It is known that for a weak acid

$$pH = ½\ pK_{acid} - ½\ lg\ C_{acid}$$

The concentration of H_3BO_3 at the end of the titration is approximately 0.1 N, and $pK_{acid} = -lg\ K_{dis.} = 9.2$.

$$So,\ pH = ½ \cdot 9.2 - ½\ lg\ 0.1 = 5.1.$$

The titration will be most accurate if you use an indicator with a titration value of pT = 5.1 or as close to this value as possible. Methyl red (pH = 5.5) is most suitable, and methyl orange (pH = 4) can also be used.

EXPERIMENTAL PART

1. Preparation of sodium tetraborate solution (primary standard)

Prepare a 0.1 N titrated solution of sodium tetraborate in a 100-ml volumetric flask. First, determine the amount of salt to be taken. 1 liter of solution should contain 0.1 mol-eq. of sodium tetraborate. The molar mass equivalent of sodium tetraborate is ½ the molar mass:

$M(Na_2B_4O_7 \cdot 10\ H_2O) = 381.4$ g/mol.

$M_E\ (Na_2B_4O_7 \cdot 10\ H_2O) = M/2 = 381.4/2 = 190.7$ g/mol-eq.

So, to prepare 100 ml of a 0.1 N solution of sodium tetraborate, you need to take the following weight of salt:

$m(Na_2B_4O_7 \cdot 10\ H_2O) = M_E \cdot C_N \cdot V = 190.7 \cdot 0.1 \cdot 0.1 = 1.907$ g.

Weigh the bullion (or watch glass) with sodium tetraborate on an analytical balance (weigh the sodium tetraborate on a technical balance beforehand).

Carefully pour the sample through a dry funnel into a volumetric flask that has been well washed and rinsed with distilled water. After that, weigh the batch with the sodium tetraborate particles again on an analytical balance and use the difference in weight to accurately determine the mass of the sample poured into the flask. Using a rinsing bottle, rinse the sodium tetraborate from the funnel into the flask. Sodium tetraborate is poorly soluble in cold water, so add hot distilled water to 2/3 of the flask volume. Stir the flask in a smooth circular motion until the sodium tetraborate is completely dissolved. After that, carefully cool the solution in the flask to room temperature under the tap and add distilled water to the mark. Close the flask with a cork and stir gently.

Determine the titer T and normality C_N of the sodium tetraborate solution using the formulas:

$T_{(borax)} = m_{(borax)}/V_{(solution)}$ (g/ml);

where $m_{(borax)}$ is the weight of sodium tetraborate (g),

$V_{(solution)}$ is the volume of the sodium tetraborate solution (volume of the measuring flask).

$C_{N(borax)} = T_{(borax)} \cdot 1000/M_{E(borax)}$.

Calculations should be made to the fourth significant digit.

For example, let's say the borax weight was 1.8893 g, then

$T_{(borax)} = 1{,}8893/100 = 0{,}01889$ (g/ml).

Having the titer of the borax solution, let's go to normal by multiplying it by 1000 ml (to convert to 1 liter) and dividing it by the molar mass of the borax equivalent:

$C_{N(borax)} = T_{(borax)} \cdot 1000/M_{E(borax)} = 0.01889 \cdot 1000/190{,}7 = 0{,}09906$.

2. Preparation of the working solution of hydrochloric acid

Prepare 500 ml of approximately 0.1 N solution from concentrated hypochlorous acid.

Use an areometer to measure the density of concentrated HCl. Knowing the density, we use the table to find the percentage concentration of hypochlorous acid and calculate how much of this acid we need to take to prepare 500 ml of a 0.1 N solution. M_E (HCl) = M/1 = 36.5 g/mol-eq.

For example, in the laboratory, the acid has a density of 1.19 g/ml. From the tables, we find that it contains 37.2% hydrogen chloride.

To prepare 0.5 liters of 0.1 N HCl solution, take 0.1 N:

In 1000 ml of solution --------- 3.65 g HCl

500 ml of solution --------- x g HCl

$$x = 500 \cdot 3{,}65/1000 = 1{,}825 \text{ g HCl.}$$

Knowing that the acid in the laboratory is 37.2%, find how many grams of this acid you need to take to make the HCl content 1.825 g:

100 g of solution contains 37.2 g of HCl

y g -------------------------- 1,825 g HCl

$$y = 1{,}825 \cdot 100/37{,}2 = 4{,}9 \text{ g (37.2\% solution)}$$

To convert the weight of HCl to volume, divide the resulting mass by the density of the hydrochloric acid solution:

$V = m/\rho$; $V = 4{,}9 / 1{,}19 = 4{,}12$ ml.

Measure out 4.12 ml of concentrated hydrochloric acid with a cylinder, dilute to about 0.5 l with water, and stir the solution. The concentration of the prepared HCl solution is determined by sodium tetraborate.

QUESTIONS FOR PREPARATION

1. What is the essence of titrimetric (volumetric) analysis and how does it differ from gravimetric (weight) analysis?
2. What is the equivalence point of a titration and how is it recorded?
3. Requirements for reactions used in titrimetric analysis.
4. What are "source" substances and requirements for them?
5. Define the concepts of "titer" and "titer for the substance to be determined".
6. Methods of preparing titrated solutions.

Laboratory work 13
STANDARDIZATION OF THE CHLORIDE SOLUTION. TITRATION OF THE SODIUM HYDROXIDE SOLUTION

EXPERIMENTAL PART

1. Determination of the exact normality and titre of hydrochloric acid by sodium tetraborate

Gently wash the burette and rinse it twice with a small amount of the prepared HCl solution. After that, fill the burette almost to the top with the HCl solution, then, placing a vessel under the burette, fill the "spout" of the burette with the acid solution, making sure that no air bubbles get in. Bring the volume of acid in the burette to the "0" mark - the burette is ready for titration.

Wash the pipette thoroughly, rinse it twice with a small amount of sodium tetraborate solution, and collect 10 ml of titrated sodium tetraborate solution. Pour the collected volume of solution from the pipette into a 100-ml titration conical flask. Do not blow out the last drops of solution from the pipette, but remove them by touching the end of the pipette to the flask wall. Add 1-2 drops of methyl orange to the flask and titrate with HCl from the burette until the color changes from a single drop of yellow to a slightly pink color that does not disappear with stirring. To better determine the color change, place white paper under the flask with the sodium tetraborate solution.

