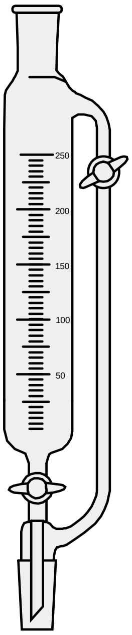
MINISTRY OF HEALTHCARE OF UKRAINE
PIROGOV VINNYTSYA NATIONAL MEDICAL UNIVERSITY

THE PHARMACEUTICAL CHEMISTRY CHAIR

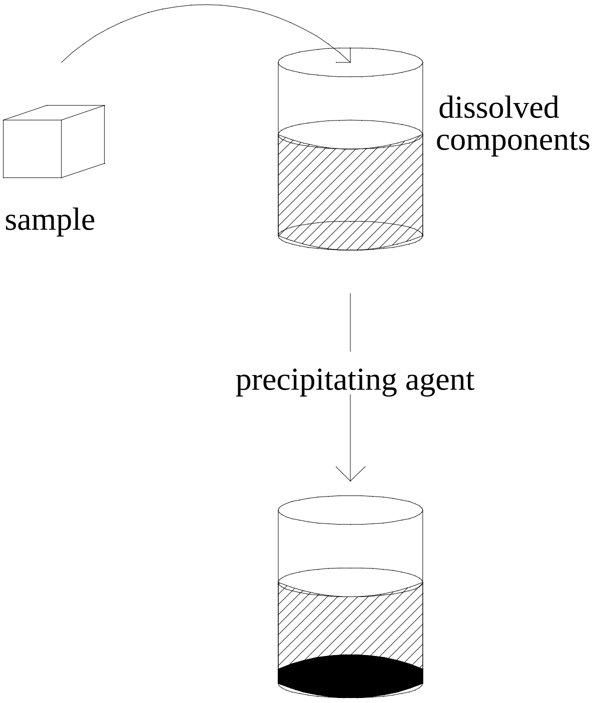


Analytical chemistry

Part I

Qualitative analysis

**Educational manual is prepared for foreign students
of the pharmaceutical faculty**



Vinnytsya 2012

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The educational manual to practical classes in analytical chemistry for foreign students of the pharmaceutical higher school and the pharmaceutical faculties of the III-IV levels of “Quantitative analysis” accreditation.

Introduction

The analytical chemistry is one of the fundamental chemical disciplines, which is the basis for the subsequent study of such core of disciplines as pharmaceutical chemistry, pharmacognosicy, forensic chemistry, technology of drugs, etc. for future specialists in pharmacy.

Analytical Chemistry is the science of the methods for studying the composition of material. It consists of two basic divisions: qualitative analysis (what is present) and quantitative analysis (how much is present).

The aim of analytical chemistry teaching is creating the theoretical basis of chemical analysis for the students and also practical skills and experience of making it.

The given manual for practical classes in analytical chemistry is intended for self-preparation of students for practical classes, carrying-out the experiment.

Each topic includes:

- brief exposition of theoretical material which accentuates student’s attention on the topic’s base position;
- laboratory work which reveals the possibilities of analytical methods learning information facts;
- control tasks for each topic which help to check the degree of material learning.

The manual consists of three parts:

- qualitative analysis;
- quantitative analysis;
- instrumental methods of analysis.

The first part “Qualitative analysis” contains descriptions of analytical reactions for detection cations and anions which are present in drugs.

TOPIC PLAN OF LECTURES
Specialitys “Pharmacy” and “Clinical pharmacy”

№	Theme of lectures	Number of hours
1	2	3
1.	Analytical chemistry and chemical analysis. Qualitative and quantitative analysis. Methods of qualitative analysis and their classification. Analytical reactions and requirements to them. Classification of ions.	2
2.	The mass action law in the heterogenius systems. Solubility of substances in water. Ions equilibrium between the substance in its solid and dissolved forms liquid. Ion product, solubility product, activity product. Conditions of precipitate formation. Influence of difference substances on precipitate solubility.	2
3.	The mass action law in the homogenous systems (equilibrium in buffer solutions and salts which hydrolyze).	2
4.	The mass action law in the homogenous systems (complex compounds). Masking ions which interrupt. Organic reagent in qualitative analysis.	2
TOTAL OF MODULE 1		8

TOPIC PLAN OF PRACTICAL LESSONS
Speciality “Pharmacy”

№	Theme of practical lessons	Number of hours
1	2	3
1.	Rules of safety appliance in chemical laboratory. Acidic-basic classification of cations. Characteristic reactions of the I analytical group cations and condition of their detection. The analysis of a mix of the I analytical group cations. *Laboratory experiment.* Problem solving: “Test sensitivity. Reaction’s specificity and selectivity”.	4
2.	Group reagent for the II analytical group cations. Characteristic reactions of the II analytical group cations and condition of their detection. The analysis of a mix of the II analytical group cations. *Laboratory experiment.* Problem solving: “Ionization theory”.	4

1	2	3
3.	Group reagent for the III analytical group cations. Characteristic reactions of the III analytical group cations and condition of their detection. The analysis of a mix of the III analytical group cations. *Laboratory experiment.* Problem solving: “Solubility equilibria. Solubility – product constant for a sparingly soluble salt”.	4
4.	Tests on analysis of I-III analytical groups cations. The analysis of a mix of I-III analytical groups cations.	4
5.	Control experimental task of a mix of I-III analytical groups cations. Comprehensive check of thematic module 1.	4
6.	Group reagent for the IV analytical group cations. Characteristic reactions of the IV analytical group cations and condition of their detection. The analysis of a mix of the IV analytical group cations. *Laboratory experiment.* Problem solving: “Acid – base equilibria. Salt’s hydrolysis and buffer solution’s”.	4
7.	Group reagent for the V analytical group cations. Characteristic reactions of the V analytical group cations and condition of their detection. The analysis of a mix of the V analytical group cations. *Laboratory experiment.* Problem solving: “Oxidation-reduction equilibria”.	4
8.	Group reagent for the VI analytical group cations. Characteristic reactions of the VI analytical group cations and condition of their detection. The analysis of a mix of the VI analytical group cations. *Laboratory experiment.* Problem solving: “Complex ion equilibria”.	4
9.	Tests on analysis of cations of IV-IV analytical groups. The analysis of a mix of cations of IV-IV analytical groups.	4
10.	Control experimental task of a mix of I-III analytical groups cations. Comprehensive check of thematic module 2.	4
11.	Characteristic reactions of the I-III analytical group anions and condition of their detection. *Laboratory experiment.*	4
12.	Characteristic reactions of the organic acids anions and condition of their detection. The analysis of a mix of the anions. *Laboratory experiment.*	4
13.	Mixture analysis of unknown composition. Comprehensive check of thematic module 3.	2
14.	Comprehensive check of module 1. Qualitative analysis.	4
TOTAL OF MODULE 1		56

TOPIC PLAN OF PRACTICAL LESSONS
Speciality “Clinical pharmacy”

№	Theme of practical lessons	Number of hours
1	2	3
1-2.	Rules of safety appliance in chemical laboratory. Acidic-basic classification of cations. Characteristic reactions of the I analytical group cations and condition of their detection. The analysis of a mix of the I analytical group cations. *Laboratory experiment.* Problem solving: “Reaction’s specificity and selectivity”, “Ionization theory”.	4
3.	Group reagent for the II analytical group cations. Characteristic reactions of the II analytical group cations and condition of their detection. The analysis of a mix of the II analytical group cations. *Laboratory experiment.*	2
4.	Group reagent for the III analytical group cations. Characteristic reactions of the III analytical group cations and condition of their detection. The analysis of a mix of the III analytical group cations. *Laboratory experiment.* Problem solving: “Solubility equilibria. Solubility – product constant for a sparingly soluble salt”.	2
5.	Group reagent for the IV analytical group cations. Characteristic reactions of the IV analytical group cations and condition of their detection. The analysis of a mix of the IV analytical group cations. *Laboratory experiment.* Problem solving: “Acid – base equilibria”.	2
6.	Group reagent for the V analytical group cations. Characteristic reactions of the V analytical group cations and condition of their detection. The analysis of a mix of the V analytical group cations. *Laboratory experiment.* Problem solving: “Oxidation-reduction equilibria”.	2
7.	Group reagent for the VI analytical group cations. Characteristic reactions of the VI analytical group cations and condition of their detection. The analysis of a mix of the VI analytical group cations. *Laboratory experiment.* Problem solving: “Complex ion equilibria”.	2
8.	Characteristic reactions of the I-III analytical group anions and condition of their detection. *Laboratory experiment.*	2
9.	Mixture analysis of unknown composition. Comprehensive check of module 1.	2
Comprehensive check of module 1.		2
TOTAL OF MODULE 1		20

Part I
Qualitative analysis

Many problems in analytical chemistry begin with the necessity of identifying what is present in a sample. This is the scope of a qualitative analysis.

The qualitative analysis is a process for identification of a substance, which allows to determine what chemical elements are included into the sample tested, what ions, functional groups or molecules are in its composition.

Although modern analytical chemistry is dominated by sophisticated instrumentation, the roots of analytical chemistry and some of the principles used in modern instruments are taken from traditional techniques many of which are still used nowadays.

The classical laboratory courses in inorganic and organic qualitative analysis are based on chemical tests to identify inorganic ions (cations and anions) and organic functional groups.

The characteristic qualitative analytical reactions are used in the chemical methods of the qualitative analysis. They are characterized by the certain external reactions: precipitates forming of with a certain colour in solutions, colour changes in solution or alloy, elimination of evolving gaseous products without odour or with a certain odour, etc. Substance, which is used for carrying out a qualitative analytical reaction, is called a reagent.

The chemical methods are characterized by high selectivity, simple performance, reliability but their sensitivity is not high: 10^{-5}-10^{-6} mol/dm^3. In the cases when higher sensitivity is needed, the physical or physico-chemical (instrumental) methods of analysis are used.

Carrying out the qualitative analysis the certain weight of the sample is needed. Depending on the taken value for sample analysis the methods are divided into macro- (0.5-l.0g of substance or 20-50 cm^3 of solution are used), semimicro- (0.01-0.10 g of dry substance or 0.5-5.0 cm^3 of solution are used), micro- (0.010-0.00l g of substance and 0.05-0.50 dm^3 of solution are used) and ultramicromethods of the qualitative analysis.

The semimicroanalysis is more frequently used in the analytical practice. The analytical reactions are carried out with the help of dropping bottles. The separation of the solid and liquid phases is performed by centrifuge.

The methods of performing analytical reactions

Analytical reactions are performed by dry or wet method. In the first case tested the sample tested and the analytical reagent are taken in a solid state and they are subjected to heating at high temperature. They are:

- Flame test – the test involves introducing a sample of the element or compound to hot, non-luminous flame, and observing the colour that appears in result;

- Bead test – the reactions for borax bead formation – sodium tetraborate $Na_2B_40_7 \cdot 10H_20$ on heating combines readily with a number of coloured transition metal oxides such as Co, Ni, Cr, Cu, Mn, etc. to form the corresponding metaborates(glassy mass) which possess characteristic colours;

- the reactions of caking with some dry reagents (Na_2CO_3, $KClO_3$, KNO_3) for obtaining the characteristically coloured products.

The reactions performed by the dry method are usually used in the preliminary tests.

The reactions performed by the wet method are the main ones in the qualitative analysis. They are accompanied by an external effect: changing of the solution coloration, the forming or dissolving the precipitation, evolving of gas.

Conditions of the analytical reactions

While performing the analytical reaction in the qualitative analysis one should keep the following requirements:

- creation and maintenance of a certain value of pH solution in the reaction;
- creation of a certain concentration the reactants.

One of the important requirements to the analytical reactions is their high sensitivity.

The sensitivity of a reaction is the least concentration of ions, which can be found with the help of this reaction in the definite conditions of its performance.

The sensitivity of the analytical reaction depends on the conditions of its performance: pH medium, solution ion strength, the presence of side-reactions, etc.

For increasing the sensitivity of reactions the concentration of the substance in the solution is increased, more often by evaporation.

The analytical reactions used in the qualitative analysis are divided into specific and selective ones.

The specificity characterizes the ability to detect the presence of an unknown element in the presence of other elements.

Specific reactions give an analytical effect only with one individual substance. A specific reaction on the definite ions allows to determine these ions in the conditions of the experiment in the presence of other ions without their preliminary separation. For example, specific reaction on NH_4^+-ions is their interaction with alkaline solutions while heating. Ammonium evolved is determined by its odour or by the colour change of a wet red litmus paper:

$$NH_4^+ + OH^- \xrightarrow{t} NH_3\uparrow + H_2O$$

The reaction, which gives identical or similar analytical effect in the presence of the limited number of ions, is called as a non-specific or **selective** one.

There are a few specific reactions in the qualitative analysis, that’s why selective or non- specific reactions are more often used.

According to this there are two methods of the qualitative analysis, they are fractional and systematic.

In the **fractional analysis** the composition of the analyzed sample is determined by the specific reactions in delimited conditions. The performance of the fractional analysis is carried out in two stages: at first, the influence of the components impeding is removed by different reactions and then the determined ions are detected.

The **systematic course of the analysis** is that complex mixture of ions is separated by the so-called group reactants into some separate groups. Then individual ions are detected in the range of each of these groups by the definite characteristic reactions. Thus, the ions are divided into groups and detected in every group in a definite consequence.

Laboratory Safety and Work Instructions

Your personal laboratory safety
depends mostly on YOUSELF!

All students must read and understand the information in this document with regard to laboratory safety and emergency procedures prior to the first laboratory session. Effort has been made to address situations that may pose a hazard in the lab but the information and instructions provided cannot be considered all-inclusive.

Students must adhere to written and verbal safety instructions throughout the academic term.

With good judgement, the chance of an accident in this course is very small. Nevertheless, research and teaching workplaces are full of potential hazards that can cause serious injury and or damage to the equipment.

Personal and General laboratory safety

1. Never eat, drink, or smoke while working in the laboratory.
2. Read the labels carefully.
3. Do not use any equipment unless you are trained.
4. Wear safety glasses or face shields when working with hazardous materials and/or equipment.
5. Wear gloves when using any hazardous or toxic agent.
6. Clothing: When handling dangerous substances, wear gloves, laboratory coats, and safety shield or glasses. Shorts and sandals should never be worn in the lab.
7. If you have long hair or loose clothes, make sure it is tied back or confined.
8. Keep the work area clear of all materials except those needed for your work. Coats should be hung in the hall or placed in a locker. Extra books, purses, etc. should be kept away from the equipment that requires air flow or ventilation to prevent overheating.
9. Disposal - Students are responsible for the proper disposal of used material if any in appropriate containers.
10. Equipment Failure - If a piece of equipment fails while being used, report it immediately to your lab assistant or tutor. Never try to fix the problem yourself because you could harm yourself and others.
11. If leaving a lab unattended, turn off all ignition sources and lock the doors.
12. Never pipette anything by mouth.
13. Clean up your work area before leaving.
14. Wash hands before leaving the lab and before eating.

Electrical safety

1. Obtain permission before operating any high voltage equipment.
2. Maintain an unobstructed access to all electrical panels.
3. Avoid using extension cords whenever possible. Extension cords should not go under doors, across aisles, be hung from the ceiling, or plugged into other extension cords.
4. Never, ever modify, attach or otherwise change any high voltage equipment.
5. When you are adjusting any high voltage equipment or a laser which is powered with a high voltage supply, USE ONLY ONE HAND. Your other hand should be placed in a pocket or behind your back. This procedure eliminates the possibility of an accident where high voltage current flows up one arm, through your chest, and down the other arm.

Chemical safety

1. Treat every chemical as if it were hazardous.
2. Make sure all chemicals are clearly and currently labeled with the substance name, concentration, date, and name of the individual responsible.
3. Never return chemicals to reagent bottles. (Try for the correct amount and share any excess.)
4. Use volatile and flammable compounds only in a fume hood.
5. Never allow a solvent to come in contact with your skin. Always use gloves.
6. Never "smell" a solvent!! Read the label on the solvent bottle to identify its contents.
7. Dispose of waste and broken glassware in proper containers.
8. Clean up spills immediately.
9. Do not store food in laboratories.

Handling liquid chemicals

Take an appropriate container to the reagent shelf. Avoid measuring volumes of strong acids and alkaline solutions with your graduated cylinder held at eye level. Support your graduated cylinder on your bench. Add hazardous liquids a little at a time, inspecting after each addition.

Reagent in dropper bottle

If the general supply bottle is equipped with a dropper, use it, but be sure that the dropper never touches your container or the contents in it. Never put it down on the bench top, but return it immediately the right reagent bottle.

Reagent in a stopper bottle

If the general supply bottle is equipped with a stopper, the stopper should either be held during the transfer or placed on its flat top. Do not lay the stopper on its side on the bench top. Pour chemicals from the general supply bottle into your container. Be sure that the proper stopper is returned to the supply bottle; do not interchange stoppers.

Mixing

If liquid chemicals are to be mixed with water, always add the concentrated chemical to water rather than water to chemical. This keeps the new solution dilute at all times and avoids many accidents. Usually addition should be done slowly, using small quantities. It is especially important to add acid to water because of the heat generated.

Pipetting

Liquids are drawn into the pipette by applying a slight vacuum at the top, using a small rubber suction bulb but NEVER THE MOUTH. Use pipette fillers.

Heating

Liquids in beakers and flasks can be heated by placing them on a ring or tripod stand on wire gauze with the container preferably supported by a clamp. Liquid should never be heated in a graduated cylinder or in other columetric glassware.

Disposal

Check with your laboratory instructor before disposing of any chemicals down the drain. If the liquid chemical can be disposed of in the sink, dispose of it by rinsing it down the sink with large amounts of water. Avoid unnecessary splashing during this process by pouring the chemical directly down the drain while the water is running vigorously.

Handling solid chemicals

Take an appropriate container to the reagent shelf where the general supply is kept. Solids are somewhat more difficult to transfer than are liquids, so a wide-mouthed container such as a beaker is preferable.

During the transfer, hold the stopper or lay it on the bench without contaminating the stopper. Solid chemicals are most easily poured by tipping the general supply bottle and slowly rotating it back and forth. Mere tipping of the bottle alone often causes large chunks to come out very suddenly which leads to spills. If you use your own spatula, be sure that it is absolutely clean. Return the proper stopper to the general supply bottle; do not interchange stoppers.

Mixing

If the solid is to be mixed with a liquid, add the solid to the liquid. Additions should be made in small amounts except for the special circumstances.

Disposal

If the laboratory instructor directs you to dispose of any solid chemicals in the sink, flush it down the drain with copious amounts of running water. All other solids should be disposed of in special containers provided for this purpose.

Chemical spills in the laboratory

In all cases, immediately warn your group-mates and the laboratory instructor of the spill. Locate spill cleanup materials. Laboratories should be equipped with spill cleanup kits. Wear the appropriate personal protective equipment (e.g., gloves, goggles) when cleaning up spills.

Non volatile and non flammable materials

If the material is not particularly volatile, nor toxic, and poses, no fire hazard the liquid can be cleaned up by using an absorbent material which neutralizes them, for example, sodium bicarbonate solution or powder for acids, or sodium thiosulfate solution for bromine. Rubber or plastic gloves should be worn while using absorbent materials. A dustpan and brush should be used to remove the absorbent material. Then, the contaminated area should be cleaned with detergent and water and the area mopped dry.

Volatile, flammable and toxic spill materials

Warn everyone in the laboratory to extinguish flames, disconnect spark-producing equipment, shut down all experiments, and evacuate the laboratory. The laboratory instructor and safety personnel will handle the cleaning up.

Acid Spills

Apply neutralizer (or sodium bicarbonate) to perimeter of spill. Mix thoroughly until fizzing and evolution of gas ceases. NOTE: It may be necessary to add water to the mixture to complete the reaction. Neutralizer has a tendency to absorb acid before fully neutralizing it. Check mixture with pH indicator paper to assure that the acid has been neutralized.

Put the mixture into a plastic bag, tie shut, fill out a waste label, and place it in the fume hood. Inform the supervisor.

Caustic Spills

Apply neutralizer to perimeter of spill. Mix it thoroughly until fizzing and evolution of gas ceases. Check the mixture with pH indicator paper to assure that the material has been completely neutralized.

Put the mixture into a plastic bag, tie shut, fill out a waste label, and place it in the fume hood. Inform the supervisor.

Solvent Spills

Apply activated charcoal to the perimeter of the spill. Mix thoroughly until material is dry and no evidence of liquid solvent remains.

Put the absorbed solvent into a plastic bag (if compatible), tie shut, fill out and attach a waste label, and place it in the fume hood. Inform the supervisor.