After achieving a change in the color of the indicator from one drop of HCl, determine the volume of hydrochloric acid used during the titration from the burette and record it.

Repeat the titration three times, taking a new portion of HCl each time, setting the liquid level in the burette to zero.

From the three results, we calculate the average value of V (HCl), which we use in the calculations.

The normality and titer of the hypochlorous acid solution are calculated by the formula:

$C_N\,(HCl) = V_{(borax)} \cdot C_{N(borax)} / V_{(HCl)}$.

$T\,(HCl) = C_N\,(HCl) \cdot \frac{M_E\,(HCl)}{1000}$ g/ml

$M_E\,(HCl) = \frac{M}{1} = \frac{36,45}{1} = 36,45$ g/mol-eq.

We save the acid for the next titration. To do this, each student writes his or her name on a label and sticks it on the jar of acid.

2. Determination of the unknown mass of sodium hydroxide in solution

After receiving a certain volume of sodium hydroxide solution from the laboratory assistant, add 1-2 drops of phenolphthalein and titrate with hydrochloric acid solution (first add hydrochloric acid solution to the bulletin to the zero mark).

Measure the volume used for titration.

Calculations:

1. Determine the titre of HCl with NaOH (i.e., how much NaOH in grams reacts with 1 ml of HCl):

$$T(_{HCl/NaOH}) = C_H(HCl)\,\frac{M_E(NaOH)}{1000}\ .$$

$$M_E(NaOH) = \frac{M}{1} = \frac{40}{1} = 40 \text{ g/mol-eq.}$$

2. The mass of alkali (m_{NaOH}) contained in the solution is determined from the formula:

m (NaOH in solution) = $T(_{HCl/NaOH}) \cdot V(HCl)$ (g).

QUESTIONS FOR PREPARATION

1. What is the essence of the acid-base titration method?
2. How is the stoichiometric point determined in acid-base titration?
3. Why can't NaOH and HCl solutions be classified as primary standards?
4. What substance can be used to standardize hydrochloric acid? Give the appropriate reaction.

Laboratory work 14.
DETERMINING THE ACIDITY OF BREAD AND MILK

THEORETICAL INFORMATION

The acidity of bread is expressed in degrees of acidity. A degree of acidity is the amount of ml of 1 N solution of caustic soda or caustic potassium necessary to neutralize the acids contained in 100 g of bread crumb.

The acidity of bread is due to the presence of lactic and acetic acids in its composition, which are formed during the fermentation of the dough and subsequent baking.

Moderate acidity of bread gives it a pleasant taste and promotes more complete digestion; bread with high acidity can be harmful to health due to increased fermentation processes in the gastrointestinal tract. In addition, sour bread is a good environment for the development of mold that has come from the air. The acidity of rye bread should not exceed 12°, rye-wheat bread - 11°, wheat bread - 3-4°.

Titratable acidity is a criterion for assessing the quality of milk during its preparation. In milk and dairy products (except butter), it is expressed in conventional units - Turner degrees (°T). Degrees of acidity are defined as the number of milliliters of a 0.1n alkali solution required to neutralize 100 ml of milk.

The acidity of freshly milked milk is 16...18°T. This acidity is caused by acid salts - dihydrophosphates and dihydrocitrates (about 9...13°T), proteins - casein and whey proteins (4...6°T), carbon dioxide, acids (lactic, citric, ascorbic, free fatty acids) and other milk components (in total about 1...3°T).

During storage, the titratable acidity of raw milk increases as lactic acid bacteria develop in the milk, converting lactose into lactic acid. Therefore, milk with an acidity of 21°T is accepted as non-vintage.

EXPERIMENTAL PART
1. Determining the acidity of bread

An average sample of bread is taken, a slice is taken from the middle of the bread, the crust and crust layer are cut off, and the crumb is taken for analysis.

Weigh out 25 g of pulp to the nearest 0.01 g and place it in a dry 500-ml conical flask with a wide neck and a well-fitting stopper. Next, 250 ml of distilled water heated to 60° is measured out. About 1/4 of this volume is poured into the bread weight, which is quickly rubbed with a glass rod until a homogeneous mass is obtained. After a few minutes, the remaining amount of water is added to the resulting mass. The flask is covered with a cork and shaken vigorously for 3 minutes. The mixture is then left to rest for 10 minutes.

Carefully pour the settled liquid layer into a beaker through cheesecloth. From the beaker, take 20 ml of the solution into a 100 ml conical flask, add 2-3 drops of phenolphthalein solution and titrate with 0.1 N alkaline solution until a light pink color appears that does not disappear within 1 minute. Acidity in degrees (T) is calculated by the formula:

$$T = \frac{V \cdot N \cdot 250 \cdot 4}{V_1},$$

where V is the volume of alkali solution used for titration, ml;

N - alkali normality, mol-eq/l;

4 is the conversion factor per 100 g of weight;

250 is the volume of liquid used to process the sample;

V_1 is the volume of the sample taken for titration, ml.

2. Determination of milk acidity

Pipette 10 ml of milk, 20 ml of distilled water, 2-3 drops of phenolphthalein into a 100 ml conical titration flask, mix well, and titrate with 0.1 N alkaline solution until a light pink color appears and does not disappear within 1 minute. The acidity in degrees (T) is calculated by the formula:

$$T = \frac{V \cdot N \cdot 100}{V_1},$$

where V is the volume of alkali solution used for titration, ml;

N - alkali normality, mol-eq/l;

100 is the volume of liquid taken for analysis;

V_1 is the volume of milk whose acidity is determined, ml.

QUESTIONS FOR PREPARATION

1. Classification of titrimetric analysis methods.
2. Acid-, alkalimetry, titration curves of strong acid with strong base, weak acid with strong base, weak base with strong acid.
3. Indicators of acid-base titration, their pH values.
4. Calculations in titration analysis.

Laboratory work 15
DETERMINATION OF WATER HARDNESS

THEORETICAL INFORMATION

Water is widely used in machinery, chemical production as a solvent and reagent, as well as for washing various substances, for cooling units, steam boilers, etc.