Mercury Spills

Using a mercury vacuum, vacuum all areas where mercury was spilled with particular attention to corners, cracks, depressions and creases in flooring or table tops.

Clean up small spills with a mercury spill kit, dampen the mercury sponge with water, then wipe the contaminated area. Do this procedure slowly to allow for complete absorption of all free mercury. A silvery surface will form on the sponge.

Put the contaminated sponge in its plastic bag, tie shut, fill out and attach a waste label, and place it in the fume hood.

Chemical spills on a person

Over the body

Within seconds, quickly remove all contaminated clothing while person is under safety shower. Rinse the affected body area with cold water for at least fifteen minutes. If pain continues or resumes, rinse it with a larger amount of water. Wash off chemicals with a mild detergent solution. Do not apply any materials such as neutralizing agents or salves, to the area. Obtain medial assistance immediately.

On small area of body

Immediately rinse the area thoroughly with cold water. Wash with mild detergent solution. If there is no visible burning, wash out the area with warm water and soap.

In the eyes

You will need to assist the person who has chemicals spattered in the eyes. Immediately drench the eyes at the nearest emergency eyewash station. Force the eye or eyes open to get water into them. The speed of your response to this emergency is extremely important. Inform the laboratory instructor of the accident immediately.

Swallowing chemicals

The laboratory instructor should determine what specific substance is ingested.

The person should be forced to drink copious amounts of water while en route to medical assistance. The Health Center or Hospital should be informed while the person is in transit as to what chemicals are involved.

Burns

For burns by hot objects, flames or chemical, rinse the affected area with cold water for several minutes. Inform the laboratory instructor of the burning and he will arrange transportation to the infirmary if necessary.

Injury or illness

Render assistance if necessary. For minor cuts, wash them thoroughly, apply a good antiseptic, and a band-aid. For major cuts, severe bleeding or serious illness, send someone for help and administer first aid. Only a physician is trained to treat serious injury or illness. Inform the instructor immediately.

Additional Safety Guidelines

- Never do unauthorized experiments.
- Never work alone in laboratory.
- Keep your lab space clean and organized.
- Do not leave an on-going experiment unattended.
- Always inform your instructor if you break a thermometer. Do not clean mercury yourself!!
- Never taste anything. Never pipette by mouth; use a bulb.
- Never use open flames in laboratory unless instructed by TA.
- Check your glassware for cracks and chips each time you use it. Cracks could cause the glassware failure during usage and cause serious injury to you or lab mates.
- Maintain unobstructed access to all exits, fire extinguishers, electrical panels, emergency showers, and eye washes.
- Do not use corridors for storage or work areas.
- Do not store heavy items above table height. Any overhead storage of supplies on top of cabinets should be limited to lightweight items only. Also, remember that a 36" diameter area around all fire sprinkler heads must be kept clear at all times.
- Areas containing lasers, biohazards, radioisotopes, and carcinogens should be posted accordingly. However, do not post areas unnecessarily and be sure that the labels are removed when the hazards are no longer present.

- Be careful when lifting heavy objects. Only shop staff may operate forklifts or cranes.
- Clean your lab bench and equipment, and lock the door before you leave the laboratory.

Qualitative analysis of cations

Qualitative analysis of inorganic compounds allows to determine a composition both individual inorganic substances and their mixtures. The majority of nonorganic compounds are electrolytes and behave as ions in water solutions. According to that the qualitative analysis of inorganic compounds is divided into the cations and anions analysis.

According to their properties, cations are classified into groups.

Each group has a common reagent which can be used to separate them from the solution. To obtain meaningful results, the separation must be done in the certain sequence, as some ions of an earlier group may also react with the reagent of a later group, causing ambiguity as to which ions are present.

There are some methods of cations analysis systematic course: hydrogen-sulphidous, ammoniac-phosphate, acid-base etc.

Table 1

Cations classification by sulfur-hydrogen method

Group	Cations	Group reactant	Compounds solubility
I	K^+, Na^+, NH_4^+, Mg^{2+}	No	Sulphides, carbonates, chlorides and hydroxides, are dissolved in water
II	Ba^{2+}, Sr^{2+}, Ca^{2+}	$(NH_4)_2CO_3$, $NH_3 \cdot H_2O+NH_4C1$, pH = 9,25	Carbonates not dissolved in water
III	Fe^2, Fe^{3+}, Cr^{3+}, AI^{3+}, Mn^{2+}, Ni^{2+}, Zn^{2+},Co^{2+}	$(NH_4)_2S$, $NH_3 \cdot H_2O+NH_4C1$, pH = 9,25	Sulphides are not dissolved in water, but are dissolved in diluted acids
IV	Cu^{2+}, Hg^{2+}, Bi^{3+}, Sn^{2+}, Sn (IV), Sb (III), Sb (V), As (III), As (V)	H_2S, HC1, pH = 0,5	Sulphides, are not dissolved in water and diluted acids
V	Ag^+, Pb^{2+}, Hg_2^{2+}	HC1	Chlorides, are not dissolved in water and diluted acids

Table 2

Cations classification by ammoniac-phosphate method

Group	*Cations*	*Group reactant*	*Compounds solubility*
I	Ag^+, Pb^{2+}, Hg_2^{2+}	HC1	Chlorides, are not dissolved in water
II	Sn^{2+}, Sn (IV), Sb (III), Sb (V)	HNO_3	Metantimony and metatin acids, are not dissolved in water
III	Ba^{2+}, Sr^{2+}, Ca^{2+}, Mg^{2+}, Mn^{2+}, Fe^{2+}, Al^{3+}, Cr^{3+}, Fe^{3+}	$(NH_4)_2HPO_4$, concentrated $NH_3{\cdot}H_2O$	Phosphates, are not dissolved in water and ammonia excess
IV	Cu^{2+}, Cd^{2+}, Hg^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}	$(NH_4)_2HPO_4$, concentrated $NH_3{\cdot}H_2O$	Phosphates, are not dissolved in water, but are dissolved in ammonia excess
V	Na^+, K^+, NH_4^+	No	Chlorides, nitrates and phosphates, are dissolved in water

Table 3

Cations classification by acid-base method

Group	*Cations*	*Group reactant*	*Compounds solubility*
I	Na^+, K^+, NH_4^+	No	Chlorides, sulphates and и hydroxides, are dissolved in water
II	Ag^+, Pb^+, Hg_2^{2+}	HC1	Chlorides, are not dissolved in water
III	Ba^{2+}, Sr^{2+}, Ca^{2+}	$H_2SO_4 + C_2H_5OH$	Sulphates, are not dissolved in water
IV	Al^{3+}, Zn^{2+}, Cr^{3+}, Sn (II), Sn (IV), As (III), As (V)	Excess of concentrated NaOH + 3% H_2O_2	Hydroxides are not dissolved in water, but are dissolved in alkali excess
V	Fe^{2+}, Fe^{3+}, Mg^{2+}, Mn^{2+}, Bi^{3+}, Sb (III), Sb (V)	Excess of concentrated $NH_3{\cdot}H_2O$	Hydroxides, are not dissolved in water, alkali and ammonia excess
VI	Co^{2+}, Ni^{2+}, Cd^{2+}, Cu^{2+}, Hg^{2+}	Excess of concentrated $NH_3{\cdot}H_2O$	Hydroxides, are not dissolved in water, caustic soda solution excess, but are dissolved in ammonia excess

In the manual the qualitative cations analysis is described by acid-base method on the example of ions which are the most frequently make up medicinal preparations or reactants used in the pharmaceutical analysis.

Module 1.Qualitative analysis

The specific objectives:

Learn and perform qualitative reactions of cations I-VI analytical groups (acid-base classification). Pay attention to the reaction, which State Pharmacopoeia of Ukraine applies to confirm quality and purity of drugs. Examine and make specific reactions of anions I-III analytical groups and pharmacopoeias analytical reaction.

Study the features of the analysis of anions by fractional method, the reaction for detection of the anions-oxidants, anions-reductions, the anions of volatile acids. Identify the reasons and learn a systematic course of analysis for selected groups of anions. Justify the need to perform analytical operation "soda extraction" before the analysis of anions.

Learn the basic principles of the strong electrolyte solutions theory: analytical ion concentration, activity, the relationship between them; ionic strength. Weak electrolytes: the constant of ionization; the relationship between degree of dissociation and constant of ionization; equilibrium in water, the ionic product of water, pH.

Learn different types of chemical equilibrium in analytical chemistry:

- heterogeneous (sediment - a saturated solution); solubility; the solubility product constant; criteria for precipitation; fractional precipitation;
- homogeneous – acid-base equilibrium in buffer solution, solutions of salts which hydrolyze and solutions of amphoteric compounds; calculating pH of buffer solutions and solutions of different types of salt; the degree and constant of hydrolysis;
- homogeneous – the redox equilibrium in analytical chemistry; redox potentials (normal, real or equilibrium, formal); Nernst equation; electromotive force and direction of redox reactions;
- homogeneous – the equilibrium of complex formation reactions; constant of instability; formation constant; calculating the equilibrium concentrations of ions in solutions of complex compounds

Explain the role of different types of chemical equilibrium and their application in analytical chemistry and chemical analysis.

Topic 1
Chemistry of the Ist Group Cations
Analysis systematic course of the Ist analytical group cations

1. The main purpose of the topic:

Chemical compounds of the first analytical group cations are widely used in medical practice. For example, a 0.9% aqueous solution of sodium chloride (isotonic solution) was used to maintain blood plasma volume. Sodium bicarbonate is used to maintain acid-base balance. Potassium chloride is a drug that is used to cure arrhythmias. Potassium iodide is a source of iodine when it is deficient in the body. Ammonia solution 10% is used for breathing stimulation. Ammonia chloride is used as a diuretic for cordial hypostases healing.

Introduction to the qualitative reactions of the 1st analytical group cations will allow future professionals to identify drugs that contain these cations, as well as help in the further study of relevant disciplines: pharmaceutical chemistry, pharmacology, technology of medicine, etc.

2. Basic questions:

2.1. The first analytical group cations (acid – base classification), general characteristic.
2.2. Characteristic reactions of K^+ cations.
2.3. Characteristic reactions of Na^+ cations.
2.4. Characteristic reactions of NH_4^+ cations.
2.5. The analysis of a mix of the Ist analytical group cations.

3. Brief exposition of theoretical material:

General characteristic of the Ist analytical group cations K^+, Na^+, NH_4^+

The cations of the following alkaline metals such as potassium, sodium and also complex ammonium ion belong to the first analytical group. The composition of Na^+ and K^+ electron shells are similar to the composition of electron shells of inert gases atoms Ar and He respectively. The polarizing ability of these cations is small, because they have large radii. Chemical properties of NH_4^+ ion are close to potassium ions, as their ionic radii are very close. K^+, Na^+, NH_4^+ form compounds with ionic type of chemical bound and most of them are readily dissolved in water. Therefore I analytical group cations have no group reactant. Na^+ and K^+ ions are stable to action of oxidizers and regenerators.

K^+, Na^+ and NH_4^+ hydrotised ions are colourless. Salts of these ions have colour, if there are painted anions in their composition. For example, Na_2CrO_4 is yellow, $KMnO_4$ is violet.

K^+ and Na^+ compounds easily form oversaturated solutions. That is why for crystallization acceleration of their precipitates it is necessary to rub the inner wall of a test tube, where the reaction proceeds, with a glass stick.

4. Control test and patterns of responses:

4.1. Please, choose a reagent that can help you to detect potassium cations in solution of a sample:

a) tartaric acid ($H_2C_4H_4O_6$);

b) hexahydroxoantimonate (V) potassium ($K[Sb(OH)_6]$);

c) the Nessler's reagent ($K_2[HgI_4]$ + KOH).

Answer:

Tartaric acid: Potassium can be precipitated from aqueous solution as white precipitate by addition of the reagent tartaric acid $H_2C_4H_4O_6$ and sodium acetate:

$$CH_3COO^- + H_2C_4H_4O_6 \rightarrow CH_3COOH + HC_4H_4O_6^-$$

$$HC_4H_4O_6^- + K^+ \rightarrow KHC_4H_4O_6\downarrow \quad \mathrm{pH} = 7$$

Ammonium ions interfere with this test. Ammonium ions can be precipitated from aqueous solution as white precipitate by addition of the reagent tartaric acid $H_2C_4H_4O_6$ and sodium acetate too.

5. Tasks for homework (write in a textbook for protocols):

5.1. Why do cations of the Ist analytical group have no group reagent?

5.2. Suggest a specific reaction to identify ammonium ions. Why is this reaction specific?

5.3. Why do you need to remove ammonium cations from a solution prior to the detection of cations K^+ and Na^+?

5.4. Write the scheme for separation and identification ions in the following sample solutions that contains:

- K^+, NH_4^+, H^+;
- Na^+, NH_4^+, OH^-;
- Na^+, K^+, OH^-.

The situation tasks are solved according to the systematic analysis of the Ist analytical group cations mixture.

6. Laboratory experiment

Laboratory experiment 1.1.

Characteristic reactions of the Ist analytical group cations and condition of their detection

Potassium (K^+) ions reactions

1. Reaction with tartaric acid $H_2C_4H_4O_6$

Potassium can be precipitated from aqueous solution as white precipitate by adding the reagent tartaric acid $H_2C_4H_4O_6$ and sodium acetate:

$$CH_3COO^- + H_2C_4H_4O_6 \rightarrow CH_3COOH + HC_4H_4O_6^-$$

$$HC_4H_4O_6^- + K^+ \rightarrow KHC_4H_4O_6\downarrow \quad \text{white} \quad \mathrm{pH}=7$$

$KHC_4H_4O_6$ soluble in the strong acids and bases:

$$KHC_4H_4O_6\downarrow + H^+ \rightarrow K^+ + H_2C_4H_4O_6$$

$$KHC_4H_4O_6\downarrow + OH^- \rightarrow K^+ + C_4H_4O_6^{2-} + H_2O$$

Ammonium ions interfere with this test.

Procedure: Pour 3-5 drops of potassium salt aqueous solution into a small test tube; add 3 drops of tartaric acid and sodium acetate and rub the inner wall side of test tube by a glass stick. Soon white crystalline precipitate will be formed. Divide the precipitate into two test tubes and dissolve the first part of the precipitate in acid and the second part in base.

2. Reaction with sodium hexanitrocobaltate (III) $Na_3 [Co(NO_2)_6]$

Potassium can be precipitated from aqueous solution as yellow precipitate by adding of the reagent sodium hexanitrocobaltate (III) $Na_3[Co(NO_2)_6]$:

$$2K^+ + Na_3[Co(NO_2)_6] \rightarrow NaK_2[Co(NO_2)_6] \downarrow + 2Na^+ \quad \text{yellow} \quad pH=7$$

The precipitate is dissolved in mineral acids with formation of unstable acid $H_3[Co(NO_2)_6]$ at $pH < 4$:

$$NaK_2[Co(NO_2)_6] \downarrow + 3H^+ \rightarrow 2K^+ + Na^+ + H_3[Co(NO_2)_6]$$

Alkalis decompose the reactant with brown precipitate $Co(OH)_3\downarrow$ formation $pH>7$:

$$[Co(NO_2)_6]^{3-} + 3OH^- \rightarrow Co(OH)_3\downarrow + 6NO_2^- \quad \text{brown}$$

Ammonium ions interfere with this test. We should prepare breezy solution of hexanitrocobaltate (III) sodium because this reagent can be decomposed in time.

Procedure: Pour 3-5 drops of the potassium salt into a small test tube, add 3 drops of hexanitrocobaltate (III) sodium $Na_3[Co(NO_2)_6]$.

3. Flame painting reaction

Potassium salts give a characteristic violet colour to the flame; the test is very sensitive.

Procedure: The flame test for potassium is very sensitive, and traces of potassium ion will give characteristic violet colour to the flame. Just about every solution has a trace of potassium and thus will give a positive result. For performing the flame test, obtain a piece of platinum or Nichrome wire that has been sealed in a piece of glass tubing. Clean the wire by clipping it in 12 M HC1 that is contained in a small test tube and heat the wire in the hottest part of your Bunsen burner flame. Repeat this operation until no colour is seen when the wire is placed in the flame. Several cleanings will be required before this is achieved. Then pour 10 drops of the solution to be analyzed into a clean test tube and perform a flame test on it. If the sample being tested is unknown to you, run a flame test with distilled water and then another with 0.2M KCl solution.

Sodium (Na^+) ions reactions

1. Reaction with potassium hexahydroxoantimonate (V) $K[Sb(OH)_6]$

Sodium can be precipitated from aqueous solution as white precipitate by addition of the reagent potassium hexahydroxoantimonate (V) $K[Sb(OH)_6]$:

$$Na^+ + [Sb(OH)_6]^- \rightarrow Na[Sb(OH)_6]\downarrow \quad pH=7 \quad \text{white}$$

The pH of the solution must be neutral (pH=7)

The cooling of the solution and rubbing the inner wall of test tube with a glass stick assists the formation of precipitate Na[Sb(OH)$_6$]. In strongly alkaline media the precipitate does not form.

In acid media the reactant decomposes with formation of white amorphous precipitate of metantimony acid HSbO$_3$:

$$[Sb(OH)_6]^- + H^+ \rightarrow H[Sb(OH)_6]$$

$$H[Sb(OH)_6] \rightarrow HSbO_3\downarrow + 3H_20$$

Which by mistake can be taken as precipitate of Na[Sb(OH)$_6$].

Ammonium and magnesium ions interfere with this test reaction because of ions NH$_4^+$ hydrolysis the media becomes acid, therefore the reactant destroys with formation of HSbO$_3$.

2. Reaction with zink threeuranil octaacetictate (Mikrokristalloskopic)

Sodium can be precipitated from aqueous solution as yellow crystalline precipitate by addition of the reagent zink threeuranil octaacetictate in acetic acid:

$$Na^+ + Zn\left[(UO_2)_3(CH_3COO)_8\right] + CH_3COO^- + 9H_2O \rightarrow NaZn\left[(UO_2)_3(CH_3COO)_9\right]\cdot 9H_2O$$

The reaction is carried out on a glass slide. In 2-3 min. observe the formation of yellow octahedral and tetrahedral crystals by the microscope.

3. *Flame painting reaction*

The flame test for sodium is very sensitive, and traces of sodium ion will give acharacteristic yellow colour to the flame. Just about every solution has a trace of sodium and thus will give a positive test. On the basis of the intensity and duration of the yellow colour, you can decide whether Na$^+$ is merely a contaminant or present in substantial quantity. Using a clean wire, perform a flame test on your original (untreated) unknown. To help you make a decision as to the presence of sodium, run a flame test with distilled water and then with 0,2 M NaCl solution.

Ammonium (NH$_4^+$) ions reactions

1. Reaction with strong bases

The ammonium ion, NH$_4^+$ is the conjugate acid of the base ammonia, NH$_3$. The test for NH$_4^+$ takes advantage of the following equilibrium:

$$NH_4^+ + OH^- \xrightarrow{t} NH_3\uparrow + H_2O$$

Thus, when this strong base is added to solution of ammonium salt and this solution is heated, NH$_3$ gas is evolved.

Gaseous ammonia can be determined:

- by odour;
- by colouring of humid red litmus paper in dark blue colour.

Litmus paper should not touch test tube walls to prevent hit of alkali on the paper, otherwise colour changing will take place under the action of alkali solution under ammonium ions absence.

The reaction is sensitive and specific because ammonium ions are determined by other cations

Procedure: Pour 10 drops of the original sample to be analyzed in an evaporating dish or into a test tube. Add 10 drops of 3M NaOH to the test tube. Heat the test tube in a boiling-water bath for some minutes. Moisten a strip of red or neutral litmus paper with distilled water and hold the paper above the test tube. Let stand for a few minutes. The presence of NH_4^+ ions is confirmed if the paper turns blue.

2. Reaction with Nessler's reagent $K_2[HgI_4]$ + KOH

Ammonium ions with Nessler reagent ($K_2[HgI_4]$ + KOH) form red-brown or yellow-brown (at small concentrations of an ammonium ion) amorphous precipitate of mercury amide complex (II):

$$NH_4^+ + 2[HgI_4]^{2-} + 2OH^- \rightarrow [(IHg)_2NH_2]I\downarrow + 5I^- + 2H_2O \quad \text{redish-brown}$$

All cations that can react with bases, interfere with this test (for instance Cr^{3+}, Fe^{3+}, Co^{2+}). Sn^{2+}, Sb^{3+} and Hg^{2+} also interfere, because they destroy the Nessler's reagent.