The properties of water are significantly affected by the impurities dissolved in it. These impurities are necessary for human, animal and plant life, but they are often harmful when water is used for technical purposes. For example, for steam boilers, impurities of calcium and magnesium salts are particularly harmful, as they form a dense deposit on the boiler walls at high temperatures.

The content of Ca^{2+} and Mg^{2+} ions in natural water causes water hardness. During the boiling of hard water, sediments (scale) are formed on the walls of cookware (boilers), consisting of calcium and magnesium carbonates, products of thermal decomposition of water-soluble hydrogen carbonates.

The total content of magnesium and calcium salts in water is called its total hardness.

The total hardness of water is divided into temporary, or carbonate, and permanent, or non-carbonate.

Temporary water hardness is caused by the presence of calcium and magnesium bicarbonates and can be eliminated by boiling the water for a long time:

$$Me(HCO_3)_2 \overset{t}{=} MeCO_3\downarrow + CO_2\uparrow + H_2O.$$

The constant hardness of water is caused by the presence of strong acid salts in the water - sulfates and chlorides of magnesium and calcium; boiling cannot eliminate the constant hardness.

Water hardness is usually expressed in terms of the number of milliequivalents (mEq) of Mg^{2+} and Ca^{2+} ions contained in 1 liter of water (1 mEq = 20.04 mg/l Ca^{2+} or 12.16 mg/l Mg^{2+}).

Water containing less than 4 meq/l of Mg^{2+} and Ca^{2+} ions is called soft, 4 to 8 - medium, and more than 8 - hard.

The essence of the definition is the interaction of hydrogen carbonates with hydrochloric acid:

$$HCO_3^- + H^+ \rightarrow CO_2 + H_2O.$$

According to the law of equivalents, the number of milliequivalents of acid that was used to react is equal to the number of milliequivalents of hydrogen carbonates in the volume of water used for determination. Converting this number to a volume of 1 liter, we get the value of temporary hardness.

EXPERIMENTAL PART

1. Determination of temporary (carbonate) water hardness

Pour 100 ml of the test water into a 200-250 ml conical flask rinsed with distilled water, add 2-3 drops of methylorange indicator, and titrate with a titrated solution of hydrochloric acid until a slightly yellow color appears. The titration process is carried out by adding drops of HCl from the burette, continuously stirring the contents of the flask. The color of the solution is best observed if the flask is placed on a sheet of white paper. Measure the volume (V) of acid used for the titration.

Repeat the titration 2-3 times and take the average of the close results.

Calculating the results of the experiment:

The temporary water hardness is calculated using the formula:

$$d_H = \frac{V_{(HCl)} \cdot C_{N\ (HCl)}}{V_{(H_2O)}} \cdot 1000\ \frac{meq}{l},$$

where V(HCl) is the volume of hydrochloric acid solution used for titration, ml;

C_N (HCl) is the normality of the HCl solution, mol-eq/l;

$V(H_2O)$ is the volume of water taken for analysis (ml).

2. Determination of the total stiffness

Take 100 ml of the test water sample into a titration flask and add 5 ml of ammonia buffer solution (pH 10). Then add 2-3 drops of the solution (a little dry powder can be added) of the indicator Eriochrome Black T until a wine-red color is obtained and titrate with Trilon B working solution until the color changes to blue (with a greenish tint).

The water hardness in milliequivalents per liter (d_H) is calculated using the formula:

$$d_H = \frac{V_{Trilon} \cdot C_{N\ Trilon}}{V\ (H_2O)} \cdot 1000\ \left(\frac{meq}{l}\right),$$

where V_{Trilon} is the volume of Trilon B working solution used for titration, ml;

$C_{N\ Trilon}$ - concentration of trilon B solution; mol-eq/l;

$V(H_2O)$ is the volume of water taken for determination, ml.

3. Calcium hardness determination

After determining the total water hardness using Trilon B, we find the sum of the meqs of Calcium and Magnesium. Then, using Trilon B in the presence of a murexide indicator, the calcium content is determined and the difference is the magnesium content.

Pipette 100 ml of the test water into a 200-250 ml conical flask. Add 2 ml of 2 M NaOH solution and 10-15 mg of dry murexide indicator. Titrate with Trilon B solution with vigorous stirring. The color change from red to lilac indicates the end of the titration.

The content of Ca^{2+} ions in the water under study is calculated by the formula:

$$C_{(Ca^{2+})} = \frac{V_{Trilon} \cdot C_{N\,Trilon}}{V_{(H_2O)}} \cdot 1000 \ \frac{meq}{l},$$

where V_{Trilon} is the volume of trilon B working solution used for titration, ml;
$C_{N\,Trilon}$ - concentration of trilon B solution; mol-eq/l;

$V(H_2O)$ is the volume of water taken for determination, ml.
The content of Mg^{2+} ionsis calculated by the difference:

$$C_{(Mg^{2+})} = d_H - C_{(Ca^{2+})}.$$

QUESTIONS FOR PREPARATION

1. What salts determine water hardness?
2. Temporary and permanent rigidity.
3. Methods of eliminating stiffness.
4. Determination of temporary stiffness.
5. Determining the constant stiffness.

Laboratory work 16
PERMANGANATOMETRY

THEORETICAL INFORMATION

Permanganatometry is a method of titrimetric analysis in which a substance is determined by titration with a solution of potassium permanganate. Titration with $KMnO_4$ is used to determine many reducing agents. Depending on the pH of the medium, $KMnO_4$ is reduced in different ways. For example, in an acidic environment, the reaction proceeds according to the following equation:

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

The molar mass of the equivalent:

$$M_E\,(KMnO_4) = \frac{M}{5} = \frac{158{,}03}{5} = 31{,}61 \text{ g/mol-eq.}$$

The reaction takes place in a neutral or slightly alkaline environment:

$$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4\,OH^-.$$

The molar mass of the equivalent:

$$M_E\,(KMnO_4) = \frac{M}{3} = \frac{158{,}03}{3} = 52{,}68 \text{ g/mol-eq.}$$

Potassium permanganate does not meet the requirements for starting materials. It always has small amounts of contaminants (MnO_2 , sulfates, chlorides), oxidizes organic matter and decomposes slowly during storage.

Given these properties, the working solution of $KMnO_4$ is prepared by dissolving an approximate weight weighed on a chemical balance in an amount close to the calculated amount. The solution should be dissolved in boiled and cooled water, after dissolution, let it stand for 7-10 days, and then carefully pour the $KMnO_4$ solution into a clean dark glass beaker, close it with a glass cork.

In titrimetric analysis, the reduction of $KMnO_4$ in an acidic environment is used because under these conditions, the solution to be titrated becomes discolored as long as the reducing agent is present in the solution.

EXPERIMENTAL PART

1.Preparation of oxalic acid solution (primary standard)

To establish the normality of a $KMnO_4$ solution, usually use oxalic acid $H_2C_2O_4 \cdot 2H_2O$ or sodium oxalate $Na_2C_2O_4$.

Oxalic acid is oxidized by a solution of potassium permanganate according to the following equation:

$2KMnO_4 + 5\ H_2C_2O_4 + 3H_2SO_4 = 2MnSO_4 + 10CO_2\uparrow + K_2SO_4 + 8H_2O$.

The oxidation of oxalic acid follows the scheme:

$$C_2O_4{}^{2-} - 2\ e^- \rightarrow 2CO_2.$$

The equation shows that during oxidation, each $C_2O_4{}^{2-}$ ion loses 2 electrons, so the molar mass of the oxalic acid equivalent is half of its molar mass:

$$M_E\ (H_2C_2O_4 \cdot 2H_2O) = \frac{M}{2} = \frac{126{,}06}{2} = 63{,}03\ \frac{g}{\text{mol-eq}}.$$

You need to prepare 100 ml of a 0.05 N solution, so the weight of the acid is:

m ($H_2C_2O_4 \cdot 2H_2O$) = M_E ($H_2C_2O_4 \cdot 2H_2O$)$\cdot$ $C_N \cdot$ V = = 63.03$\cdot$ 0.05$\cdot$ 0.1 = 0.31515 (g).

Weigh the oxalic acid on an analytical balance, transfer it to a 100-mL flask, dissolve it in distilled water, and bring it to the mark (dash) with water, after which the solution in the flask is thoroughly mixed.

Calculate the titer and normality of oxalic acid:

$$T(H_2C_2O_4 \cdot 2H_2O) = \frac{m(H_2C_2O_4 \cdot 2H_2O)}{V_{\text{solution}}}.$$

$$C_N(H_2C_2O_4) = T\ (H_2C_2O_4 \cdot 2H_2O) \cdot \frac{1000}{M_E\ (H_2C_2O_4 \cdot 2H_2O)}\ .$$

2.Determination of the titer and normality of $KMnO_4$ by oxalic acid

Fill the burette with $KMnO_4$ solution (you can measure the volume by the upper meniscus of the liquid in the burette).

Pour 20 ml of water, 10-15 ml of 2N solution of H_2SO_4 into a 100 ml conical flask and heat the contents of the flask to a temperature of 75-80°C (do not bring to a boil). Take 10 ml of the oxalic acid solution with a pipette and transfer it to the flask.

After that, the contents of the flask are titrated with a solution of $KMnO_4$. The first drops of $KMnO_4$ discolor very slowly, but further discoloration is faster and the working solution can be added in larger portions. At the end of the titration, the solution turns pink, which does not disappear for a long time. Measure the V of the solution used for titration. Perform the exact titration three times and take the average volume of the solution used for the titration.

Based on the results, calculate the normality and titer of the potassium permanganate solution:

$$C_N\ (KMnO_4) = \frac{V\ (H_2C_2O_4) \cdot C_H\ (H_2C_2O_4)}{V\ (KMnO_4)}\ .$$

$$T\ (KMnO_4) = \frac{M_E\ (KMnO_4) \cdot C_H\ (KMnO_4)}{1000}\ .$$

3. Determination of the concentration of Fe^{2+} ions in a solution of Mohr's salt

A solution of ferric (II) salt is titrated in an acidic environment with a working solution of $KMnO_4$. The reaction proceeds according to the following ionic equations:

Fe^{+2} - 1e $^{-}\rightarrow$ Fe^{+3}.

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

MnO_4^- + 5 Fe^{+2} + 8H^+ $\rightarrow$ 5Fe^{+3} + Mn^{+2} + 4H_2O.

or in molecular form:

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

For analysis, prepare the solution in a 100-ml volumetric flask. Pipette 25 ml of this solution into the titration flask, add 10 ml of 2 N H_2SO_4 and titrate with $KMnO_4$. Measure the volume (V) used for titration. Titration is carried out three times and the average value of V($KMnO_4$) used for titration is taken for calculations.

Calculations.

1. Calculate the titer (T) of the KMnO solution$_4$ for iron:

$$T(\text{KMnO}_4/\text{Fe}) = C_N(\text{KMnO}_4) \cdot \frac{M_E\,(\text{Fe}^{+2})}{1000}.$$

2. Determine the mass of Fe^{+2} in an aliquot (25 ml) of the solution:

$$m\,(\text{Fe}^{+2}) = T\,(\text{KMnO}_4/\text{Fe}) \cdot V\,(\text{KMnO}_4).$$

3.Calculate the concentration of Fe^{+2} ions in a solution of Mohr's salt in g/l:

$$C\,(\text{Fe}^{+2}) = \frac{m\,(\text{Fe}^{+2})}{25} \cdot 1000.$$

QUESTIONS FOR PREPARATION

1. Reactions used in redox titration.
2. The essence of the permanganate method.
3. Determination of the equivalent mass of potassium permanganate depending on the reaction conditions.
4. Working solutions for the permanganate method.
5. What substances can be quantified by permanganate analysis?

Laboratory work 17
MEASUREMENT OF pH OF AQUEOUS SOLUTIONS BY IONOMETRY

THEORETICAL INFORMATION

Potentiometry, or the method of potentiometric analysis, is based on the use of the dependence of the electromotive force (EMF) of an electrochemical circuit on the activity (concentration) of the analyzed ion.