Procedure: Pour 2-3 drops of the ammonium salt into a small test tube, add 2-3 drops of $K_2[HgI_4]$ + KOH (reagent Nessler).

3. Reaction with tartaric acid and hexanitrocobaltate (III) sodium

NH_4^+ can be precipitated from aqueous solution as white and yellow precipitate by adding tartaric acid and $Na_3[Co(NO_2)_6]$:

$$CH_3COO^- + H_2C_4H_4O_6 \rightarrow CH_3COOH + HC_4H_4O_6^-$$

$$HC_4H_4O_6^- + NH_4^+ \rightarrow NH_4HC_4H_4O_6\downarrow \quad \text{white}$$

$$2NH_4^+ + Na_3[Co(NO_2)_6] \rightarrow (NH_4)_2Na[Co(NO_2)_6]\downarrow + 2Na^+ \quad \text{yellow}$$

Procedure: Pour 2-3 drops of the ammonium salt into two small test tubes, add 3-4 drops of $H_2C_4H_4O_6$ and CH_3COONa to the first test tube and 3-5 drops of $Na_3[Co(NO_2)_6]$ to another.

Table 4

The action of some reagents on the Ist analytical group cations

Reagent	Cations		
	K^+	Na^+	NH_4^+
KOH, NaOH	—	—	NH_3↑is evolved (when heating)
K_2CO_3, Na_2CO_3	—	—	NH_3↑ is evolved (when heating)
$NaHC_4H_4O_6$	White crystalline precipitate of $KHC_4H_4O_6$, is soluble in acids and alkalies	—	White crystalline precipitate of $NH_4HC_4H_4O_6$, is soluble in acids and alkalies
$Na_3[Co(NO_2)_6]$	Yellow crystalline precipitate of $K_2Na[Co(NO_2)_6]$, is soluble in mineral acids	—	Yellow crystalline precipitate of $(NH_4)_2Na[Co(NO_2)_6]$, is soluble in mineral acids
$Na_2Pb[Cu(NO_2)_6]$	Black crystalline precipitate of $K_2Pb[Cu(NO_2)_6]$	—	Black crystalline precipitate of $(NH)_2Pb[Cu(NO_2)_6]$
$K[Sb(OH)_6]$	—	White crystalline precipitate of $Na[Sb(OH)_6]$	White amorphous precipitate of $HSb0_3$
$Zn(UO_2)_3(CH_3COO)_8$, CH_3COOH	—	$NaZn(U0_2)_3(CH_3COO)_9 \cdot 9H_20$	—
$K_2[HgJ_4]$, KOH	—	—	Red-brown or yellow-brown amorphous precipitate of $[(IHg)_2NH_2]I$↓

Analysis systematic course of the Ist analytical cations group mixture

1. Preliminary observations and tests

The tested sample can be in a dry form (in the form of bases, salts, and salt mixtures) or in the form of solution. The tested sample is examined and the appearance (colour, form of crystals, odor etc.) is described. When analysing the dry sample its solubility in water is tested.

pH of the media is defined in the obtained solution, or in the initial solution with the help of indicator paper. If the sample is easily soluable in water and has acid media reaction ammonium cations are probably present in it (explain it).

The reaction of flame colouring is carried out. The part of the sample is taken by the cleared and overheated nichromic loop and placed into the colourless flames part of the burner. If the sample is in the form of solution, it should be previously evaporeated to dryness.

2. Ammonium cations detection

2.1. The action of alkalis

Measure out 10 drops (0,5 mL) of the test solution to a test tube. Add 10 drops of 2M NaOH. Heat the test tube in a boiling-water bath for some minutes. Moisten a strip of red or neutral litmus paper with distillated water and hold the paper above the test tube. Let stand for a few minutes. Blue litmus paper indicates the presence of the NH_4^+ - cations.

2.2. The action of Nessler reagent ($K_2[HgI_4]$ + KOH)

3-5 drops of Nessler reagent are added to 2-3 drops of the tested solution.

3. Potassium cations detection

3.1. Solution preparation for potassium cations detection

Measure out 5 drops of the test solution in an evaporating dish, add 5 drops 2M solution of NaOH or Na_2CO_3, heat the evaporating dish in a boiling-water bath for some minutes. Dissolve the dry balance in distillated water. Test it for completeness removing of NH_4^+ using the Nessler's reagent. After ammonium ions removal 2M acetic acid solution is added by drops to the obtained solution till neutral reaction (sample with indicators), evaporate in a water bath and cool it.

3.2. Potassium cations detection by the action of sodium hexanitrocobaltate solution (III) $Na_3[Co(NO_2)_6]$

Add 2 drops of sodium hexanitrocobaltate (III) $Na_3[Co(NO_2)_6]$ to the solution. The formation of yellow precipitate, confirms the presence of K^+.

3.3. Potassium cations detection by the action of tartaric acid $H_2C_4H_4O_6$

Add 2 drops of tartaric acid $H_2C_4H_4O_6$ to the solution. The formation of a white precipitate, confirms the presence of K^+.

4. Sodium cations detection

4.1. Solution preparation for sodium cations detection

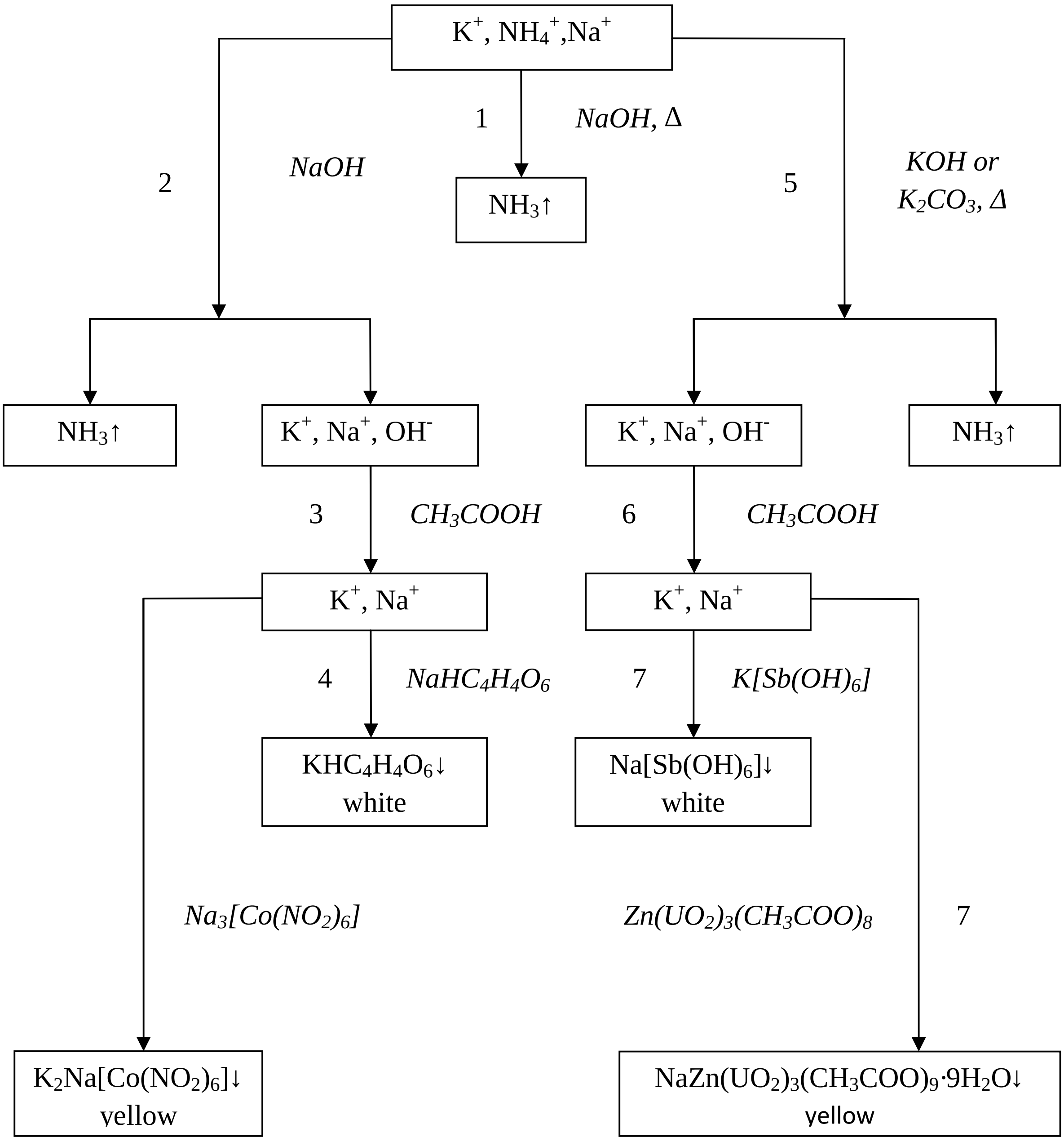
Measure out 5 drops of the test solution in an evaporating dish, add 5 drops 2M solution of KOH or K_2CO_3, and heat the evaporating dish in a boiling-water bath for some minutes. Dissolve the dry balance in distillated water. Test it for completeness removing of NH_4^+ using the Nessler's reagent. After ammonium ions removal 2M acetic acid solution is added by drops to the obtained solution till neutral reaction (sample with indicators), evaporate it in a water bath and cool it.

4.2. Sodium cations detection by the action of potassium hexahydroxostibate solution (V) $K[Sb(OH)_6]$

Add 2 drops of potassium hexahydroxoantimonate (V) $K[Sb(OH)_6]$ to the solution. The formation of white precipitate, confirms the presence of Na^+.

Scheme 1

SCHEME OF ANALYSIS SYSTEMATIC COURSE THE Ist ANALYTICAL GROUP



Topic 2
Sensitivity of Chemical Reactions

1. The main purpose of the topic:

Analytical reactions of qualitative analysis should be conducted under certain conditions (pH, concentration of reactants, temperature, etc.). In pharmaceutical analysis in accordance with the tasks, the sensitivity analysis of reaction, the limiting ratio, completeness of the reaction are important criteria. Comprehension of these characteristics allows you to find the acceptable concentration of foreign ions in the studied solution, parameters sensitivity analysis and reactions, students and professionals choose to analyze the necessary reagents and use certain amounts of certain concentrations of the reacting solutions.

2. Basic questions:

2.1. Requirements for analytical reactions.
2.2. Specific and Selective reactions.
2.3. Chemistry Reaction’s Sensitivity.
2.4. Parameters of chemical reactions sensitivity, relationship between the parameters of sensitivity.
2.5. Ways of improving the analytical reaction sensitivity.
2.6. Fractional and Systematic analysis. The group reagents, requirements for it.

3. Brief exposition of theoretical material:

The most important characteristics of all methods of qualitative analysis are specificity and sensitivity. Sensitivity is defined as the smallest quantity of an element that can be detected by a given method. Sensitivity of modern methods is expressed in magnitudes of the order of 1 mg (one millionth part of a gram).

Sensitivity − is the smallest concentration that can be determine in the chemical reaction. Parameters of sensitivity of chemical reactions:

C (C_{min}) − minimal concentration, g/ml − the lowest concentration at which ion can be detected in a solution of sample;

V (V_{min}) − volume, ml − a minimum volume of solution needed to determine this ion;

m − openear (detection) minimal − the least amount of substance, which present in the analysed solution and can be detected with the reagent. It is calculated in μg. 1 μg = 0,000001 g;

W − maximum of dilution - ($W = 1/C_{min}$) – quantity (ml) of solution, containing 1 g of the analysed substance, which can be detected with a definite reaction (reagent).

$$m = \frac{V \cdot 10^6}{W} = C_{min} \cdot V \cdot 10^6$$

It is a formula of interrelationship between these parameters of sensitivity.

Most sensitive of analytical reaction, when lesser detection minimal and minimal concentration of the analyzed solution and more minimal dilution.

Ways to improve the sensitivity of the analytical reaction:

1. Increasing the concentration of analyzed substance in solution, which analyzed and reagent that is added;
2. Creating conditions for accelerating the formation of precipitate (cooling solution, bringing of crystallization centers, addition an organic solvent, etc.);
3. Diminution the solubility of precipitate augmentation of organic non-electrolytes, such as ethanol, benzene, etc;
4. Using the masking of interfering ion;
5. Removing the impurities from the solution which is analyzed.

4. Control test and patterns of responses:

4.1. Detection minimal of calcium (II) cations for reaction with sulfate ions is equal to 0,04 mg. Minimal dilute equal to 1250000 ml/g. Calculate the volume of solution needed to determine this ion.

Answer:

The formula of interrelationship between parameters of sensitivity is:

$$m = c_{\min} \cdot V_{\min} \cdot 10^6 = \frac{V_{\min} \cdot 10^6}{W}$$

According to this formula:

$$V_{\min} = \frac{m \cdot W}{10^6} = \frac{0{,}04 \cdot 1250000}{10^6} = 0{,}05 \ (ml)$$

5. Tasks for homework (write in a textbook for protocols):

5.1. Detection minimum Cu^{2+} ions in 0.05 ml of the analyzed solution is equal to 0.2 micrograms. Calculate the minimal dilute.

Topic 3
Chemistry of the IInd Group Cations
Analysis systematic course of the IInd analytical group cations

1. The main purpose of the topic

Many medicines, which contain compounds of silver, lead and mercury cations, are used in medical practice because they possess antiseptic properties.

Silver (I) nitrate aqueous solutions (w=1-2%) are applied as antiseptic agent for treating eye and skin diseases. Colloid solutions of silver collargol, protargol (complex salt of albumen with silver) are applied for washing of the urinary tract, in ophthalmology and dermatology as facilities astringent and antiseptic.

The lead oxide PbO is the basic operating matter of plaster leaden; it is applied on the diseases of skin festering and inflammatory diseases. Lead (II) acetate solution (w=2%) is used for treating an eczema and dermatitis.

Mercury (I) chloride (calomel) is applied as diuretic and purgative. It should be remembered that mercury and its salts are very toxic!

Comprehension of the characteristic reactions of cations of these metals and conditions of their performance is making for students the theoretical base of chemical analysis, practical skills and experience of making it and also bases the subsequent study of such core of disciplines as pharmaceutical chemistry, pharmacognosicy, forensic chemistry, technology of drugs, etc. for future specialists in pharmacy.

2. Basic questions:

2.1. The second analytical group cations (acid-base classification), general characteristic.

2.2. Group reagent for the IInd analytical group cations and requirements of application.

2.3. Characteristic reactions of Ag^+ cation.

2.4. Characteristic reactions of Hg_2^{2+} cation.

2.5. Characteristic reactions of Pb^{2+} cation.

2.6. Analysis systematic course of the IInd analytical group cations.

3. Brief exposition of theoretical material:

General characteristic of the IInd analytical group cations Ag^+, Hg_2^{2+}, Pb^{2+}

The cations of the d-elements Ag^+, Hg_2^{2+} and the p-elements Pb^{2+} are referred to the IInd analytical group.

The IInd analytical group cations form nonsoluble halogenids (except silver phtoride), sulphites, sulphides, chromates, phosphates, arsenites, arsenates, hydroxides (oxides) and carbonates. That is explained by high polar action of these cations.

A group reagent of the IInd analytical group is 2M solution of HC1, which allows to separate these cations in the form of precipitates of the following chlorides. Cations of the analytical groups Ist, III^{d}-VIth still remain in the solution. The reactions of the complex formation are characteristic for the IInd analytical group cations. And reactions of oxidation-reduction are typical for ions Hg_2^{2+} (especially reactions of disproportion). That's why analysis systematic course of the mixture of the IInd analytical group of cations is based on the precipitation reactions, complex formation and oxidation-reduction.

The complex formation reactions with ammonium are used in the analysis systematic course for AgCl and Hg_2Cl_2 separation and simultaneous Hg^{2+} ions revealing.

The salts of IInd analytical group cations in the most cases are colourless, but sometimes there are coloured cations in their composition, they have colouring.

4. Control test and patterns of responses:

4.1. Hydrochloric acid solution was added to the solution containing cations of the second analytical group. It resulted in generation of white precipitate that was soluble in ammonium solution. What cations are contained in the solution? Write the equations of the conforming reactions.

Answer:

The solution contains cation Ag^+:

$$Ag^+ + Cl^- \rightarrow AgCl\downarrow \quad \text{white}$$

All cations of the second analytical group form white precipitates with hydrochloric acid but only silver (I) chloride is soluble in ammonium solution:

$$AgCl\downarrow + 2NH_3 \cdot H_2O \rightarrow [Ag(NH_3)_2]^+ + Cl^- + 2H_2O$$

4.2. Calomel is applied as diuretic and purgative. Suggest the analytical reaction for identification of this drug. Write the equations of the conforming reactions and explain the analytical effects.

Answer:

Calomel (Hg_2Cl_2) is white substance, slightly soluble in water. After adding aqueous ammonia, mercury (I) chloride turns black due to formation of fine metallic mercury:

$$Hg_2Cl_2\downarrow + 2NH_3 \cdot H_2O \rightarrow [NH_2Hg_2]Cl\downarrow + 2H_2O + NH_4Cl$$

$$[NH_2Hg_2]Cl\downarrow \rightarrow NH_2HgCl\downarrow + Hg\downarrow \qquad \text{black}$$

4.3. Solution contains Ag^+ and Pb^{+2} cations. Is it possible to detect Pb^{+2} cation in the presence of Ag^+ cation by sodium sulfide solution? Write the equations of the conforming reactions and explain the analytical effects.

Answer:

It isn't possible to detect Pb^{+2} cation in the presence of Ag^+ cation by sodium sulfide solution because Pb^{+2} and Ag^+ cations form black precipitates with sulfide-ions:

$$Pb^{2+} + S^{2-} \rightarrow PbS\downarrow$$

$$2Ag^+ + S^{2-} \rightarrow Ag_2S\downarrow$$

Precipitates are both dissolved in dilute nitric acid by heating:

$$3PbS\downarrow + 8H^+ + 2NO_3^- \rightarrow 3Pb^{2+} + 3S\downarrow + 2NO\uparrow + 4H_2O$$

$$3Ag_2S\downarrow + 8H^+ + 2NO_3^- \rightarrow 3Ag^+ + 3S\downarrow + 2NO\uparrow + 4H_2O$$

5. Tasks for individual work (write in a textbook for protocols):

5.1. How can one separate lead chloride from other chlorides of IInd analytical group cations during the analysis of this group of cations admixture?

5.2. Which reactions are used for separation lead chloride from silver and mercury (I) chlorides?

5.3. Explain amphoteric properties of lead compounds. Write the equations of the conforming reactions.

5.4. Which reactions are used for separation of silver chloride from mercury (I) chloride?

5.5. Suggest the systematic analysis of solution which contains ions:

- Ag^+, Hg_2^{2+};
- Hg_2^{2+}, Pb^{2+};
- Ag^+, Pb^{2+}.

The situation problems are solved according to the analysis systematic course of the IInd analytical group cations mixture.

6. Laboratory experiment

Laboratory experiment 3.1

Characteristic reactions of the IInd analytical group cations

1. Reaction with group reagent (precipitating agent) HCl

As the chlorides of Pb^{2+}, Ag^+ and Hg_2^{2+} are insoluble, they may be precipitated and separated from the cations of another groups by the addition of HCl:

$$Ag^+ + Cl^- \rightarrow AgCl\downarrow \quad \text{white}$$
$$Pb^{2+} + 2Cl^- \rightarrow PbCl_2\downarrow \quad \text{white}$$
$$Hg_2^{2+} + 2Cl^- \rightarrow Hg_2Cl_2\downarrow \quad \text{white}$$

A slight excess of HCl is used to ensure complete precipitation of the cations and to reduce the solubility of the chlorides by the common-ion effect.

$$AgCl\downarrow + Cl^- \rightarrow [AgCl_2]^-$$
$$PbCl_2\downarrow + Cl^- \rightarrow [PbCl_3]^-$$
$$Hg_2Cl_2\downarrow + Cl^- \rightarrow [Hg_2Cl_3]^-$$

Lead chloride is soluble in boiling water, whilst Hg_2Cl_2 and AgCl are insoluble. It is separated from the other two insoluble chlorides by dissolving it in hot water.