The dependence of the electromotive force, denoted by *E, of* an electrochemical chain on the activity (concentration) of the analyzed ion is described by the Nernst equation:

$$E = E^0 + \frac{S}{n} \lg a,$$

where $E°$ is the standard EMF of the circuit, V;

n is the charge of the analyzed ion with the corresponding sign;

S is the steepness of the electrode function of the indicator electrode, selective to a single-charge ion;

a - activity of the analyzed ion.

For potentiometric measurements, electrochemical circuits containing two electrodes are used: an indicator and a reference electrode. If both electrodes are immersed in the analyte solution, the circuit is called a circuit without , transfer. If the reference electrode is connected to the analyzed solution through a salt bridge, such a circuit is called a circuit with transfer.

In potentiometric analysis, a transfer circle is mainly used. Such a circle is depicted schematically as follows:

Indicator electrode	Analyzed solution	Salt bridge	Reference electrode

An indicator electrode is an electrode whose potential determines the activity of the analyzed ion according to the Nernst equation. A reference electrode is an electrode whose potential is constant and does not depend on the concentration of the ions being analyzed. The salt bridge is used to prevent mixing of the test solution and the reference electrode solution. Saturated salt solutions with similar cation and anion mobility values are used as a salt bridge: KCl, KNO_3 , etc.

Two types of indicator electrodes are used in potentiometric analysis:

- electrodes on the surface of which electron exchange reactions take place, they are called electron exchange or redox electrodes. Such electrodes are made of chemically inert metals: platinum, gold, etc. In analytical practice, a platinum spot electrode EPV-1-100 and a membrane redox electrode are used;

- electrodes on the surface of which ion exchange reactions take place. They are called ion exchange or ion selective electrodes. The main element of ion-selective electrodes is an ion-sensitive membrane, so they are also sometimes called membrane electrodes.

Depending on the type of membrane, ion-selective electrodes are divided into:

- electrodes with solid membranes
- electrodes with glass membranes;
- electrodes with liquid membranes.

When measuring the emf of electrochemical circuits used in potentiometry, it is necessary to measure very low currents (10^{-13} -10^{-14} A) to avoid causing electrode polarization. This is possible only when using the compensation method of measuring the emf. Nowadays, the industry produces special devices for this purpose: pH meters and ionometers.

Potentiometric analysis methods are divided into two types:

- direct potentiometry or ionometry
- Potentiometric titration.

EXPERIMENTAL PART

Standard buffer solutions should be prepared at the beginning of the assay. Standard buffer solutions are recommended to be prepared from standard titers. If they are not available, they can be prepared from reagents.

Potassium tetraoxalate solution, pH = 1.68, with a concentration of 0.05 mol/dm^3 (12.7 ± 0.02 g $KH_3C_4O_8 \cdot 2H_2O$, in 1 dm^3 solution at 20° C).

Potassium hydrophthalate solution, pH = 4.01, with a concentration of 0.05 mol/dm^3 (10.21 ± 0.02 g $KHC_8H_4O_4$ in 1 dm^3 solution at 20° C).

A solution of potassium dihydrogen phosphate, pH = 6.86, with a concentration of 0.025 mol/dm^3 , and sodium hydrogen phosphate, with a concentration of 0.025 mol/dm^3 (3.40 ± 0.01 g $KH_2PO_4$and 3.55 ± 0.01 g NaH_2PO_4 in 1 dm^3 solution at 20° C)

A solution of sodium tetraborate, pH = 9.18, with a concentration of 0.01 mol/ dm^3 (3.81 ± 0.01 g $Na_2B_4O_7 \cdot 10H_2O$, borax, in 1 dm^3 solution at 20° C)

When preparing buffer solutions of phosphate (pH = 6.86) and borax (pH = = 9.18), use distilled water free of carbon dioxide. It is recommended to store the buffer solutions in an airtight glass or plastic container.

Measurement of the hydrogen index is carried out using a pH meter. A diagram of the device is shown in the figure.

a) Rinse the working parts of the electrodes with distilled water. Carefully remove water droplets from the electrodes (without friction) with a piece of filter paper.

б) The electrodes are immersed in a small portion of the solution to be analyzed and poured out. For measurements, a fresh dose of the solution is poured in, which should completely cover the spherical glass membrane (40-60 ml).

The working part of the electrode should not touch the bottom of the glass.

To measure the pH of solutions using the pH scale of the instrument, you must first calibrate the instrument. For this purpose, measure the pH of a standard buffer solution for which the pH value is known. If necessary, use the calibration knob to set the instrument to the appropriate pH value, taking into account the temperature of the solution. Then check the instrument readings in three standard buffer solutions with different pH values. The measurement error in each of the buffers should be within ±0.05 pH.

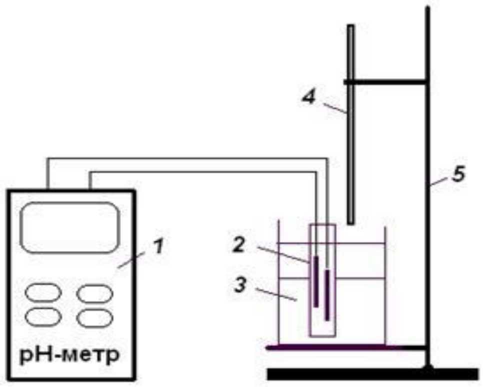


Fig. 4. Diagram of a pH meter
1 - pH meter;
2 - combined electrode;
3 - a glass with the solution;
4 - burette;
5 - tripod.

In this way, the device is calibrated using standard pH buffer solutions. The measurement results are recorded in a table.

pH of the standard buffer solution	1,68	4,01	6,86	9,18
pH measured experimentally				

After the calibration of the device is completed, the pH of the test solution is measured. The measurement is performed three times.

QUESTIONS FOR PREPARATION

1. What type of electrode is a glass electrode? What are its disadvantages and advantages?

2. Explain the mechanism of the potential jump at the glass-solution interface.

3. How is the electrode prepared for work?

4. What is the essence of glass electrode calibration. What is the reason for this procedure?

5. Write a diagram of a galvanic cell used to measure pH?

6. What is the structure of a silver chloride electrode? What type of electrode does it belong to? Why is this electrode used as a reference electrode?