Silver chloride is separated from Hg_2Cl_2 by the addition of aqueous NH_3. Silver chloride is dissolved because Ag^+ forms a soluble complex cation with NH_3:

$$AgCl + 2NH_3 \cdot H_2O \rightarrow [Ag(NH_3)_2]^+ + Cl^- + 2H_2O$$

Mercury (I) chloride reacts with aqueous ammonia in a disproportionation reaction to form dark gray precipitate:

$$Hg_2Cl_2\downarrow + 2NH_3 \cdot H_2O \rightarrow [NH_2Hg_2]Cl\downarrow + 2H_2O + NH_4Cl$$
$$[NH_2Hg_2]Cl\downarrow \rightarrow NH_2HgCl\downarrow + Hg\downarrow \quad \text{black}$$

<u>*Procedure:*</u> Pour 3-5 drops of the silver, mercury (I) and lead salts into small test tubes, add some drops of group reagent. Dissolve the precipitates in hot distilled water, group reagent and aqueous ammonia.

2. Reaction with sulfide-ion

Lead, silver and mercury can be precipitated from aqueous solution as black solids by adding of reagent sodium sulfide:

$Pb^{2+} + S^{2-} \leftrightarrow PbS\downarrow$ black
$2Ag^{+} + S^{2-} \leftrightarrow Ag_2S\downarrow$ black
$Hg_2^{2+} + S^{2-} \leftrightarrow HgS\downarrow + Hg\downarrow$ black

These insoluble sulfides are brought into solution by treating them with hot nitric acid except HgS:

$$3PbS + 8H^{+} + 2NO_3^{-} \rightarrow 3Pb^{2+} + 3S + 2NO + 4H_2O$$

$$3Ag_2S + 8H^{+} + 2NO_3^{-} \rightarrow 3Ag^{+} + 3S + 2NO + 4H_2O$$

Procedure: Pour 3-5 drops of the silver, mercury (I) and lead salts in small test tubes, add some drops of sodium sulfide. Dissolve the precipitates of PbS and Ag_2S in hot nitric acid.

3. Reaction with sodium (or potassium) hydroxide NaOH

Lead and silver are precipitated as white precipitates by the adding NaOH. Mercury can be precipitated from aqueous solution as black precipitates by adding NaOH (or KOH):

$Ag^{+} + OH^{-} \leftrightarrow AgOH\downarrow$ white
$2AgOH \rightarrow Ag_2O\downarrow + H_2O$ brown
$Pb^{2+} + OH^{-} \rightarrow Pb(OH)_2\downarrow$ white
$Hg_2^{2+} + 2OH^{-} \leftrightarrow Hg_2O + H_2O$ black

Lead hydroxide can be dissolved in excess of NaOH or KOH:

$$Pb(OH)_2\downarrow + 2OH^{-} \rightarrow [Pb(OH)_4]^{2-}$$

Procedure: Pour 3-5 drops of the silver, mercury (I) and lead salts into small test tubes, add some drops of sodium or potassium hydroxide. Dissolve lead hydroxide in excess of NaOH or KOH.

4. Reaction with potassium iodide KI

Lead and silver are precipitated as yellow precipitates by adding KI. Mercury can be precipitated from aqueous solution as green precipitates by adding KI:

$Ag^{+} + I^{-} \leftrightarrow AgI\downarrow$ yellow
$Pb^{2+} + 2I^{-} \leftrightarrow PbI_2\downarrow$ yellow
$Hg_2^{2+} + 2I^{-} \leftrightarrow Hg_2I_2\downarrow$ green

Lead iodide can be dissolved in hot acetic acid and in excess of iodide solution:

$$PbI_2 + 2I^{-} \rightarrow [PbI_4]^{2-}$$

Procedure: Pour 3-5 drops of the silver, mercury (I) and lead salts into small test tubes, add some drops of potassium iodide. Pour 10 drops of acetic acid into the test tube with lead iodide, heat the test tube and then quickly cool it.

5. Reaction with potassium chromate K_2CrO_4

The presence of Pb^{2+} is confirmed by the formation of yellow precipitate, $PbCrO_4$, upon the adding K_2CrO_4:

$Pb^{2+} + CrO_4^{2-} \leftrightarrow PbCrO_4\downarrow$ yellow

Mercury can be precipitated from aqueous solution as red precipitate by adding K_2CrO_4:

$$Hg_2^{2+} + CrO_4^{2-} \leftrightarrow Hg_2CrO_4\downarrow \qquad \text{red}$$

Silver can be precipitated from aqueous solution as light-red precipitate by adding K_2CrO_4:

$$2Ag^{+} + CrO_4^{2-} \leftrightarrow Ag_2CrO_4\downarrow \qquad \text{light-red}$$

All chromates can be dissolved in inorganic acids:

$$2Ag_2CrO_4\downarrow + 2H^{+} \rightarrow 4Ag^{+} + Cr_2O_7^{2-} + H_2O$$

Lead chromate can be dissolved in NaOH or KOH:

$$PbCrO_4\downarrow + 4OH^{-} \rightarrow [Pb(OH)_4]^{2-} + CrO_4^{2-}$$

Silver chromate can be dissolved in aqueous ammonia:

$$Ag_2CrO_4\downarrow + 4NH_3 \cdot H_2O \rightarrow 2[Ag(NH_3)_2]^{+} + CrO_4^{2-} + 4H_2O$$

Procedure: Pour 3-5 drops of the silver, mercury (I) and lead salts in small test tubes, add some drops of potassium chromate. Dissolve all chromates in acid; lead chromate in NaOH or KOH and silver chromate in aqueous ammonia.

6. Reaction with carbonate-ions

Silver and mercury cations can be precipitated from aqueous solution as yellow solids by the adding carbonate-ions:

$$2Ag^{+} + CO_3^{2-} \leftrightarrow Ag_2CO_3\downarrow \qquad \text{yellow}$$

$$Hg_2^{2+} + CO_3^{2-} \leftrightarrow Hg_2CO_3\downarrow \qquad \text{yellow}$$

$$Hg_2CO_3\downarrow \rightarrow HgO\downarrow + Hg\downarrow + CO_2\uparrow \qquad \text{black}$$

Lead cations can be precipitated from aqueous solution as white precipitates by adding the carbonate-ions:

$$2Pb^{2+} + 3CO_3^{2-} + 2H_2O \leftrightarrow (PbOH)_2CO_3\downarrow + 2HCO_3^{-} \qquad \text{white}$$

Procedure: Pour 3-5 drops of the silver, mercury (I) and lead salts into small test tubes, add some drops of carbonate-ions.

6. Reaction with sulfate-ions

Lead, silver and mercury can be precipitated from aqueous solution as white precipitates by adding sulfate-ions.

$$2Ag^{+} + SO_4^{2-} \leftrightarrow Ag_2SO_4\downarrow \qquad \text{white}$$

$$Hg_2^{2+} + SO_4^{2-} \leftrightarrow Hg_2SO_4\downarrow \qquad \text{white}$$

$$Pb^{2+} + SO_4^{2-} \leftrightarrow PbSO_4\downarrow \qquad \text{white}$$

Lead sulfate is dissolved in NaOH or KOH and hot 30% aqueous solution of ammonia acetate:

$$PbSO_4\downarrow + 4OH^{-} \rightarrow [Pb(OH)_4]^{2-} + SO_4^{2-}$$

$$2PbSO_4\downarrow + 2CH_3COO^{-} \rightarrow [Pb(CH_3COO)_2 \cdot PbSO_4] + SO_4^{2-}$$

Procedure: Pour 3-5 drops of silver, mercury (I) and lead salts into small test tubes, add some drops of sulfate-ions. Dissolve lead sulfate in NaOH or KOH and 30% solution of ammonia acetate.

Table 5

Action of some reagents to the IInd analytical group cations

Reagents	Cations		
	Ag^+	Hg_2^{2+}	Pb^{2+}
Na_2S or H_2S	Ag_2S – black precipitate is solved in HNO_3 with hitting	HgS+ Hg – black precipitate is solved in «Czar vodka», bromin water	PbS – black precipitate is solved in HNO_3 with hitting
NaOH or KOH	Ag_2O – brown precipitate, is solved in $NH_3{\cdot}H_2O$ and HNO_3	Hg_2O – black precipitate, is solved in HNO_3	$Pb(OH)_2$ – white precipitate $Pb(OH)_2$ is solved in alkalis and HNO_3
KI	AgI – yellow precipitate, is solved in $NH_3{\cdot}H_2O$	Hg_2I_2 – green precipitate, is solved in the excess of the reagent.	PbI_2 – golden yellow precipitate, is solved in hot water, in the excess of the reagent and in CH_3COOH
H_2SO_4	Ag_2SO_4 – white precipitate from concentrated solutions, is solved in hot water	Hg_2SO_4 – white precipitate, is solved in «Czar vodka»	$PbSO_4$ – white precipitate is solved in alkalis, 30% solution CH_3COONH_4 and concentrated HCI and H_2SO_4

Analysis systematic course of the IInd analytical cations group mixture

1. Preliminary tests and observation (see page 23)

2. Precipitation of Group II Cations

Measure out 10 drops (~0,5 mL) of the test solution or the unknown one into a small test tube. Add 15 drops of 2 M HC1, stir them thoroughly, and then centrifuge the test tube. Test it for completeness of precipitation by adding some drops of 2 M HC1 to the clear supernate. If the supernate turns cloudy, this shows that not all of the group II cations have precipitated; add another two drops of 2 M HC1, stir and centrifuge them. Repeat this process until no more precipitate forms. All of the group II cations must be precipitated. Wash the precipitate by adding five drops of cold distilled water and stirring.

3. Separation and Identification of Pb^{2+}

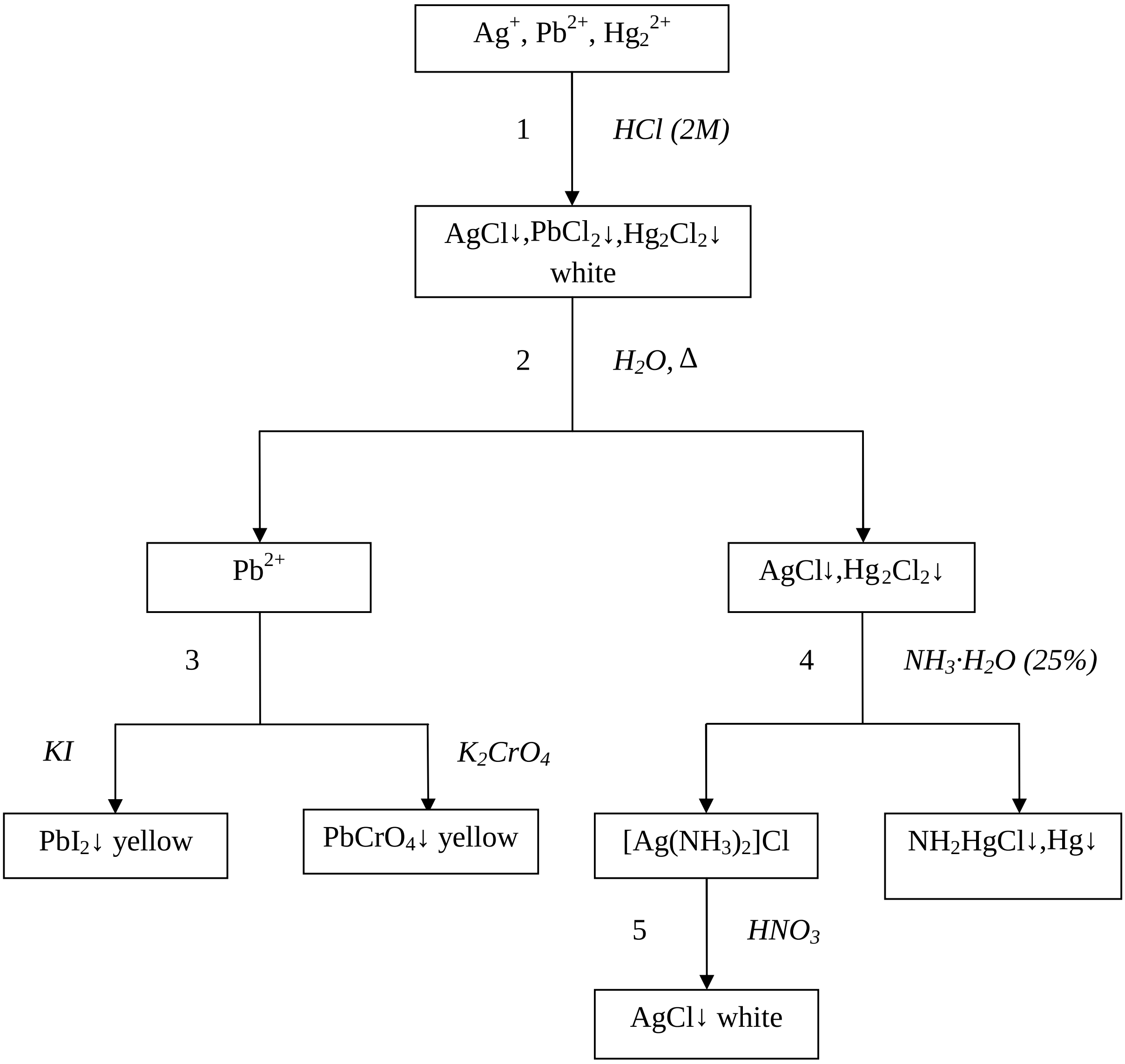
Add 15 drops of distilled water to the precipitate and place the test tube in a hot-water bath. Stir using a stirring rod and heat for 1 min or longer. Quickly centrifuge and decant the hot supernate into a clean test tube. Repeat this procedure two more times, combining the supernate, which should contain Pb^{2+} if is present. Save the precipitate for Procedure 3. Add three drops of 1M K_2CrO_4 or KI to the supernate. The formation of yellow precipitate confirms the presence of Pb^{2+}.

4. Separation and Identification of Ag^+ and Hg_2^{2+}

Add 10 drops of 6 M aqueous ammonia to the precipitate from Procedure 2. The formation of black precipitate indicates the presence of mercury. Centrifuge and decant the clear supernate into a clean teat tube. Add 20 drops of 6 M HNO_3 to the decantate. Stir the solution and test its acidity. Continue to add HNO_3 dropwise until the solution is acidic. White cloudiness confirms the presence of Ag^+.

Scheme 2

SCHEME OF ANALYSIS SYSTEMATIC COURSE THE IInd ANALYTICAL GROUP



Topic 4
Ionization Theory

1. The main purpose of the topic

When we perform a qualitative analysis, we deal mainly with aqueous solutions of acids, bases and salts. Knowledge of the processes that occur when substances are dissolved in water, and the law of mass action allows to calculate the concentration of ions in solution and to anticipate the completeness and the direction of the chemical reaction.

2. Basic questions:

2.1. Theories of electrolyte solutions in analytical chemistry: strong and weak electrolytes. The degree of ionization (dissociation). The basic principles of the theory of strong electrolytes.
2.2. Analytical ion concentration, activity, activity coefficient, the relationship between them. Ionic strength, dependence of it on various factors.
2.3. Weak electrolytes. Constant of ionization, the relationship between degree of dissociation and constant of ionization.
2.4. Equilibriua of ionization in water. The ionic product of water. Calculating pH, pOH values of acids and bases aqueous solutions.
2.5. Ways of expressing concentration of solution: the percent composition (by mass), normal, molar concentration.

3. Brief exposition of theoretical material:

Strong Electrolytes

Electrolytes are substances which, when dissolved in water, break up into cations (plus-charged ions) and anions (minus-charged ions). We say they ionize. These solutions conduct electricity due to the mobility of the positive and negative ions. Electrolytes conduct electricity only when molten or in aqueous solutions.

There are two classes of electrolytes: strong electrolytes and weak electrolytes.

A **strong electrolyte** is a solute that completely, or almost completely ($\rightarrow$100%), ionizes or dissociates in a solution. Originally, a "strong electrolyte" was defined as a chemical that, when in aqueous solution, is a good conductor of electricity.

For strong electrolytes, a single reaction arrow shows that the reaction occurs completely in one direction, in contrast to the dissociation of weak electrolytes, which both ionize and re-bond in significant quantities.

$$\text{Strong electrolyte (aq)} \rightarrow \text{Cation}^{+}\text{ (aq)} + \text{Anion}^{-}\text{ (aq)}$$

Virtually all salts belong to strong electrolytes. Among the most important acids and bases, the following are strong electrolytes: HNO_3, $HClO_4$, HC1, HBr, HI, KOH, NaOH, $Ba(OH)_2$, $Ca(OH)_2$.

Therefore, the number of ions in them is great. In not very dilute solutions of strong electrolytes the average distance between ions is comparatively small owing to the considerable concentration. The forces of interionic attraction and repulsion are quite great. In such solutions, the ions are not entirely free, their motion is hampered by their mutual attraction. Owing to this attraction, each ion is surrounded, as it were, with a spherical cluster of oppositely charged ions that has been named an "ionic atmosphere". When the concentration of the solution increases, the retarding action of the ionic atmosphere on the electrical conductivity of the solution manifests itself to a greater extent.

The state of the ions in a solution is assessed with the aid of a quantity called the **activity *a***. By the activity of an ion is meant its effective, conditional concentration according to which it acts in chemical reactions. The activity of an ion ***a*** equals its concentration ***c*** multiplied by the ***activity coefficient f***:

$$a = f\cdot c$$

The activity coefficients of various ions are different. In addition, they change upon a change in the conditions, particularly when the concentration of the solution changes. The activity coefficient is usually less than unity for concentrated solutions, and it approaches unity in very dilute solutions.

We can state approximately that the activity coefficient of a given ion depends only on its charge and on the **ionic strength** I of the relevant solution. The latter is denned as the half-sum of the products of the concentrations (mol/L) of all the ions in the solution and the square of their charge:

$$I = 1/2\ (C_1\cdot Z_1^2 + C_2\cdot Z_2^2 + \ldots + C_n\cdot Z_n^2)$$

An activity coefficient close to unity points to the weak interaction between ions. In dilute solutions, the nature of ions only slightly affects the values of their activity coefficients.

Weak Electrolytes

Small fractions of **weak electrolytes'** molecules ionize when dissolve in water. Some neutral molecules are present in their solutions. For example, ammonia, NH_4OH, carbonic acid, H_2CO_3, acetic acid, CH_3COOH, and most organic acids and bases are weak electrolytes. The following ionization is not complete,

$$HNO_2\,(aq) \rightleftarrows H^+\,(aq) + NO_2^-\,(\mathrm{aq})$$

In the solution, HNO_2 molecules and ions are present. Ionization can be viewed as an equilibrium established for the above reaction, for which the **equilibrium constant** is defined as

$$K_a = \frac{[H^+]\cdot[NO_2^-]}{[HNO_2]},$$

where we use [ ] to mean the concentration of the species in the [ ]. You can find the values of equilibrium constants in the reference tables.

Arrhenius says that only a part of an electrolyte dissociates into ions in a solution, and introduced the concept of the **degree of dissociation**. By the degree of dissociation of an electrolyte is meant the ratio of the number of its molecules that have broken up into ions in the given solution (X) to the total number of its molecules in the solution (C):

$$\alpha = \frac{X}{C} \cdot 100\%$$

If we denote the concentration of an electrolyte dissociating by *c*, and the degree of its dissociation in the given solution by α, then the concentration of each of the ions will be c·α, and the concentration of the undissociated molecules will be c·(1– α). Hence, the equation of the dissociation constant acquires the form:

$$K = \frac{(c\alpha)^2}{c(1-\alpha)} \qquad \text{or} \qquad K = \frac{c \cdot \alpha^2}{1-\alpha}$$

This equation expresses W. Ostwald's **dilution law**. It permits us to calculate the degree of dissociation for different concentrations of an electrolyte if we know its dissociation constant. Using this equation, we can also calculate the dissociation constant of an electrolyte knowing its degree of dissociation and the concentration.

For solutions in which the dissociation of an electrolyte is very small, the equation of Ostwald's law is simplified. Since in these cases α<<1, we may disregard the quantity α in the denominator of the right-hand side of the equation. Hence, the equation acquires the form:

$$K = c\alpha^2$$

This equation shows the relationship existing between the concentration of a weak electrolyte and the degree of its dissociation: the degree of dissociation increases upon dilution of a solution.

Water – Weak Electrolyte

Pure water conducts an electric current very poorly, but nevertheless it has a measurable electrical conductivity that is explained by the slight dissociation of water into hydrogen and hydroxide ions:

$$H_2O \rightleftarrows H^+ + OH^-$$

The electrical conductivity of pure water can be used to calculate the concentration of hydrogen and hydroxide ions in water. Let us write an expression for the dissociation constant of water:

$$K = \frac{[H^+]\cdot[OH^-]}{[H_2O]}$$

We can rewrite this equation as follows:

$$[H^+]\cdot[OH^-] = [H_2O]\cdot K$$

Replacing the product $[H_2O]\cdot K$ in the last equation with the new constant K_w, we have:

$$[H^+]\cdot[OH^-] = K_w$$

The latter K_w is called the **ion product of water**. The K_w value is depended of temperature. For pure water at 25°C $K_w = 10^{-14}$, we have $[H^+] = [OH^-] = 1\cdot10^{-7}$ mol/L. Hence, for this temperature:

$$K_w = 10^{-7} \cdot 10^{-7} = 10^{-14}$$

Solutions in which the concentrations of the hydrogen ions and hydroxide ions are the same are called neutral solutions.

The acidity or alkalinity of a solution can be expressed in another, more convenient way: instead of the hydrogen ion concentration, its common logarithm is taken with the reverse sign. The latter quantity is named the **hydrogen ion index**, but the majority chemists call it the **pH-value**, or simply the pH, which is its symbol:

$$pH = -\log[H^+]$$

$$pOH = -\lg[OH^-]$$

$$pH + pOH = 14 \quad (\text{at } 25°C)$$

For acid solutions, pH < 7, and diminishes with an increasing acidity of the solution. Conversely, for alkaline solutions, pH >7, and grows with an increasing alkalinity of the solution.

4. Control test and patterns of responses:

4.1. Calculate the ionic strength and activity of Na^+ and Cl^- ions in 0.10 M solution of NaCl.

Answer:

1). NaCl is strong electrolyte and completely dissociates in aqueous solutions:

$$NaCl \rightarrow Na^+ + Cl^-$$

Ionic strength:

$$\text{«} = \frac{1}{2}\sum c_i \cdot z_i^2 = \frac{1}{2}\left(1^2 \cdot c_{Na^+} + 1^2 \cdot c_{Cl^-}\right) = \frac{1}{2}\left(1^2 \cdot 0,01 + 1^2 \cdot 0,01\right) = 0,01$$

2). Activity coefficient for Na^+ and Cl^- ions (tables data):

$$f_{Na^+} = f_{Cl^-} = 0,89$$

3). Activity of Na^+ and Cl^- ions:

$$a_{Na^+} = a_{Cl^-} = 0,01 \cdot 0,89 = 8,9 \cdot 10^{-3} \ (mol/l)$$

4.2. Calculate the concentrations of CN^-, H^+, and OH^- in 0.1 M aqueous solution of acid HCN. What is the pH of this solution?

Answer:

HCN is weak electrolyte and partly dissociates in aqueous solutions:

$$HCN \rightleftarrows H^+ + CN^- \quad (1)$$

The K_a expression is

$$K_a = \frac{[H^+] \cdot [CN^-]}{[HCN]} \qquad (2)$$

$$K_a(HCN) = 7,2 \cdot 10^{-10} \ (\text{from reference book})$$

Let $[H^+] = x$ mol/l. According to (1) $[CN^-] = [H^+] = x$ mol/l and $[HCN] = (c - x)$ mol/l. Next, enter the known and unknown concentrations into the K_a expression and solve for x:

$$K_{іон.} = \frac{x^2}{c - x}$$

But HCN is weak electrolyte and initial concentration of acid is much greater than concentration of ions, this means that $c - x \rightarrow c,$ you can use 0 1 M for [HCN] in the K_a expression:

$$K_{\text{іон.}} = \frac{x^2}{c}$$

$$7.2 \cdot 10^{-10} = \frac{x^2}{0.1}$$

$$x = \sqrt{7.2 \cdot 10^{-10} \cdot 0.1} = 8.5 \cdot 10^{-6}\,mol/l$$

That is $[CN^–]$ = $[H^+]$ = $8.5·10^{-6}$ mol/l. For calculating the remaining concentration needed, $[OH^–]$, use the expression for K_w:

$$K_w = 1.0 \cdot 10^{-14} = [H^+]\,[OH^–]$$

$$\left[OH^-\right] = \frac{1.0 \cdot 10^{-14}}{8.5 \cdot 10^{-6}} = 1.2 \cdot 10^{-9}\,mol/l$$

Finally, here's the calculation of the pH:

$$pH = –\lg\,[H^+] = –\lg\,8.5·10^{-6} = 5.07$$

4.3. Calculate the Degree of Dissociation in a 0.2 M aqueous solution of acetic acid.

<u>Answer:</u>

The equation for the reaction is:

$$CH_3COOH \rightleftarrows CH_3COO^– + H^+$$

$K_a = 1.8 \cdot 10^{-5}$ (from reference book)

We can use the W. Ostwald's dilution law.

$$K = c\sim^2$$

$$\sim = \sqrt{\frac{k}{c}} = \sqrt{\frac{1.8 \cdot 10^{-5}}{0.2}} = 0.009$$

$$\alpha = 0.009 \cdot 100\% = 0.94\%$$

5. Tasks for individual work (write in a textbook for protocols):

5.1. Calculate the concentration of OH^- in a 0.05M aqueous solution of HCN. What is the pH and pOH of this solution?

5.2. Calculate the concentrations of H^+ in a 0.7% aqueous solution of perchloric ($HClO_4$) and hypochlorous (HClO) acids. What is the pH and pOH of this solution?

5.3 Calculate the activity of ions in the 0.001M $KAl(SO_4)_2$.

Topic 5
Chemistry of the III^{d} Group Cations
Analysis systematic course of the III^{d} analytical group cations

1. The main purpose of the topic:

The cations of the third analytical group contain many medical preparations. A wide use in medicine has found such pharmaceutical preparations: Calcium chloride, Calcium gluconas, Calcium lactas, Calcium carbonate, Barium sulfate. Pharmaceutical preparations which contain barium and calcium substances are toxic. Qualitative reactions to the named ions are used for their identification. These reactions can be used for research of objects pharmaceutical, toxicological and phytochemical of the analyses.

2. Basic questions:

2.1. The third analytical group cations (acid – base classification), general characteristic.
2.2. Group reagent for the III^{d} analytical group cations.
2.3. Characteristic reactions of Ca^{2+}.
2.4. Characteristic reactions of Sr^{2+}.
2.5. Characteristic reactions of Ba^{2+}
2.6. The analysis of a mix of the III^{d} analytical group cations.

3. Brief exposition of theoretical material:

General characteristic of the III^{d} analytical group cations Ca^{2+}, Sr^{2+}, Ba^{2+}

Cations of alkaline-earth metals are concerned such as: barium, stroncium, calcium, belonging to the main subgroup of the second group of the D.I. Mendeleyev periodic system are referred to the III^{d} analytical group. Electron structure of these ions is similar to the electronic structure of inert gases that is differing by their stability. Rather high polarizing action of the III^{d} analytical group cations result to that the majority of these cations salts are slightly soluble: sulphates, carbonates, chromates, oxalates, phosphates.

The group reagent on cations of the III^{d} analytical group is 1M solution of H_2SO_4 in the presence of ethanol ensuring cations precipitation as sulphates. Sulphates of the II analytical group cations are also precipitated by sulfuric acid that is why III^{d} analytical group cations are precipitated by group reagent (1M H_2SO_4 + C_2H_5OH) only after the IInd analytical group cations removement. Cations of the IVth -VIth analytical groups are not precipitated by sulfuric acid and stay in solution.

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

For the III^{d} analytical group cations redox reactions are not specified as they are have the constant degree of oxidation.

The majority of compounds containing cations of this analytical group have white colour, and their solutions are colourless. The coloured compounds are formed only with coloured anions, for example yellow $BaCrO_4$ is a yellow colour.

4. Control test and patterns of responses:

4.1. Solution containing cations Ca^{2+} and Sr^{2+}. Added solution of $K_4[Fe(CN)_6]$ and heated. White crystalline precipitate is formed. Explain this effect analytically. Write the chemical reactions.

Answer:

Solution of potassium $K_4[Fe(CN)_6]$ is formed, when heated and pH <7, with solutions of calcium salts white crystalline precipitate of double salt - $CaK_2[Fe(CN)_6]$, at pH> 7 in the presence of ammonia and ammonium chloride produced white crystalline precipitate $CaKNH_4[Fe(CN)_6]$:

$$Ca^{2+} + K^{+} + NH_4^{+} + \left[Fe\left(CN\right)_6\right]^{4-} \rightarrow CaKNH_4\left[Fe\left(CN\right)_6\right]\downarrow$$

Cations Sr^{2+} do not form precipitate of $K_4[Fe(CN)_6]$.

5. Tasks for individual work (write in a textbook for protocols):

5.1. Why do strontium ions interfere with ammonium oxalate test of calcium ions?
5.2. Why do not calcium ions interfere with gypsum water test of strontium ions?
5.3. Suggest the systematic analysis of solution which contains ions:

- Ba^{2+}, Sr^{2+};
- Ba^{2+}, Ca^{2+};
- Sr^{2+}, Ca^{2+}.

The situation tasks are solved according to the systematic analysis of the III^{d} analytical group cations mixture.

6. Laboratory experiment

Laboratory experiment 5.1.

Characteristic reactions of the III^{d} analytical group cations and condition of their detection

1. Reaction with precipitating agent (group reagent)

As the sulfates of Ba^{2+}, Sr^{2+} and Ca^{2+} are insoluble, they may be precipitated and separated from the cations of another groups by the adding of 1M H_2SO_4 in presence of alcohol (C_2H_5OH). The precipitate $CaSO_4$ solubility is rather high, that Ca^{2+} cations aren't precipitating completely. For solubility $CaSO_4$ decreasing ethyl alcohol is added, which has le dielectric permission than water. It leads to solubility precipitate decreasing of all the III^{d} analytical group cations:

$$Ba^{2+} + SO_4^{2-} \leftrightarrow BaSO_4\downarrow \quad \text{white}$$
$$Ca^{2+} + SO_4^{2-} \leftrightarrow CaSO_4\downarrow \quad \text{white}$$
$$Sr^{2+} + SO_4^{2-} \leftrightarrow SrSO_4\downarrow \quad \text{white}$$

$BaSO_4\downarrow$, $CaSO_4\downarrow$ and $SrSO_4\downarrow$ are insoluble in weak acetic acid CH_3COOH and in strong acid (HCl, H_2SO_4 or HNO_3).

$CaSO_4\downarrow$ is soluble in the presence of the saturated solution of ammonium sulfate:

$$CaSO_4 + (NH_4)_2SO_4 \rightarrow (NH_4)_2[Ca(SO_4)_2]$$

This feature is used for calcium ions separation in the analysis systematic course.

<u>Procedure:</u> Pour 3-5 drops of the barium, calcium and strontium salts in small test tubes, add some drops of precipitating agent. Dissolve the precipitate of $CaSO_4$ in some drops of $(NH_4)_2SO_4$.

2. Reaction with gypsum water (saturated solution of calcium sulfate)

Barium and strontium cations can be precipitated from aqueous solution as white precipitates by adding of reagent calcium sulfate. $SrSO_4$ precipitate forms slowly as turbidity at heating because of its rather high value of stability:

$$Ba^{2+} + SO_4^{2-} \leftrightarrow BaSO_4\downarrow \qquad \text{white}$$
$$Sr^{2+} + SO_4^{2-} \leftrightarrow SrSO_4\downarrow \qquad \text{white}$$

Calcium cations can’t react with calcium sulfate.

We can use this reaction to determine strontium in aqueous solution if we don’t have barium in this solution.

<u>Procedure:</u> Pour 3-5 drops of the barium and strontium salts in small test tubes, add some drops of calcium sulfate and place test tubes in a hot-water bath.

3. Reaction with sodium carbonate Na_2CO_3

Barium, strontium and calcium cations can be precipitated from aqueous solution as white solids by adding of reagent sodium carbonate:

$$Ba^{2+} + CO_3^{2-} \leftrightarrow BaCO_3\downarrow \qquad \text{white}$$
$$Sr^{2+} + CO_3^{2-} \leftrightarrow SrCO_3\downarrow \qquad \text{white}$$
$$Ca^{2+} + CO_3^{2-} \leftrightarrow CaCO_3\downarrow \qquad \text{white}$$

$BaCO_3\downarrow$, $CaCO_3\downarrow$ and $SrCO_3\downarrow$ are soluble in strong acid (HCl, HNO_3) and in weak acetic acid CH_3COOH:

$$BaCO_3 + 2H^+ \rightarrow Ba^{2+} + H_2O + CO_2\uparrow$$
$$BaCO_3 + 2CH_3COOH \rightarrow Ba^{2+} + H_2O + CO_2\uparrow + 2CH_3COO^-$$

<u>Procedure:</u> Pour 3-5 drops of the barium, calcium and strontium salts in small test tubes, add some drops of sodium carbonate. Dissolve the precipitates in some drops of strong acid.

4. Reaction with potassium chromate K_2CrO_4

Barium, strontium cations can be precipitated from aqueous solution as yellow precipitates by adding of reagent potassium chromate:

$$Ba^{2+} + CrO_4^{2-} \leftrightarrow BaCrO_4\downarrow \qquad \text{yellow}$$
$$Sr^{2+} + CrO_4^{2-} \leftrightarrow SrCrO_4\downarrow \qquad \text{yellow}$$

Calcium chromate is rather well dissolved in water ($S(CaCr0_4) = 2{,}7\cdot10^{-2}$ mol/dm^3).

$BaCrO_4\downarrow$ and $SrCrO_4\downarrow$ are soluble in strong acids (HCl, HNO_3):

$$2BaCrO_4\downarrow + 2H^+ \rightarrow 2Ba^{2+} + Cr_2O_7^{2-} + H_2O$$
$$2SrCrO_4\downarrow + 2H^+ \rightarrow 2Sr^{2+} + Cr_2O_7^{2-} + H_2O$$

$SrCrO_4\downarrow$ are soluble in weak acetic acid CH_3COOH:

$$SrCrO_4\downarrow + CH_3COOH \rightarrow Sr^{2+} + HCrO_4^- + CH_3COO^-$$

This property is used for separation and detection of Ba^{2+} cations in the presence of Sr^{2+} and Ca^{2+} cations.

Procedure: Pour 3-5 drops of the calcium, strontium and barium salts in small test tubes, add some drops of potassium chromate. Dissolve one part of the precipitates in some drops of strong acid and another part in some drops of weak acetic acid CH_3COOH.

5. Reaction with ammonium oxalate $(NH_4)_2C_2O_4$

Barium, calcium and strontium cations can be precipitated from aqueous solution as white precipitate by adding of reagent ammonium oxalate:

$$Ca^{2+} + C_2O_4^{2-} \leftrightarrow CaC_2O_4\downarrow \quad \text{white}$$
$$Sr^{2+} + C_2O_4^{2-} \leftrightarrow SrC_2O_4\downarrow \quad \text{white}$$
$$Ba^{2+} + C_2O_4^{2-} \leftrightarrow BaC_2O_4\downarrow \quad \text{white}$$

All precipitates are soluble in strong acids (HCl, HNO_3)

$$BaC_2O_4\downarrow + 2H^+ \rightarrow Ba^{2+} + H_2C_2O_4$$
$$SrC_2O_4\downarrow + 2H^+ \rightarrow Sr^{2+} + H_2C_2O_4$$
$$CaC_2O_4\downarrow + 2H^+ \rightarrow Ca^{2+} + H_2C_2O_4$$

$BaC_2O_4\downarrow$ and $SrC_2O_4\downarrow$ are soluble in hot weak acetic acid CH_3COOH.

These properties are used for Ca^{2+} ions detection in the analysis systematic course. The detection is prevented by Ba^{2+} and Sr^{2+} ions.

Procedure: Pour 3-5 drops of the calcium, strontium and barium salts in small test tubes, add some drops of ammonium oxalate. Dissolve all precipitates in some drops of strong acid (HCl, HNO_3). Dissolve $BaC_2O_4\downarrow$ and $SrC_2O_4\downarrow$ in some drops of hot acetic acid CH_3COOH.

6. Reaction with potassium hexacyanoferrate (II) solution $K_4[Fe(CN)_6]$

Calcium cations from solution of potassium hexacyanoferrate (II) $K_4[Fe(CN)_6]$ form white crystalline precipitate of calcium and potassium hexacyanoferrate (II) $CaK_2[Fe(CN)_6]$ by boiling at pH <7. In the presence of ammonia and ammonium chloride forms white crystalline precipitate less soluble salt $CaKNH_4[Fe(CN)_6]$ at pH > 7. Cations Ba^{2+} and Sr^{2+} under these conditions do not form precipitate with $K_4[Fe(CN)_6]$.

Procedure: Pour 3-5 drops of the calcium salts in small test tubes, add some drops of potassium hexacyanoferrate (II). Dissolve the precipitates in some drops of strong acid.

7. Flame painting reaction

Barium salts add a characteristic yellow-green colour to the flame. Calcium and strontium salts add a characteristic red color to the flame.

Procedure: To perform the flame test, take a piece of platinum or Nichrome wire that has been sealed in a piece of glass tubing. Clean the wire by clipping it in 12 M HC1 that is contained in a small test tube and heat the wire in the hottest part of your Bunsen burner flame. Repeat this procedure until no color is seen when the wire is placed in the flame. Several cleanings will be required before this is achieved. Then pour 10 drops of the solution to be analyzed in a clean test tube and perform a flame test on it. If the sample being tested is your unknown, run a flame test with distilled water and then another with $BaCl_2$, $Ca(NO_3)_2$ and $Sr(NO_3)_2$ solution.

Table 6

The action of some reagents on III^{d} analytical group cations

Reagent	Cations		
	Ba^{2+}	Sr^{2+}	Ca^{2+}
H_2SO_4	$BaSO_4$ - white precipitate is not dissolved in acids and alkalis	$SrSO_4$ - white precipitate is not dissolved in acids and alkalis	$CaSO_4$ - white precipitate partly dissolved in water it is dissolved in strong solutions of $(NH_4)_2SO_4$
Saturated solution of $CaSO_4$ (gypsum water)	$BaSO_4$ - white precipitate, is precipitated immediately	$SrSO_4$ - white precipitate, is precipitated gradually at heating	–
Na_2CO_3	$BaCO_3$ - white precipitate is partly dissolved in strong acids and acetic acid	$SrCO_3$-white precipitate is partly dissolved in strong acids and acetic acid	$CaCO_3$-white precipitate is partly dissolved in strong acids and acetic acid
K_2CrO_4	$BaCrO_4$ - yellow precipitate is partly dissolved in strong acids is not dissolved in acetic acid	$SrCrO_4$ - yellow precipitate is partly dissolved in strong acids and acetic acid	—
$(NH_4)_2C_2O_4$	BaC_2O_4 - white precipitate is partly dissolved in strong acids is not dissolved in acetic acid	SrC_2O_4 - white precipitate is partly dissolved in strong acids is not dissolved in acetic acid	CaC_2O_4 - white precipitate is partly dissolved in strong acids is not dissolved in acetic acid

Analysis systematic course of the III^{d} analytical cations group mixture

1. *Preliminary tests and observation (see page 23)*
2. *Precipitation of Group III^{d} Cations*

Measure out 10 drops (0.5 mL) of the test solution or the unknown into a small test tube. Add 5 drops of sulfuric acid, ethanol and mix. Centrifuge and decant the supernate into a clean test tube. Test it for completeness of precipitation by adding one drop of H_2SO_4 to the clear supernate. If the supernate turns cloudy, this shows that not all of the group III cations have precipitated; add another two drops of H_2SO_4 and centrifuge. Repeat this process until no more precipitate forms. All of the group III cations must be precipitated.

3. *Transfer of sulfates cations third analytical group into carbonates*

Precipitate from Procedure №2 transferred to porcelain cup, add 15-20 drops of saturated solution of sodium carbonate and heated on a boiling water bath for 10-15 minutes. Mixture is cooled, transferred into a test tube and centrifuge. Centrifuge rejects. This procedure is repeated at least three times. Test it for completeness of conversion of sulfate in carbonates by adding few drops of CH_3COOH to a precipitate. The precipitate dissolution indicates the complete transfer of sulphates to carbonates.

4. Separation and Identification of Ba^{2+} cation

Measure out 10 drops (0.5 mL) of the solution from Procedure №3 into a small test tube. Add 5 drops of K_2CrO_4 and 5 drops of acetic acid to the precipitate. Centrifuge and decant the supernate into a clean test tube. Barium chromate is insoluble in the weak acetic acid CH_3COOH.