Laboratory work 18
DETERMINATION OF NITRATE CONTENT IN FOOD PRODUCTS

THEORETICAL INFORMATION

The problem of toxic accumulation of nitrates in agricultural products is one of the most acute and urgent, as nitrates are characterized by a fairly wide range of toxic effects. Nitrates themselves are not toxic; it is not nitrates themselves that cause harm to the human body, but nitrites, into which they are converted under certain conditions. The greatest danger of an increased content of nitrates in the body is the ability of the nitrite ion to participate in the nitrosation reaction of amines and amides, which results in the formation of nitro compounds with carcinogenic and mutagenic effects. According to the WHO, the permissible daily dose of nitrates for an adult is 5 mg per 1 kg of body weight, i.e. 0.25 g per person weighing 60 kg. For a child, the permissible rate is no more than 50 mg.

The distribution of nitrates in vegetables is uneven, so it is necessary to properly prepare the sample for analysis. Sampling is carried out individually. If the products are stacked in several layers, a sample is taken from each layer. From the total sample, to prepare for analysis, do the following:

Potatoes. Tubers are washed with water, dried with filter paper or a clean cloth, and a quarter is taken from each tuber. The selected material is mixed and a sample for analysis weighing at least 0.25 kg is taken.

Table beets and other root vegetables. Root vegetables are washed with water, wiped, and the neck and thin end of the root are cut off. Large root crops are cut crosswise along the vertical axis and half or a quarter is used for analysis. A sample weighing 0.5-0.25 kg is taken from the material obtained.

Cabbage. Each head of cabbage is cut into 4 parts along the vertical axis and one quarter of the sample is taken for analysis. The surface of the previous cut is cut off and discarded, and the upper inedible leaves and the remainder of the head of cabbage are discarded. A sample for analysis weighing 0.5 kg is taken from the material obtained.

Leafy vegetables are cleaned from the ground, freed from inedible parts and inclusions, and a 0.25 kg sample is taken for analysis.

Bulbous plants. Discard inedible parts. Remove the top husk from the onions, cut off and discard the root base and dry neck. The bulbs are divided into two parts vertically and only one half is taken for analysis. A sample of 0.25 kg is taken from the material obtained for analysis.

Tomatoes, cucumbers. The fruits are washed with water, dried with filter paper or a clean cloth, and the stalks are removed. Large fruits are cut into 2-4 pieces along the axis, and half or a quarter is taken for analysis. A 0.5 kg sample is taken from the material obtained for analysis.

Melons and gourds. The top layer, which is not eaten, is removed from the fruit, the seeds are also removed and only the edible part is examined. Fruits are cut into 2 parts along the line from the stem attachment point to the flower droppings so that each half contains darkened and sunlit parts. If the fruits are very large, they are cut into 6-8 cm segments around the circumference of the fruit and 2-4 segments are taken from opposite sides of each fruit. A sample of 0.5 kg is taken from the material obtained for analysis.

EXPERIMENTAL PART

First, prepare a stock solution of potassium nitrate (0.1 M). To do this, dissolve 0.1011 g of potassium nitrate in a 1% solution of potassium alum in a 100 ml volumetric flask. KNO_3 working standard solutions 0.01M, 0.001M and 0.0001M are prepared by successive dilution of the stock solution with 1% potassium alum solution.

Before starting work, the nitrate-selective electrode is soaked in a 0.1M potassium nitrate solution. Before starting work, the indicator electrode and the reference electrode are rinsed in distilled water.

To build a calibration graph, the potential of working standard solutions of potassium nitrate is measured. Based on the results, a graph of the potential versus pC of nitrate solutions is plotted.

The sample for analysis is crushed, weighed 10 g, ground in a mortar with calcined sand to a homogeneous mass, and transferred with 50 ml of 1% solution of potassium alum to a 100 ml beaker. Measure the potential of the sample using a nitrate-selective electrode. The content of nitrate ions in the sample is determined according to the calibration graph.

The mass fraction of nitrates in the sample is determined by the formula

$$c = \frac{\left(V + \frac{\omega m}{100\rho}\right) 10^{-pC(NO_3)} 62 \cdot 10^{-6}}{1000m},$$

where 62 is the molar mass of the nitrate ion; m is the mass of the sample, g;
V is the volume of the extraction solution, ml; ρ is the density of water, g/ml;
ω is the mass fraction of water in the sample, %.

The value of ω is determined according to the table below.

The results of the study were compared with the values of the limit is the permissible concentration of nitrates (mg/kg) for some of the most common plant products:

- potatoes - 250; - cabbage - early (before September 1) - 900, late - 500; - carrots - early (before September 1) - 400, late - 250; - tomatoes - (open ground) - 150, (closed ground) -300 - cucumbers - (open ground) - 150, (closed ground) - 400 - table beets - 1400; - onions (turnips) - 80; - onions (feathers) - 600 (open ground), 800 (closed ground); - green crops - 2000 (open ground), 3000 (closed ground); - melons - 90 - watermelons - 60; - sweet peppers - 200 (open ground), 400 (closed ground) - zucchini - 400; - table grapes; - apples - 60; - pears - 60.