5. Identification of Sr^{2+} cation

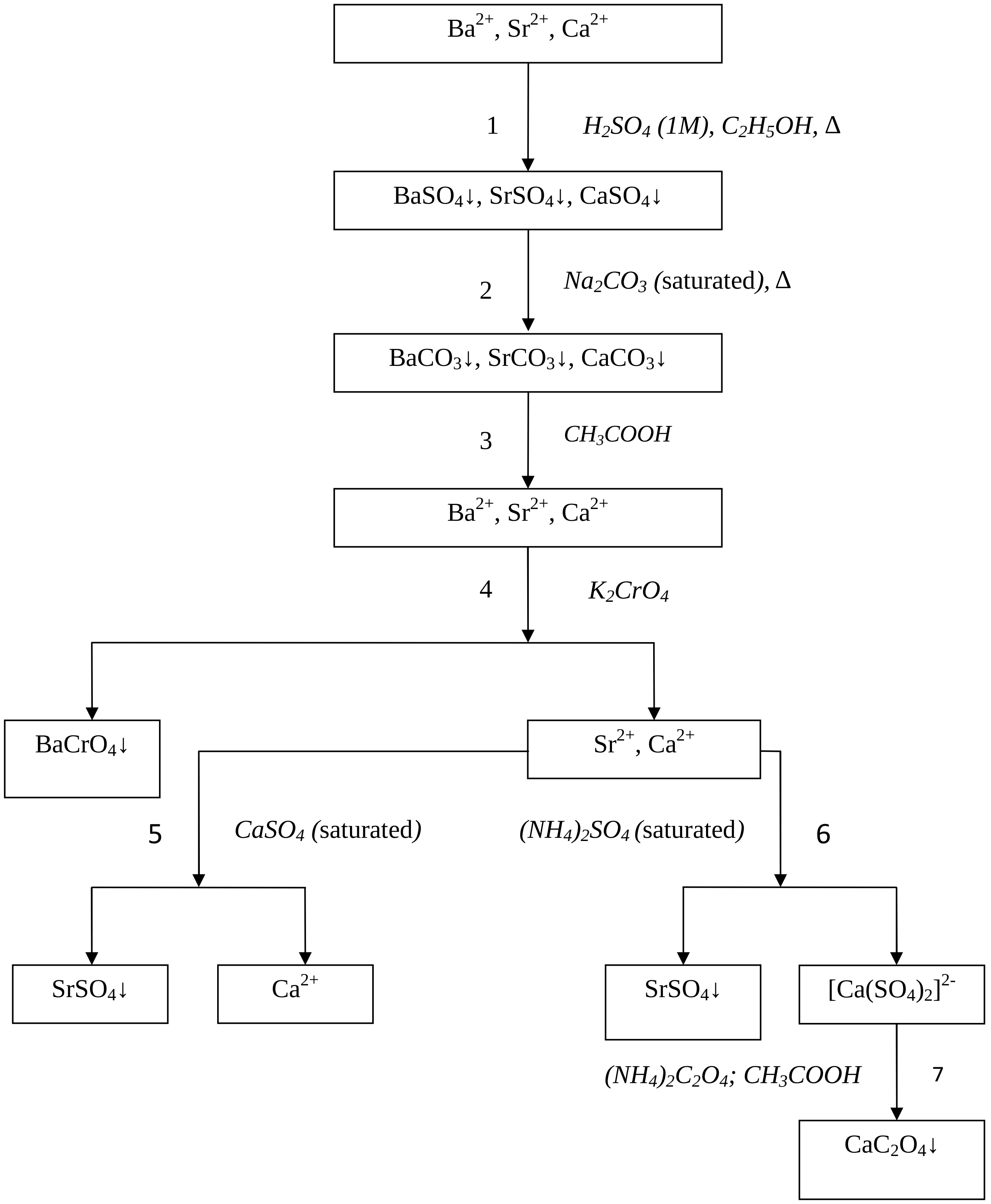
To 2-3 drops of supernate from Procedure №4 add some drops of gypsum water (calcium sulfate) and put the test tube in a hot-water bath. The formation of white precipitate indicates the presence of strontium. If strontium ions are presents then add 1,5 volumes of saturated solution of ammonium sulphate to the supernate from Procedure №4, heat on water bath during 10-15 minutes. Admixture is centrifugated and precipitate is not analyzed.

6. Identification of Ca^{2+} cation

Add some drops of ammonium oxalate $(NH_4)_2C_2O_4$ and acetic acid to the supernate from Procedure №5, put the test tube in a hot-water bath. The formation of a white precipitate indicates the presence of calcium.

Scheme 3

SCHEME OF ANALYSIS SYSTEMATIC COURSE THE III^{d} ANALYTICAL GROUP



Topic 6
Solubility Equilibria

1. The main purpose of the topic:

We use the reactions of precipitation and dissolution of precipitate, the product of solubility in the study of qualitative analysis. The term "solubility product" is important in analytical chemistry. Its application allows to understand many complex processes, namely in the processes of formation and dissolution of precipitates, in the action of the same ion on solubility, in the process of fractional precipitation, etc. The largest number of cations and anions that make up the drugs are identified by precipitation reactions.

2. Basic questions:

2.1. Solubility Equilibria and Solubility product.
2.2. Molar Solubility and Solubility.
2.3. Predicting Precipitation Reactions.
2.4. Fractional Precipitation.
2.5. The Common Ion Effect.
2.6. Effect of diverse ions on solubility of Precipitates.

4. Brief exposition of theoretical material:

When precipitate is dissolved in water, dissolving stops when saturated solution is obtained, i.e. when equilibrium sets between the solute and the molecules of the same substance in the solution. When an electrolyte dissolves, for instance, salt, not molecules, ions pass into the solution. Hence, equilibrium in a saturated solution will also set in between the precipitate salt and the ions that have passed into the solution. For example, in a saturated solution of calcium sulfate, the following equilibrium will set in:

$$CaSO_4 \leftrightarrow Ca^{2+} + SO_4^{2-}$$

The equilibrium constant for this process is

$$K = \frac{[Ca^{2+}][SO_4^{2-}]}{[CaSO_4]}$$

The denominator of the fraction—the concentration of the precipitate salt—is a constant quantity that can be introduced into the equilibrium constant. Hence, introducing the symbol

$$K\,[CaSO_4] = K^{'}$$

We obtain

$$[Ca^{2+}]\,[SO_4^{2-}] = K^{'}$$

Thus, in a saturated solution of an electrolyte, the product of the concentrations of its ions is a constant quantity at the given temperature. **Solubility product** of the compound is the product of the molar concentrations of the constituent ions, each raised to the power of its stoichiometric coefficient in the equilibrium equation. It is known as the **solubility product** (or the **solubility product constant**) of an electrolyte and is designated by the symbol K_{sp}. The value of K_{sp} indicates the solubility of an ionic compound – the smaller the value, the less soluble the compound in water.

Using $K_{sp}(CaSO_4)$ instead of K', we have:

$$K_{sp}(CaSO_4) = [Ca^{2+}][SO_4^{2-}]$$

When an electrolyte contains two or more common ions, the concentrations of these ions must be raised to the relevant powers in calculating the solubility product. For example:

$$PbI_2 \leftrightarrow Pb^{2+} + 2I^-$$

$$K_{sp}(PbI_2) = [Pb^{2+}][I^-]^2$$

There are two other ways to express a substance's solubility: **molar solubility,** which is the number of moles of solute in one liter of a saturated solution (mol/L), and **solubility,** which is the number of grams of solute in one liter of a saturated solution (g/L).

Ion Product (Q_{sp}) - the product of the concentrations of ions at any moment of time (not necessarily at equilibrium).

The ion product (Q_{sp}) can be used to determine in which direction a system must shift in order to reach equilibrium.

There are three possible situations:

$[A]^m[B]^n$ (Q_{sp}) < K_{sp} - This means there are not enough ions in the solution. In order to return to equilibrium, more of the solid salt must dissociate into its ions.

$[A]^m[B]^n$ (Q_{sp}) =K_{sp} - This means that the system is at equilibrium.

$[A]^m[B]^n$ (Q_{sp}) > K_{sp} - This means that there are too many ions in the solution. In order to return to equilibrium, the excess ions will precipitate to form more solid.

Factors Which Affect Solubility

Important solution factors which may affect the solubility of ionic substances in water.

Temperature - solubility is temperature dependent

Common ions - the presence of common ions in solution lowers solubility

pH - solution pH can affect solubility if the anion of the ionic solid is the conjugate base of weak acid

Complex ions - ammonia reacts with many metal ions in solution through complexation reactions

Common-ion effect - the decrease in the solubility of a salt that occurs when the salt is dissolved in a solution, that already contains another source of one of its ions. For example, if AgCl is added to a NaCl solution (which contains the common ion, Cl^-) the solubility of the AgCl decreases.

Fractional Precipitation

Fractional precipitation is the technique of separating two or more ions from a solution by adding a reactant that precipitates first one ion, then another, and so forth. For example, suppose a solution contains Ba^{+2} ions and Sr^{+2} ions. As we slowly add a concentrated solution of potassium chromate, K_2CrO_4, to the solution, barium chromate precipitates first (since its K_{sp} is much less than that for strontium chromate). When a larger part of the barium chromate has precipitated, strontium chromate begins to precipitate. It is therefore possible to separate Ba^{+2} ions from Sr^{+2} ions from solution by fractional precipitation.

4. Control test and patterns of responses:

4.1. The molar solubility of saturated solution of $PbCl_2$ is $1.6 \cdot 10^{-2}$M at 25°C. What is the value of K_{sp} for lead chloride at this temperature?

Answer:

The equation is*:*

$$PbCl_2 \leftrightarrow Pb^{2+} + 2Cl^-$$

The solubility product expression for $PbCl_2$ is $K_{sp} = [Pb^{2+}][Cl^-]^2$. If $1.6 \cdot 10^{-2}$ mol of $PbCl_2$ is dissolved per liter of solution, the concentration of Pb^{2+} will be $1.6 \cdot 10^{-2}$ M and the concentration of Cl^- will be twice that value, or $3.2 \cdot 10^{-2}$ M. The substitution of these values gives:

$$[Pb^{2+}] = 1.6 \cdot 10^{-2} \text{ mol/L}; [Cl^-] = 2 \cdot 1.6 \cdot 10^{-2} = 3.2 \cdot 10^{-2} \text{ mol/L}$$

$$K_{sp} = [1.6 \cdot 10^{-2} \text{ M}] [3.2 \cdot 10^{-2}]^2 = 1.6 \cdot 10^{-5}$$

The K_{sp} for $PbCl_2$ in water is $1.6 \cdot 10^{-5}$ at 25°C.

4.2. The value of K_{sp} for AgCl is $1.7 \cdot 10^{-10}$ at 25°C. What is the molar solubility of AgCl in water at that temperature?

Answer:

The equation is:

$$AgCl \leftrightarrow Ag^+ + Cl^-$$

The solubility product expression for AgCl is therefore $K_{sp} = [Ag^+] [Cl^-]$. If *x* moles of AgCl is dissolved per liter of solution, the concentrations of Ag^+ and Cl^- will both be equal to *x* at equilibrium. Thus you have:

$$K_{sp} = [x] [x] = x^2 = 1.7 \cdot 10^{-10}$$

$$x = \sqrt{1.7 \cdot 10^{-10}} = 1.3 \cdot 10^{-5} M$$

$$x = 1.3 \cdot 10^{-5} \text{M}$$

The molar solubility of AgCl in water is $1.3 \cdot 10^{-5}$ M at 25°C.

4.3. If the K_{sp} for PbI_2 is $7.1 \cdot 10^{-9}$, will precipitation of PbI_2 take place when 10 mL of $1.0 \cdot 10^{-4}$ M $Pb(NO_3)_2$ is mixed with 10 mL of $1.0 \cdot 10^{-3}$ M KI?

Answer:

$$Pb(NO_3)_2 + 2KI \rightarrow PbI_2 + 2KNO_3$$

$$PbI_2 \leftrightarrow Pb^{2+} + 2I^-$$

$$K_{sp} = [Pb^{2+}] [I^-]^2 = 7.1 \cdot 10^{-9}$$

Precipitation will take place if $[Pb^{2+}] [I^-]^2 > 7.1 \cdot 10^{-9}$

$$\left[Pb^{2+}\right] = \frac{10mL \cdot 1.0 \cdot 10^{-4} M}{20mL} = 5.0 \cdot 10^{-5} M$$

$$\left[I^-\right] = \frac{10mL \cdot 1.0 \cdot 10^{-3} M}{20mL} = 5.0 \cdot 10^{-4} M$$

$$Q = [Pb^{2+}] [I^-]^2 = (5.0 \cdot 10^{-5}) (5.0 \cdot 10^{-4})^2 = 1.3 \cdot 10^{-11}$$

Since $1.3 \cdot 10^{-11} < 7.1 \cdot 10^{-9}$, no precipitation will take place. However, if 10 mL of $1.0 \cdot 10^{-2}$ M $Pb(NO_3)_2$ is added to 10 mL of $2.0 \cdot 10^{-2}$ M KI, then

$$\left[Pb^{2+}\right] = \frac{10mL \cdot 1.0 \cdot 10^{-2} M}{20mL} = 5.0 \cdot 10^{-3} M$$

$$\left[I^{-}\right] = \frac{10mL \cdot 2.0 \cdot 10^{-2}M}{20mL} = 1.0 \cdot 10^{-2}M$$

and

$$[Pb^{2+}]\,[I^-]^2 = (5.0 \cdot 10^{-3})\,(1.0 \cdot 10^{-2})^2 = 5.0 \cdot 10^{-7}$$

Because $5.0 \cdot 10^{-7} > 7.1 \cdot 10^{-9}$, precipitation of PbI_2 will tak place in this solution.

5. Tasks for individual work (write in a textbook for protocols):

5.1. How many grams of $BaSO_4$ will be dissolved in 200 mL of water?

5.2. The K_{sp} for AgCl is $1.78 \cdot 10^{-10}$. Will AgCl be precipitated upon mixing 10 mL of 0.01M $AgNO_3$ with 10 mL of 0.01M NaCl?

5.3. The solubility product of $PbBr_2$ is $8,9 \cdot 10^{-6}$. Determine the molar solubility (a) in pure water, (b) in 0,20M KBr solution, (c) in 0,20M $Pb(NO_3)_2$ solution.

Topic 7

Analysis systematic course of mixture of the I^{st} –III^{d} analytical group cations

1. The main purpose of the topic:

Inorganic drugs, which contain more than one cation, but several are widely used in medical practice. And a lot of cations with the same reagents give similar analytical effects. The analysis of the I^{st} *–*III^{d} *analytical group cations mix is based on the comprehension of the characteristic reactions of metal cations of the* I^{st} *–*III^{d} *analytical groups, the conditions for their implementation, the properties of compounds that contain cations of these metals. But it is impossible to identify individual ions using analytical reactions in a randomly selected order. Therefore a systematic course of cations mixtures analysis is often used in practice.*

Comprehension of a systematic course of mixtures of I^{st} *–*III^{d} *analytical group cations analysis creates for students the theoretical base of chemical analysis, practical skills and experience of performance.*

2. Basic questions:

2.1. Characteristic reactions of the first analytical group cations (acid – base classification). The analysis of the I^{st} analytical group cations mix.

2.2. Characteristic reactions of the second analytical group cations. The analysis of a mix of the II^{nd} analytical group cations mix.

2.3. Characteristic reactions of the third analytical group cations. The analysis of the III^{d} analytical group cations mix.

3. Brief exposition of theoretical material:

Analysis systematic course of a mixture of the I^{st} –III^{d} analytical group cations

Mixture analysis should begin from trial tests and observations: colour, odour flame colouring, relation to water, acetic and inorganic acids, heating, definition;

environment pH etc. It allows to make preliminary conclusions about availability of some cations in a mixture. The low values of pH indicate possible presence in solution of free acids or cations, which strongly hydrolyze, for example Hg_2^{2+}.

After carrying out of preliminary tests in separate sample NH_4^+ ions are fonud by action of alkali solution at heating. If ammonium ions are identified, they must be removed from a solution, as they prevent detection of K^+, Na^+ ions.

For Na^+ ions detection to the separate portion of solution KOH or K_2CO_3 add. Then they are heated up till complete (check by Nessler reagent) ammonia removing. The cooled mixture is centrifuged. There are K^+ and Na^+ cations in centrifugate and there are oxides, carbonates and basic salts of cations of the II^nd^, III^d^ of analytical groups in precipitate. Then the centrifugate is neutralized by acetic acid, and, if necessary, evaporated, cooled and found out ions of sodium by the action of $K[Sb(OH)_6]$ $Zn(UO_2)_3(CH_3COO)_8$ solutions.

For K^+ ions detection ammonia is removed from the investigated solution by action of NaOH or Na_2CO_3 at heating till complete (check by Nessler reagent) removing of ammonia. Centrifug is neutralized by CH_3COOH, if necessary evaporated, cooled and found out K^+ by action of $NaHC_4H_4O_6$, $Na_3[Co(NO_2)_6]$ solutions or by microcrystalloscopic reaction with $Na_2Pb[Cu(NO_2)_6]$.

Cations of the II^{nd} analytical group are precipitated from the starting solution by action of 2 M solution of HCl by the way of insoluble chlorides (AgCl, Hg_2Cl_2, $PbCl_2$). Resulting precipitate is separated and anylised according to the analysis course of mixture of the II^{nd} analytical group cations. Centifugate contains cations of the III^{d} analytical group (Ba^{2+}, Sr^{2+}, Ca^{2+}) and Pb^{2+}, which are precipitated only fractionally by the action of HC1 and prevent further analysis.

1M solution of H_2SO_4 and ethanol is added to centrifugate, at that the precipitate ($BaSO_4$, $SrSO_4$, $CaSO_4$, $PbSO_4$) is formed. It is washed out by solutions of ammonium acetatete or alkali before complete Pb^{2+} cations removing. The remained precipitate is analysed according to the analysis course of the III^{d} analytical group cations mixture.

4. Tasks for individual work (write in a textbook for protocols):

4.1. Potassium chromate solution was added to the solution which contains cations of the I^{st}–III^{d} analytical groups and acetic acid. Write the equations of the conforming reactions and explain the analytical effects.

4.2. Why is it necessary to transfer sulphates of the III^{d} analytical group cations into carbonates in the cause of analysis?

4.3. Why is it necessary to separate lead sulphate $PbSO_4$ from sulphates of the III^{d} analytical group cations when systematic course of analysis of the III^{d} analytical group cations mixture is performed? What reagent can be used for this purpose? Write the equations of the conforming reactions.

4.4. Suggest the systematic analysis of solution which contains ions:

- NH_4^+, Ag^+, Hg_2^{2+}, Ca^{2+};
- K^+, Pb^{2+}, Ba^{2+}, Sr^{2+};
- Na^+, Pb^{2+}, Ca^{2+}.

The situation problems are solved according to the analysis systematic course of the III^{d} analytical group cations mixture.

5. Laboratory experiment

Laboratory experiment 5.1.

Analysis systematic course of a mixture of the Ist – III^{d} analytical group cations (without a precipitate)

1. Preliminary observations and testing (see page 23)

2. Finding ammonium cations in the separate sample

Ammonium cations are found by adding of surplus of 2M solution of sodium or potassium hydroxide under heating.

3. Finding potassium cations

Add 4-5 drops of 2M solution of sodium carbonate to 5-6 drops of the analyzable solution. The admixture is heated on water bath up to eliminating of ammonia (if ammonium ions are present). The formed precipitate of oxides, carbonates, basic salts of cations of IInd and III^{d} groups of cations are separated by centrifugation. The centrifugate is neutralized by acetic acid up to neutral medium (litmus test), concentrated by evaporation and find potassium ions by reactions with $NaHC_4H_4O_6$ or $Na_3[Co(NO_2)_6]$.

4. Finding of sodium cations

Add 4-5 drops of 1M solution of potassium carbonate to 5-6 drops of the analyzable solution. The admixture is heated on water bath up to full eliminating of ammonia (if ammonia ions are present). The formed precipitate of basic salts and carbonates of IInd and III^{d} groups cations is separated by centrifugation. The centrifugate is neutralized by acetic acid up to neutral medium (litmus test), concentrated by evaporation and sodium ions are identified by reactions with $K[Sb(OH)_6]$ or $Zn(UO_2)_3(CH_3COO)_8$.

5. Test for the presence of IInd analytical group cations in the solution

Measure out 3-5 drops of the test solution or the unknown into a small test tube. Add 5-6 drops of 2M HCl. The formation of white precipitates indicates the presence of Group II.

6. Separation of IInd analytical group cations

Measure 30-35 drops of the test solution or the unknown into a small test tube. Add 40 drops of the 2M HCl and then centrifuge them. Test it for completeness of precipitation by adding one drop of 2M HCl to the clear supernate. If the supernate turns cloudy, this shows that not all of the group II cations have precipitated, add another two drops of 2M HCl and centrifuge them. Repeat this process until no more precipitate forms. All of the group II cations must be precipitated.

The precipitate contains the group II insoluble chlorides, while the supernate liquid may contain cations from groups I, III and Pb^{2+}. Decant the supernate into a clean test tube and save it for analysis of group I and III cations.

Wash the precipitate by adding five drops of cold distilled water and stirring.

6.1 Separation and identification of Pb^{2+}

Add 15 drops of distilled water to the precipitate and place the test tube in a hot-water bath. Stir it with a stirring rod and heat the test tube for 1 min or longer. Quickly centrifuge and decant the hot supernate into a clean test tube. Repeat this procedure twice, combining the supernate, which should contain Pb^{2+} if itis present. Save the precipitate for next procedure. Add three drops of 1M K_2CrO_4 or KI to the supernate. The formation of yellow precipitate, indicates the presence of Pb^{2+}.

6.2 Separation and identification of Ag^+ and Hg_2^{2+}

Add 10 drops of 6 M $NH_3 \cdot H_2O$ to the precipitate from Procedure №2.1. The formation of dark gray precipitate indicates the presence of mercury. Centrifuge and decant the clear supernate into a clean teat tube. Add 20 drops of 6 M HNO_3 to the decantate. Stir the solution and test its acidity. Continue to add HNO_3 dropwise until the solution is acidic. A white cloudiness confirms the presence of Ag^+.

7. Test for the presence of III^d analytical group cations in the solution

Add 10 drops of the supernate from Procedure №2 into a small test tube. Add some drops of 1M H_2SO_4 and C_2H_5OH. The formation of white precipitate indicates the presence of Group III cations. Centrifuge. The precipitate contains the group III insoluble sulfates and $PbSO_4$, while the supernate liquid may contain cations from group I.

8. Separation of Pb^{2+} cations and identification cations of III^d analytical group

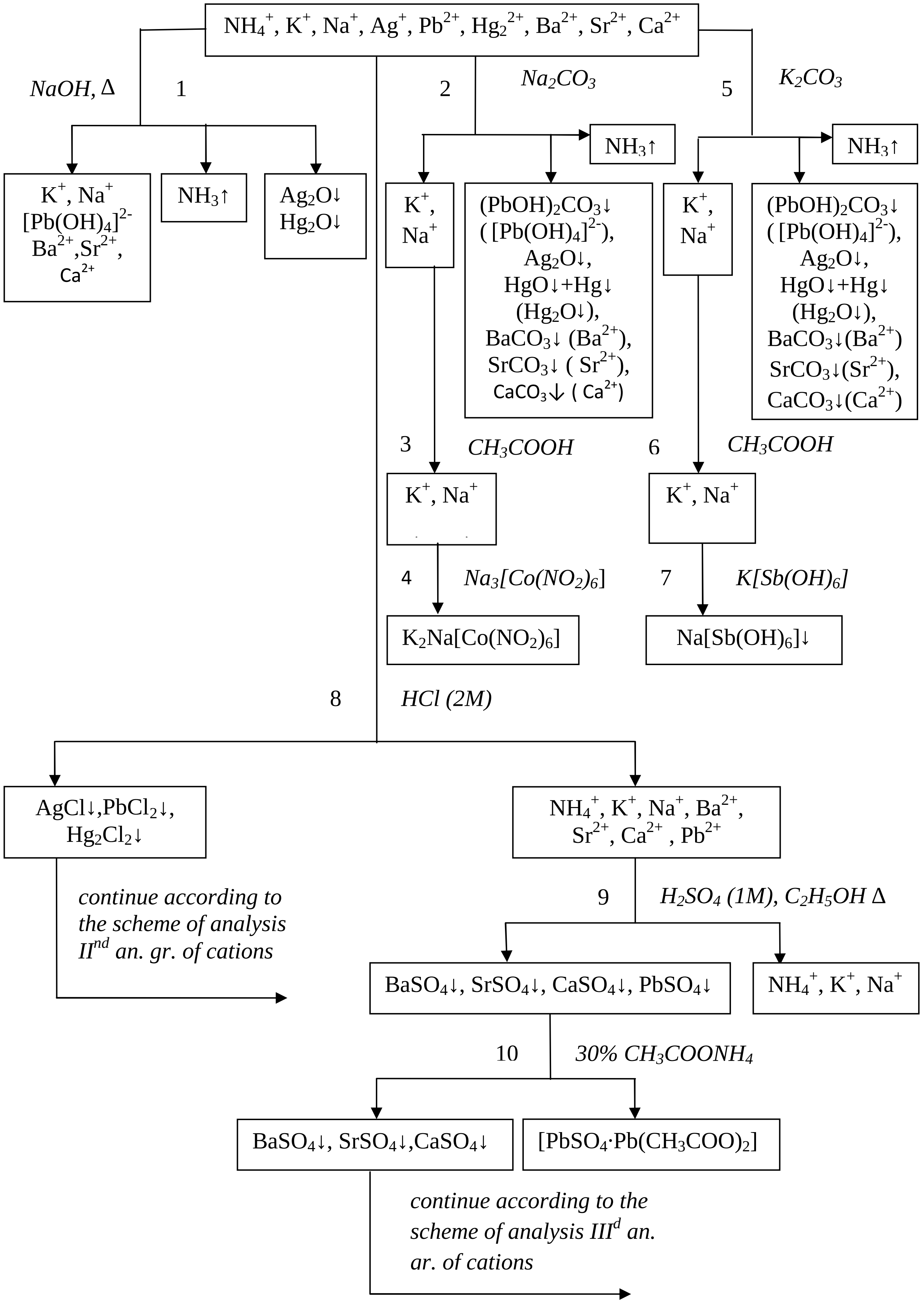
Add the precipitate from Procedure 3 into a small test tube. Add 15-20 drops of 30% CH_3COONH_4 and put the test tube in a water bath. Quickly centrifuge it. The precipitate contains the group III insoluble sulfates. Transfer the contents to an evaporating dish, add 30 drops of Na_2CO_3. Boil the mixture for 3 min. Add more Na_2CO_3 and boil 3 min. Repeat this operation three time. Dissolve the precipitate in some drops of acetic acid. Add some drops of K_2CrO_4. The formation of yellow precipitate indicates the presence of barium.

Centrifuge and divided the supernate into the two test tubes. Add some drops of gypsum water (calcium sulfate) to the supernate and put the test tube in a water bath. The formation of white precipitate indicates the presence of strontium.

Add some drops of ammonium oxalate $(NH_4)_2C_2O_4$ and acetic acid to another supernate, put the test tube in a water bath. The formation of white precipitate indicates the presence of calcium.

SCHEME OF ANALYSIS SYSTEMATIC COURSE THE Ist-III^{d} ANALYTICAL GROUP CATIONS

Scheme 4



Topic 8
Analysis systematic course of mixture of the Ist – III^{d} analytical groups cations
Experimental control problem

Objective: identifying cations of the Ist – III^{d} analytical groups in the mixture, using analysis systematic course of mixture of the Ist – III^{d} analytical groups cations.

Laboratory experiment 8.1.

Each student receives solution from the teacher and applying systematic analysis of a mix of the Ist – III^{d} analytical group cations detects what cations are present in it. Describe in writing procedure of the analysis, the reactions, observations and conclusions in the laboratory copybook.

Thematic Module 1

Objective: checking the students comprehension that they were given at the lectures and practical lessons in the following sections:

1. Characteristic reactions of the Ist analytical group cations. Analysis systematic course of the Ist analytical group cations (topic 1).
2. Sensitivity of Chemistry Reactions (topic 2).
3. Characteristic reactions of the IInd analytical group cations. Analysis systematic course of the IIst analytical group cations (topic 3).
4. Ionization theory (topic 4).
5. Characteristic reactions of the III^{d} analytical group cations. Analysis systematic course of the III^{d} analytical group cations (topic 5).
6. Solubility Equilibria (topic 6).
7. Analysis systematic course of mixture of the Ist – III^{d} analytical group cations (topic 7).

Control card of thematic module 1 includes the tasks:

- 8 tests. You must choose the correct answer and give a brief explanation, write the corresponding equations of chemical reactions;
- 4 calculation problems. You must write the corresponding equations of chemical reactions, write the formula that used in the course of solving the problem, and perform the necessary calculations to indicate the unit of measurement calculated parameters.

Topic 9
Chemistry of the IVth Group Cations
Analysis systematic course of the IVth analytical group cations

1. The main purpose of the topic:

Many medicines, which contain compounds of aluminum, lead and mercury cations are used in medical practice because they possess antiseptic properties.

Aluminum hydroxide in the form of suspensions in the mixture with magnesium hydroxide (almagelum) is used for treating gastritis and stomach ulcer as an antiacidic, absorbent and covering agent. Alums $KAl(SO_4)_2 \times 12H_2O$ *are applied as a hemostatic agent.*

Zinc sulphate suppresses reproduction of microorganizms. Therefore zinc sulphate solutions (w=0.25% and w=0.3%) are applied in medical practice as eye drops. The zinc oxide ZnO *is used in dermatology as ointments and powders as an astringent and antimicrobial agent.*

Arsenic oxide possesses a necrotizing effect when applied topically, that's why it is used in stomatology. Sodium arsenate in therapeutic doses stimulates the formation of red blood cells, so it is used as a fortifying agent.

Chromium, arsenic, tin as microelements take a very important biological part in the human's organism. But in the high doses the metals and their compounds are very poisonous.

Comprehension of the characteristic reactions of cations of these metals and conditions of their performance is making for students the theoretical base of chemical analysis, practical skills and experience of making it and also bases the subsequent study of such core of disciplines as pharmaceutical chemistry, pharmacognosicy, forensic chemistry, technology of drugs, etc. for future specialists in pharmacy.

2. Basic questions:

2.1. Cations of the IVth analytical group (acid – base classification), general characteristic.
2.2. Group reagent for the IVth analytical group cations and condition of their application.
2.3. Characteristic reactions of Al^{3+} cation.
2.4. Characteristic reactions of Cr^{3+} cation.
2.5. Characteristic reactions of Zn^{2+} cation.
2.6. Characteristic reactions of Sn^{2+} cation.
2.7. Characteristic reactions of Sn(IV).
2.8. Characteristic reactions of As(III).
2.9. Characteristic reactions of As(V).
2.10. Analysis systematic course of the IVth analytical group cations.

3. Brief exposition of theoretical material:

General characteristic of the IVth analytical group cations
Al^{3+}, Cr^{3+}, Zn^{2+}, Sn^{2+}, Sn(IV), As(III), As(V)

Cations of p-elements: Al^{3+}, Sn^{2+}, Sn (IV), As (III), As (V), and of d-ements: Cr^{3+}, Zn^{2+} belong to the IVth analytical group.

Cations of p- and d-elements have strong polarizing activity that stipulates formation of many slightly soluble compounds (sulfides, phosphates, carbonates, hydroxides etc.).

Ions of p-elements (Sn, As) and of d-elements (Cr) with incomplete 18-electronic shell are easily engaged in oxidation-reduction reactions, which are used in the analysis for the detection and separation of these ions.

Hydroxides of IVth analytical group cations are amphoteric, therefore under the action of NaOH solution excess they are transferred to appropriate hydroxoanions.

Group reagent of this group is 6 M solution of NaOH in the presence of 3 % solution of H_2O_2. At action of group reagent at first precipitates of hydroxides fall, which is dissolved in NaOH excess. H_2O_2 presence stipulates the formation of hydroxoanions and oxoanions of these elements at the highest rates of oxidation. At the same time the cations of Vth, VIth analytical groups are precipitated as oxyhydroxides, but hydroxoanions and oxoanions of IVth analytical group remain in the solution. These anions are capable of hydrolysis, but in a different degree. That property is used in the analysis systematic course for separation of $[Al(OH)_6]^{3-}$ and $[Sn(OH)_6]^{2-}$ ions as appropriate hydroxides.

4. Control test and patterns of responses:

4.1. NaOH solution excess was added to solution containing cations of the IVth analytical group cations, and then solution was boiled. It resulted in generation of green precipitate. Write the equations of the conforming reactions and explain the analytical effects.

Answer:

6M solution of NaOH is group reagent of this group IVth analytical group cations. At action of group reagent at first precipitates of hydroxides of cations fall:

$$A1^{3+} + 3OH^- \rightleftarrows A1(OH)_3\downarrow$$
$$Zn^{2+} + 2OH^- \rightleftarrows Zn(OH)_2\downarrow$$
$$Cr^{3+} + 3OH^- \rightleftarrows Cr(OH)_3\downarrow$$
$$Sn^{2+} + 2OH^- \rightleftarrows Sn(OH)_2\downarrow$$
$$[SnCl_6]^{2-} + 4OH^- \rightleftarrows Sn(OH)_4\downarrow + 6Cl^-$$

All precipitates are white except $Cr(OH)_3\downarrow$ (green).

Hydroxides of cations of the IVth analytical group have amphoteric properties therefore they are dissolved in alkali excess:

$$Al(OH)_3\downarrow + 3OH^- \rightleftarrows [Al(OH)_6]^{3-}$$
$$Zn(OH)_2\downarrow + 2OH^- \rightleftarrows [Zn(OH)_4]^{2-}$$
$$Cr(OH)_3\downarrow + 3OH^- \rightleftarrows [Cr(OH)_6]^{3-}$$
$$Sn(OH)_2\downarrow + 4OH^- \rightleftarrows [Sn(OH)_6]^{4-}$$
$$Sn(OH)_4\downarrow + 2OH^- \rightleftarrows [Sn(OH)_6]^{2-}$$

Arsenic as the element of secondary subgroup of the V^th^ group of the periodic system has expressed non-metallic properties, and in acids and alkalis solutions it predominantly acts as AsO_3^{3-} AsO_4^{3-} anions.

Unlike other ions hydroxoanions of $[Cr(OH)_6]^{3-}$ and $[Sn(OH)_6]^{4-}$ when boiling hydrolyzed nonreversibly:

$$[Cr(OH)_6]^{3-} + 3H_2O \xrightarrow{\Delta} H_3[Cr(OH)_6] + 3OH^-$$

$$[Sn(OH)_6]^{4-} + 4H_2O \xrightarrow{\Delta} H_4[Sn(OH)_6] + 4OH^-$$

Obtained acids are nonresistant and destoy:

$$H_3[Cr(OH)_6] \xrightarrow{\Delta} Cr(OH)_3\downarrow + 3H_2O \quad \text{green}$$

$$H_4[Sn(OH)_6] \xrightarrow{\Delta} Sn(OH)_2\downarrow + 4H_2O \quad \text{white}$$

Thus, the described analytical effect indicates the presence of Cr^{3+} cations in the solution.

5. Tasks for individual work (write in a textbook for protocols):

5.1. What properties of hydroxides of IV^th^ analytical group cations their dissolution in excess of NaOH solution are based on? Write the equations of the conforming reactions.

5.2. Which reactions are used for separation of Al^{3+}, Sn(IV) from another cations of Group IV? Write the equations of the conforming reactions and explain the analytical effects.

5.3. Why can Cr^{3+} cations be identified by action of group reagent of IV^th^ analytical group cations in the presence of 3 % solution of H_2O_2? Write the equations of the conforming reactions.

5.4. Suggest the systematic analysis of solution which contains ions:

- Al^{3+}, Zn^{2+}, Sn^{2+};
- Cr^{3+}, Zn^{2+}, As(III);
- Al^{3+}, Cr^{3+}.

The situation problems are solved according to the analysis systematic course of the IV^th^ analytical group cations mixture.

6. Laboratory experiment

Laboratory experiment 6.1.

Characteristic reactions of the IV^th^ analytical group cations and condition of their detection

1. Reaction with precipitating agent NaOH

All cations of Group IV may be precipitated and separated from the cations of another groups by the addition of 4M NaOH:

$Al^{3+} + 3OH^- \leftrightarrow Al(OH)_3$ white
$Cr^{3+} + 3OH^- \leftrightarrow Cr(OH)_3$ gray-green
$Zn^{2+} + 2OH^- \leftrightarrow Zn(OH)_2$ white
$Sn^{2+} + 2OH^- \leftrightarrow Sn(OH)_2$ white

All hydroxides are amphoteric and are dissolved in excess sodium hydroxide NaOH, forming the soluble complex ions:

$$Al(OH)_3 + 3OH^- \rightarrow [Al(OH)_6]^{3-}$$
$$Cr(OH)_3 + 3OH^- \rightarrow [Cr(OH)_6]^{3-}$$
$$Zn(OH)_2 + 2OH^- \rightarrow [Zn(OH)_4]^{2-}$$
$$Sn(OH)_2 + 2OH^- \rightarrow [Sn(OH)_4]^{2-}$$
$$Sn(OH)_4 + 2OH^- \rightarrow [Sn(OH)6]^{2-}$$

All hydroxides can also be dissolved in strong acids:

$$Al(OH)_3 + 3H^+ \rightarrow Al^{3+} + 3H_2O$$
$$Cr(OH)_3 + 3H^+ \rightarrow Cr^{3+} + 3H_2O$$
$$Zn(OH)_2 + 2H^+ \rightarrow Zn^{2+} + 2H_2O$$
$$Sn(OH)_2 + 2H^+ \rightarrow Sn^{2+} + 2H_2O$$

The $Cr(OH)_3$ is also dissolved, being oxidized by H_2O_2 to form CrO_4^{2-}:

$$\begin{array}{l|l} -3e + [Cr(OH)_6]^{3-} + 2OH^- \leftrightarrow CrO_4^{2-} + 4H_2O & 2 \\ +2e + H_2O_2 \leftrightarrow 2OH^- & 3 \\ \hline \end{array}$$
$$[Cr(OH)_6]^{3-} + 3H_2O_2 \rightarrow 2CrO_4^{2-} + 8H_2O + 2OH^-$$

yellow

<u>Procedure:</u> Pour 3-5 drops of the aluminum, chromium and zinc salts in small test tubes, add 2 drops of 4M sodium hydroxide. Dissolve all precipitates in 4M NaOH and in strong acid. Pour 3-5 drops of the chromium salt in a small test tube, add 10 drops of 4M NaOH and H_2O_2. Heat the test tube in a boiling-water bath for some minutes.

2. Properties of the $[Al(OH)_6]^{3-}$, $[Cr(OH)_6]^{3-}$ and $[Zn(OH)_4]^{2-}$

When the solution is treated with aqueous ammonium chloride, aluminum and chromium precipitates as $Al(OH)_3$ and $Cr(OH)_3$:

$$[Al(OH)_6]^{3-} + 3NH_4^+ \leftrightarrow Al(OH)_3 + 3NH_4OH \qquad \text{white}$$
$$[Cr(OH)_6]^{3-} + 3NH_4^+ \leftrightarrow Cr(OH)_3 + 3NH_4OH \qquad \text{gray-green}$$

$Zn(OH)_2$ is not precipitated because zinc hydroxide is dissolved in aqueous ammonium chloride:

$$[Zn(OH)_4]^{2} + 2NH_4^+ \leftrightarrow Zn(OH)_2 + 2NH_4OH$$
$$Zn(OH)_2 + 6NH_4OH \rightarrow [Zn(NH_3)_6]^{2+} + 6H_2O + 2OH^-$$

<u>Procedure:</u> Pour 3-5 drops of the aluminum, chromium and zinc salts in small test tubes, add 10 drops of 4M sodium hydroxide and ammonium chloride.

Zinc (Zn^{2+}) ions reactions (colorless)

1. Zinc can be precipitated from aqueous solution as white salt by adding of the reagent potassium hexacyanoferrate (II), $K_4[Fe(CN)_6]$:

$$3Zn^{2+} + 2K_4[Fe(CN)_6] \leftrightarrow K_2Zn_3[Fe(CN)_6]_2\downarrow + 6K^+ \qquad \text{white}$$

<u>Procedure:</u> Pour 2-3 drops of the zinc salt in a small test tube, add 3 drops of $K_4[Fe(CN)_6]$. Heat the test tube in a boiling-water bath for some minutes.

2. Reaction by dry method

$$Zn(NO_3)_2 + Co(NO_3)_2 \rightarrow CoZnO_2 + 4NO_2 + O_2$$

<u>Procedure:</u> Moisten a piece of filter paper with aqueous zinc nitrate and cobalt nitrate and burn this paper in the evaporating dish. In the presence of Zn^{2+} the ash turns green. Cr^{3+}, Al^{3+}, Ni^{2+} and Cu^{2+} - ions interfere with this test for zinc ions.

3. Reaction with ditizon

The presence of Zn^{2+} is confirmed by the formation of a red inorganic and organic layer, when an organic compound called ditizon is added to solution.

<u>Procedure:</u> Pour 2-3 drops of the zinc salt in a small test tube, add some drops of ditizon.