Data on the conversion of pC (NO_3^-) to the mass fraction of nitrate

$pC_{NO_3^-}$	Mass fraction of nitrate, mln^{-1}									
	Hundredths of pC_{NO3^-}									
	0,00	0,01	0,02	0,03	0,04	0,05	0,06	0,07	0,08	0,09
2,0	30900	30200	29510	28840	28180	27540	26920	26300	25700	25120
2,1	24550	23990	23440	22910	22390	21880	21380	20890	20420	19950
2,2	19500	19050	18620	18200	17780	17380	16980	16600	16220	15850
2,3	15490	15140	14790	14450	14130	13800	13490	13180	12680	12590
2,4	12300	12020	11750	11480	11220	10960	10720	10470	10230	10000
2,5	9772	9550	9333	9120	8913	8730	8511	8318	8128	7943
2,6	7762	7586	7413	7244	7079	6918	6761	6607	6457	6310
2,7	6166	6026	5888	5754	5623	5495	5370	5248	5129	5012
2,8	4898	4786	4677	4571	4467	4365	4266	4169	4047	3981
2,9	3890	3802	3715	3631	3548	3467	3388	3311	3236	3162
3,0	3090	3020	2951	2884	2818	2754	2692	2630	2570	2512
3,1	2455	2399	2344	2291	2239	2188	2138	2089	2042	1995
3,2	1950	1905	1862	1820	1778	1738	1698	1660	1622	1585
3,3	1549	1514	1479	1445	1413	1380	1349	1318	1283	1259
3,4	1230	1202	1175	1148	1122	1096	1072	1047	1023	1000
3,5	877	955	933	912	891	871	851	832	813	794
3,6	766	759	741	724	708	692	676	661	646	631
3,7	617	603	589	575	563	549	537	525	513	501
3,8	490	479	468	457	447	437	427	417	407	398
3,9	389	380	371	363	355	347	339	331	324	316
4,0	309	302	295	288	283	275	269	263	257	251

QUESTIONS FOR PREPARATION

1. What are the main sources of nitrates in the human body?
2. What is the toxic effect of nitrates on the human body?
3. Describe the method for determining nitrates in plant material.
4. What are the permissible nitrate levels in potatoes, beets, onions, and apples?
5. What is the harm caused by excess nitrates in food?
6. What parts of plants accumulate the most nitrates?
7. How can we reduce the nitrate content of vegetables and fruits?

Laboratory work 19

REFRACTOMETRIC DETERMINATION OF SODIUM CHLORIDE CONTENT IN FOOD PRODUCTS

THEORETICAL INFORMATION

Refraction, or refraction (from the Latin refractus - refracted), is a change in the direction of straight-line propagation of light when it passes from one medium to another.

Refraction, as well as absorption, of light is the result of its interaction with the medium.

The relative refractive index $n_{relative}$. is the ratio of the speeds of light in two media:

$$n_{relative} = V_1 / V_2 .$$

where V_1 and V_2 are the speeds of light propagation in medium I and II, respectively, provided that $V_1 > V_2$.

The value of the refractive index depends on the nature of the substance, its density, the wavelength of the incident light, temperature, and pressure.

According to the laws of light refraction, when light passes from an optically less dense medium I to a medium with a higher optical density II, the angle of incidence α *is* always greater than the angle of refraction β (Fig. 5), and the following equations hold:

$$n_{relative} = \sin\alpha / \sin\beta = n_2 / n_1 .$$

where α *is the* angle of incidence of light, β *is the* angle of refraction of light,

n_1 and n_2 are the refractive indices of media I and II (Fig. 5).

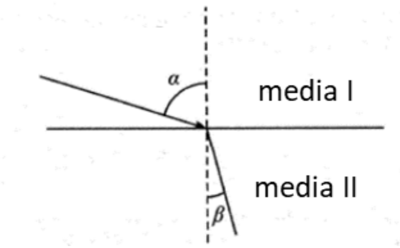


Fig. 5. Refraction of a light beam at the boundary between an optical medium (I) and another optical medium (II).

Refractometry (from Latin *refractus* - refracted and Greek *metreo* - measure) is a method of studying substances based on the determination of the refractive index and some of its functions. Refractometric analysis is used for the identification of chemical compounds, quantitative and structural analysis, and determination of physical and chemical parameters of substances.

For liquids and solids, the refractive index n *is* most often determined relative to air, and for gases, relative to vacuum.

The values of n depend on the wavelength l *of* light and temperature. For example, the refractive index at 20°C for the D-line of the spectrum of the sodium atom (l = 589.3 nm) is n_D^{20} . For gases, the pressure dependence of n must be taken into account.

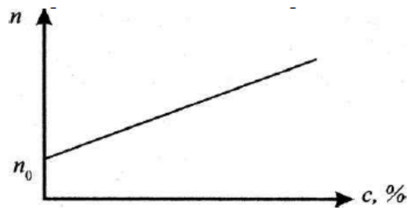
The effect of temperature on the refractive index is determined by two factors: a change in the concentration of a substance and the dependence of the polarizing bridges of molecules on temperature.

Instruments used to measure n are called refractometers. There are two main types of refractometers: Abbe refractometers and Pulfrich refractometers. Measurements of n are based on determining the value of the refractive index.

For Abbe refractometers, the main and characteristic unit is a prismatic block consisting of measuring and illuminating prisms. The measurement accuracy of the refractive index is ±(1-2-10^{-4}), the measurement limits are 1.3-1.7.

Pulfrich-type refractometers have a higher measurement accuracy ±(1-2-10^{-5}), the measurement limit is much higher - 1.9. These instruments do not have a prismatic block.

The dependence of the refractive index *n of* a homogeneous two-component system on its composition is determined experimentally by determining the refractive index for a number of standard systems in which the content of the components is known. On the basis of the data obtained, a graduation graph is constructed in the coordinates: refractive index - content.



Dependence of the refractive index on the concentration of a solute.

Knowing the refractive index of the system under study, the graph can be used to determine its concentration.

EXPERIMENTAL PART

To prepare the refractometer for operation, the prism surfaces are wiped with alcohol and distilled water and left open until completely dry. Apply 2-3 drops of distilled water to the surface of the lower prism using a pipette or glass rod without touching the glass, and close the upper prism. In the eyepiece of the viewing device, align the chiaroscuro border with the center of the grid crosshairs by rotating the adjusting mechanism. At the level of the center of the crosshairs, the refractive index of light is recorded on the lower scale (for distilled water, the refractive index is 1.330). At the end of the measurement, lift the illuminating prism and wipe both prisms with filter paper.

To construct the calibration graph n = f(C), take appropriate aliquots of the standard solution and prepare a series of solutions of concentrations 1, 2, 3, 4, 5 g/100 ml in 25 ml flasks. Bring the solutions to the mark with distilled water, mix thoroughly and leave for 15-20 minutes for homogenization.

Perform 2-3 measurements of the refractive index for each concentration, find the average value, plot it on graph paper, and construct a calibration graph of the relationship n = f(C).$_{NaCl}$

Similarly, the refractive index of the brine solution under study is measured, the corresponding concentration is found from the calibration graph, and the mass of NaCl is calculated.

QUESTIONS FOR PREPARATION

1. What is the refractometric method of analysis based on?
2. What is the refractive index, its physical meaning?
3. What parameters does the refractive index depend on?
4. Light dispersion, how does it affect the refractive index?
5. What physical phenomenon is the refractometer based on?
6. What are the main components of a refractometer and what is the principle of their operation?

Laboratory work 20
PHOTOMETRIC DETERMINATION OF IONS COPPER Cu^{2+}

Theoretical information

Photocolorimetric analysis is based on comparing the color intensity of the test solution and a standard solution of a certain concentration.

Molecular absorption methods of analysis are based on two basic laws. The first of them, the **Bouguer-Lambert** law, states that the relative amount of light absorbed by a permeable medium does not depend on the intensity of the primary radiation. Each layer of equal thickness absorbs an equal proportion of the monochromatic radiation flux.

Mathematically, this relationship is expressed in the following equation:

$$I = I_0 \cdot 10^{-kl} \text{ or } \frac{I}{I_0} = 10^{-kl},$$

where I_0 is the intensity of radiation incident on the substance;

And - the intensity of radiation that has passed through the substance;

l is the thickness of the layer through which monochromatic radiation passes;

k is the absorption coefficient.

The second law is **Beer's** law: the absorption of a radiation flux is directly proportional to the number of particles of the absorbing substance. Beer's law actually expresses the dependence of the absorption coefficient on the concentration of the absorbing substance in a homogeneous solution:

$$k = \varepsilon c,\ k = \kappa c,$$

where ε and k are proportionality coefficients.

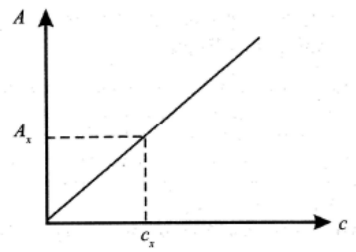
The combined **Bouguer-Lambert-Beer** law: The absorption of monochromatic light by a solution is directly proportional to the concentration of the absorbing substance and the thickness of the solution layer through which it passes.

The Bouguereau-Lambert-Beer law is the basic law of light absorption and is the basis for most photometric analysis methods. Mathematically, it is expressed as follows:

$$I = I_0 \cdot 10^{-kcl} \text{ or in logarithmic form } lg\frac{I_0}{I} = kcl.$$

The value lg I_0/I is called the optical density of the absorbing substance and is denoted by the letter *A* or *D*.

The dependence *A* - f(*c*) *is* straightforward (for monochromatic radiation fluxes).



Dependence of the optical density *A* on the concentration of the solution *c*.

The value of the absorption coefficient *k* depends on the way the concentration of a substance in solution is expressed and the thickness of the absorbing layer. If the concentration is expressed in mol/dm^3 , and the thickness of the layer is in centimeters, it is called the molar absorption coefficient (index) and is denoted by ε.

It is equal to the optical density of a solution with a concentration of 1 M and a layer thickness of 1 cm. In this case, the Bouguer-Lambert-Beer law has the form:

$$A = \varepsilon\text{-}c\text{-}b.$$

The main methods of photometric measurements are the calibration graph method, the method of comparisons, the method of additions, etc.

The method of comparison is based on the ratio of the optical density of the standard and test solutions, which are prepared and photometrically measured under the same conditions:

$$A = \varepsilon \cdot l \cdot c \; ; A_x = \varepsilon \cdot l \cdot c_x.$$

Since the values of ε and l are constant by the condition, then $c_x = \frac{A_x \cdot c}{A}$.

EXPERIMENTAL PART

The method is based on the formation of a blue complex compound by Cu^{2+} ions with an aqueous ammonia solution:

$$Cu^{2+} + 4NH_4OH \rightarrow [Cu(NH_3)_4]^{2+} + 4H_2O.$$

For the study, a standard solution of copper (II) sulfate 0.5 mg/ml is used, which is prepared by dissolving 1.9647 g of $CuSO_4 \cdot 5H_2O$ in a 1-liter volumetric flask with 5 ml of concentrated sulfuric acid.

To build a calibration graph, 1.0 - 2.0 - 3.0 - 4.0 - 5.0 ml of standard solution of copper (II) sulfate is placed in a series of 100 ml volumetric flasks, neutralized with ammonia solution (1:1) until a slight turbidity appears, then 30 ml of ammonia solution is added, brought to the mark with distilled water and mixed.

Measure the optical density of the solutions relative to distilled water in cuvettes with l = 5 cm. Based on the results of the measurements, plot a calibration graph in the coordinates: optical density (A) - concentration of Cu^{2+} (C (Cu^{2+}), mg/ml).

The test solution is analyzed according to the method described above. The concentration of copper(II) is determined graphically, and the mass of copper(II) is calculated by the formula: $m(Cu^{2+}) = C_x \cdot Vm_{.flask}$,

where m (Cu^{2+}) is the mass of Cu^{2+} [mg]; Cx is the concentration of Cu^{2+} , which is found using a calibration graph [mg/ml]; $Vm_{.flask}$ is the volume of the measuring flask [ml].

The measurement results are recorded in a table.

№ flask	$V_{standard\ solution}$, ml	C (Cu^{2+}), mg/ml	A
1			
2			
3			
4			
5			
sample		C_x =	A_x =

QUESTIONS FOR PREPARATION

1. What is the photometric method of analysis based on?
2. What optical phenomena occur when light passes through colored solutions?
3. What requirements must the solutions to be analyzed meet?
4. How is the first law of light absorption formulated?
5. How is the second law of light absorption formulated?
6. What is the principle of filter selection?
7. What is the principle of cuvette selection?
8. What parameters affect the value of ε?
9. What is the purpose of filters and photocells in a photoelectrocolorimeter?

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FOR NOTES

A-46 **Analytical chemistry [**Text]: methodical instructions for laboratory classes for applicants for the first (bachelor's) level of higher education of the educational and professional program "Food Technologies" of the field of knowledge 18 Production and Technologies, specialty 181 Food Technologies full-time and part-time forms of study / compiled by. I. A. Moroz - Lutsk: Lutsk NTU, 2023. 72 p.

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