Chromium (Cr^{3+}) ions reactions (dark-green)

1. Reaction with hydrogen peroxide

$$Cr^{3+} + 3OH^- \leftrightarrow Cr(OH)_3\downarrow \qquad \text{gray-green}$$

$$Cr(OH)_3 + 3OH^- \rightarrow [Cr(OH)_6]^{3-}$$

$$\begin{array}{l|l} -3e + [Cr(OH)_6]^{3-} + 2OH^- \leftrightarrow CrO_4^{2-} + 4H_2O & 2 \\ +2e + H_2O_2 \leftrightarrow 2OH^- & 3 \\ \hline \end{array}$$

$$2[Cr(OH)_6]^{3-} + 3H_2O_2 \rightarrow 2CrO_4^{2-} + 4H_2O + 2OH^-$$

yellow

<u>Procedure:</u> Pour 2-3 drops of the chromium salt in a small test tube, add 10 drops of 2M NaOH and 2-3 drops of 3% hydrogen peroxide. Heat the test tube in a boiling-water bath for some minutes.

2. The formation of a H_2CrO_6

<u>Procedure:</u> Pour 2-3 drops of the chromium salt in a small test tube, add 5-10 drops of 2M NaOH. Add 1 drop of 30% or 6-8 drops of 3% hydrogen peroxide. Heat the test tube in a boiling-water bath for 3-4 minutes. In the presence of Cr^{3+} the solution turns yellow. Add some drops of nitric acid HNO_3. The solution turns orange.

$$2CrO_4^{2-} + H^+ \rightarrow Cr_2O_7^{2-} + OH^- \qquad \text{orange}$$

Add 2-3 drops of 3% hydrogen peroxide and 6-8 drops of chloroform. The formation of blue colour indicates the presence of chromium.

$$Cr_2O_7^{2-} + 4H_2O_2 + 2H^+ \rightarrow 2H_2CrO_6 + 3H_2O \qquad \text{blue}$$

3. Oxidation Cr^{3+} cations to the $Cr_2O_7^{2-}$ anions, in acidic solution, by potassium permanganate.

<u>Procedure:</u> Pour 4-5 drops of the $Cr_2(SO_4)_3$ in a small test tube, add 3-4 drops of sulfuric acid and 10 drops 0,1N solution of potassium permanganate. Heat the test tube in a boiling-water bath for some minutes. The solution turns orange.

4. Oxidation Cr^{3+} cations to the $Cr_2O_7^{2-}$ anions, in acidic solution, by $(NH_4)_2S_2O_8$.

<u>Procedure:</u> Pour 5-6 drops of the $(NH_4)_2S_2O_8$ solution in a small test tube, add 1 drop of silver nitrate and 2-3 drops of chromium sulfate or chromium nitrate. Heat the test tube in a boiling-water bath for some minutes. The solution turns orange. Then cool the test tube and add 2-3 drops of 3% solution of H_2O_2 and 6-8 drops of chloroform. The organic layer turns blue.

Aluminum (Al^{3+}) ions reactions (colorless)

The confirmatory test for aluminum involves dissolving the aluminum hydroxide in acid and then re-precipitating it again with ammonia in the presence of Aluminon (alizarin) reagent. As the aluminum hydroxide precipitates, it absorbs the Aluminon reagent and assumes red coloration known as a “lake”.

$$Al^{3+} + 3NH_3 \cdot 3H_2O \rightleftarrows Al(OH)_3\downarrow + 3NH_4^+$$

$$Al(OH)_3 + H_2Alis \rightleftarrows Al(OH)_2(HAlis)\downarrow + H_2O$$

red lake

<u>Procedure:</u> Pour 3 drops of aluminum salt in a small test tube, add 4 drops of sodium hydroxide. Dissolve aluminum hydroxide in acid and add 3 drops of aqueous ammonia and Aluminon reagent.

Tin (Sn^{2+} and Sn^{4+}) ions reactions (colorless)

In the presence of hydrochloric acid, tin(II) in aqueous solution (1) is precipitated by hydrogen sulphide as *brown* SnS, and (2) will reduce mercury(II) chloride first to mercury(I) chloride (white precipitate) and then to metallic mercury. Tin(IV) in aqueous acid gives *yellow* precipitate with hydrogen sulphide, and no reaction with mercury(II) chloride.

Arsenic (As(III)) ions reactions (colorless)

Depending on its toxicity, it is often necessary to be able to detect arsenic when present only in small amounts in other substances.

1. Arsenic present only in traces (in any form) can be detected by reducing it to arsine (AsH_3) and then applying tests for the latter. In Marsh's test, dilute sulfuric acid is added dropwise through a thistle funnel to some arsenic-free zinc in a flask; hydrogen is evolved and led out of the flask by a horizontal delivery tube. Then the arsenic containing compound is added to the zinc-acid solution, and the delivery tube is heated in the middle. If arsenic is present, it is reduced to arsine by the zinc-acid reaction, for example:

$$\begin{array}{l|l} +8e + AsO_4^{3-} + 11H^+ \leftrightarrow AsH_3\uparrow + 4H_2O & 1 \\ -2e + Zn^0 \leftrightarrow Zn^{2+} & 4 \\ \hline AsO_4^{3-} + 4Zn + 11H^+ \rightarrow AsH_3\uparrow + 4Zn^{2+} + 4H_2O & \end{array}$$

$$\begin{array}{l|l} +e + Ag^+ \leftrightarrow Ag\downarrow & 6 \\ -6e + AsH_3\uparrow + 3H_2O \leftrightarrow AsO_3^{3-} + 9H^+ & 1 \\ \hline 6Ag^+ + AsH_3\uparrow + 3H_2O \rightarrow AsO_3^{3-} + 9H^+ + 6\,Ag\downarrow & \end{array}$$

The evolved arsine is decomposed to arsenic and hydrogen at the heated zone of the delivery tube; hence arsenic deposits as a shiny black mirror beyond the heated zone.

<u>Procedure:</u> Pour free zinc to a small test tube, add 5-7 mL 5HCl and 10 drops of arsenic solution. Moisten the filtration paper with aqueous $AgNO_3$ and put the paper on the test tube. The paper turns black.

2. Silver nitrate react with arsenic ions $AgNO_3$

Arsenic can be precipitated from aqueous solution as yellow solids by adding the reagent silver nitrate.

$$AsO_3^{3-} + 3Ag^+ \rightarrow Ag_3AsO_3 \qquad \text{yellow}$$

<u>Procedure:</u> Pour 2-3 drops of arsenic salt into a small test tube, add 2-3 drops of silver nitrate.

Table 7

Action of some reagents to the IVth analytical group cations

Reagent	Cations						
	As(III), AsO_3^{3-}	As(V), AsO_4^{3-}	Al^{3+}	Cr^{3+}	Zn^{2+}	Sn^{2+}	Sn(IV), $[SnCl_6]^{2-}$
KOH or NaOH	—	—	$Al(OH)_3$↓ white	$Cr(OH)_3$↓ green	$Zn(OH)_2$↓ white	$Sn(OH)_2$↓ white	$Sn(OH)_4$↓ white
			precipitates are dissolved in reagent excess				
H_2O_2 in alkali media	AsO_4^{3-} colour-less solution	AsO_4^{3-} colour-less solution	$[Al(OH)_6]^{3-}$ colourless solution	CrO_4^{2-} yellow solution	$[Zn(OH)_4]^{2-}$ colourless solution	$[Sn(OH)_6]^{4-}$ colourless solution	$[Sn(OH)_6]^{2-}$ discolor solution
$K4[Fe(CN)_6]$	—	—	—	—	$K_2Zn_3[Fe(CN)_6]_2$↓ white, is dissolved in HCl	$Sn_2[Fe(CN)_6]_2$↓ white, is dissolved in HCl	$Sn_2[Fe(CN)_6]_2$↓ white, is dissolved in HCI
CH_3COONa	—	—	$AI(OH)_2CH_3COO$↓ white, is dissolved in acids and alkalis	—	—	—	—
$HgCI_2$	—	—	—	—	—	Hg↓ - black	—
Zn, HC1	AsH_3↑ gas with chara-cterize small	AsH_3↑ gas with chara-cterize small	—	—	—	—	—
Ditizone solution in $CHCl_3$	—	—	—	—	Zinc ditizonate - red precipitate	—	—
Alyzarin	—	—	"aluminum varnish" - red precipitate	—	—	—	—
$Na_2B_4O_7 \cdot 10H_2O$ (borax bead formation)	—	—	—	$Cr(BO_2)_3$- emerald green bead	—	—	—

Analysis systematic course of a mixture of the IVth analytical group cations

1. Preliminary observations and testing (see page 23)

2. Identification of As(III), As(V)

Pour free zinc into a small test tube, add 5-7 mL 5HCl and 10 drops of arsenic solution. Moisten the filtration paper with aqueous $AgNO_3$ and put the paper on the test tube. If the paper turns black, it indicates the presence of arsenic.

3. Reaction with precipitating agent

Measure out 20-25 drops of the solution into a small test tube. Add 1mL of 4M NaOH and 5 drops of 3% hydrogen peroxide. Heat the test tube in a boiling-water bath for some minutes. The formation of yellow solution indicates the presence of chromium.

4. Reaction with ammonium chloride

Add ammonium chloride to the solution from Procedure №2 and place the test tube in a hot-water bath. The formation of precipitates indicates the presence of $Al(OH)_3$ and $Sn(OH)_4$. Centrifuge and decant the supernate into a clean test tube.

5. Identification of Al^{3+} *and* Sn^{2+}

Add some drops of 2M HCl to the precipitate from Procedure №3. Divide the solution into two test tubes. Add 3 drops of aqueous ammonia and Aluminon reagent to the first test tube. The formation of red precipitate indicates the presence of aluminum.

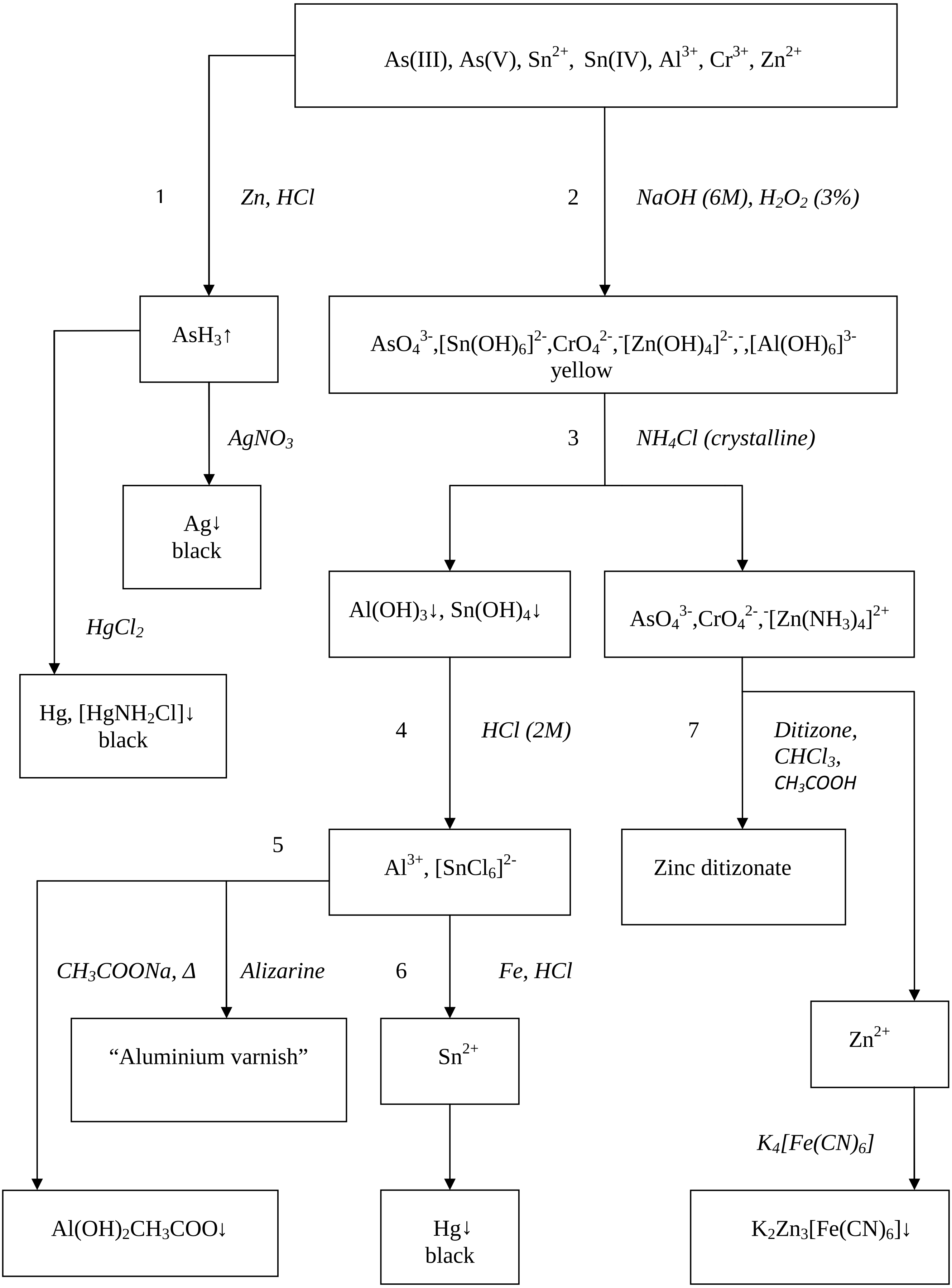
Add 3-4 drops of 2M hydrochloric acid solution and metal iron to another supernate, put the test tube in a hot–water bath for 3 min. Centrifuge and add it to the supernate mercury salt (II). The formation of black precipitate indicates the presence of Sn^{2+}.

6. Identification of Zn^{2+}

Add some drops of the reagent potassium hexacyanoferrate (II), $K_4[Fe(CN)_6]$ to the supernate from Procedure №3. Heat the test tube in a boiling-water bath for 3 min. The formation of white precipitate indicates the presence of zinc.

SCHEME OF ANALYSIS SYSTEMATIC COURSE THE IV^th ANALYTICAL GROUP

Scheme 5



Topic 10
Acid – Base Equilibrium

1. The main purpose of the topic:

Acid-base reactions - neutralization, hydrolysis are widely used in analytical chemistry. For determine the possible occurrence and direction of these reactions it is necessary be able to make calculations using values of equilibrium constants of ionic reactions.

Every analytical test should take place under certain conditions. Therefore it is necessary to know everything about the processes that are taking place in the solutions, including the process of hydrolysis, and factors to influence them. Buffer systems are widely used to ensure the certain pH value.

2. Basic questions:

2.1. Acid-Base Theories: Arrhenius theory of electrolytic dissociation; Protolytic acid-base theory Bronsted-Lowry; Electronic theory of acids and Lewis bases.
2.2. Calculation of pH and pOH in solutions of strong, weak acids and bases, polyprotic acids.
2.3. Salts in solution. Salt hydrolysis. Calculation pH of salt solutions. Using the hydrolysis process in the analysis.
2.4. Buffer systems, their characteristics. Calculation pH in buffer solutions. Buffer capacity, used in the analysis.
2.5. Amphoteric hydroxides. Equilibrium in their solutions.

3. Brief exposition of theoretical material:

Acid-Base Theories

In addition to the operational definitions for acids and bases, a number of theories have been developed to explain the behaviors of these substances. One of earliest and simplest is the **Arrhenius Theory**. According to this theory, acids and bases are defined in terms of their behavior in water:

- Acid: is dissolved in water to form H^+ ions
- Base: is dissolved in water to form OH^- ions

Under the Arrhenius model the acids which dissociate completely are **strong** while those which dissociate only partly are **weak**. The bases are similar. Reactions move in the direction which produces **salt**.

Because it is so simple to use, it is easy to fall into the terminology of the Arrhenius model when discussing acid/base behavior informally. But the model suffers from some real deficiencies, not the least of which is the unrealistic aqueous H^+ which is the "acid particle". Protons are so small and the unit charge therefore is so concentrated that very few probably exist in water independently. There is also the problem of bases which contains no OH^- in their formulas (like ammonia). And finally there is the restriction of water as the solvent.

These limitations and others led to a new model suggested in the 1920's by the Danish chemist **Bronsted** and the British chemist **Lowry**:

- Acid: a proton donor
- Base: a proton acceptor

This model broadens the scope of acid/base chemistry considerably since the only requirement is the transference of a proton. In a way it makes these reactions analogous to redox chemistry in which electron transfer occurs. Water is no longer required as a solvent and exchange can even take place between different phases. There is another important aspect of the Bronsted-Lowry model: acids and bases are relative to one another based on the competition for protons. A substance which is acid in one reaction may well behave as a base in another. The products of these reactions are not salts but other acids and bases.

In the Bronsted-Lowry model reactions proceed in the direction which converts stronger acids and bases to weaker acids and bases.

There is the third model for the acid/base behavior that is even broader than that suggested by Bronsted and Lowry.

Gilbert N. **Lewis** (the "dot man") suggested that acid/base behavior can be described in terms of **electron pairs**. In his model acids accept electron pairs and the bases donate them. One way of visualizing this process is to think of molecules with lone pairs as bases and those with incomplete octets as acids.

That, of course, is only the beginning. This approach broadens acid/base behavior to a considerable extent beyond even what Bronsted and Lowry suggested.

Calculation of pH and pOH in solutions of strong, weak acids and bases, polyprotic acids

Strong acids and bases are completely or almost completely ($\rightarrow$100%) ionized or dissociated in solution. For example, HCl is strong electrolyte:

$$HCl \rightarrow H^+ + Cl^-$$

Concentration of ions in the solution equal to the concentration of acid:

$$C(H^+) = C(Cl^-) = C(HCl)$$

$$pH = -\lg C(H^+)$$

$$pOH = 14 - pH \text{ (at 25°C)}$$

Sodium hydroxide is strong electrolyte:

$$NaOH \rightarrow Na^+ + OH^-$$

$$C(OH^-) = C(Na^+) = C(NaOH)$$

$$pOH = -\lg C(OH^-)$$

$$pH = 14 - pOH \text{ (at 25°C)}$$

Weak acids and bases are dissociated only partly. For example, acetic acid is weak electrolyte:

$$CH_3COOH \rightleftarrows CH_3COO^- + H^+$$

The K_a expression is:

$$K_a = \frac{[H^+]\cdot[CH_3COOH^-]}{[CH_3COOH]}$$

$$K_a = 1.74\cdot10^{-5} \text{ (from reference table)}$$

See the calculation of pH and pOH values in example 4.2. of topic 4.

Ammonia hydroxide (ammonia solution) is weak electrolyte:

$$NH_4OH \rightleftarrows NH_4^+ + OH^- \quad (1)$$

The K_b expression is:

$$K_b(NH_4OH) = \frac{[NH_4^+]\cdot[OH^-]}{[NH_4OH]}$$

$K_b = 1.76\cdot10^{-5}$ (from reference table)

According to the reaction (1): $[OH^-]=[NH_4^+]=x$ mol/l and $[NH_4OH]=(c- x)\approx c$ mol/l

The K_b expression:

$$K_b = \frac{x^2}{c} \Rightarrow x = \sqrt{K_b \cdot c}$$

$$pOH = -\lg C(OH^-)$$

$$pH = 14 - pOH \text{ (at 25°C)}$$

Polyprotic acids (H_3PO_4, H_2SO_4, H_2S etc.) contain more than one mole ionizable hydronium ions per mole of acids. They ionize to give more than one H^+ ions per molecule. The possible forms of three polyprotic acids are given below after their dissociation into H^+ ions.

These acids are ionized in several stages, giving out one proton at each stage. The acidity constants for these acids may be written as K_1, K_2, K_3 ... For polyprotic acids, the following is always true: $K_1 > K_2 > K_3 > ...$

For example, carbonic acid H_2CO_3 are ionized in two stages:

$$H_2CO_3 \rightleftarrows H^+ + HCO_3^-, \qquad K_1 = 4{,}1\cdot10^{-7}$$

$$HCO_3^- \rightleftarrows H^+ + CO_3^{2-}, \qquad K_2 = 4{,}8\cdot10^{-11}$$

If you need calculate the pH of the polyprotic weak acid solution you must be remembered that the ionization takes place mainly at the first stage

Salt Hydrolysis

By hydrolysis is meant the reaction of substance with water in which the constituent parts of the substance combine with the constituent parts of water.

Compounds of various classes are subjected to hydrolysis. In the present section, we treat one of the most important cases — the hydrolysis of salts. Salt is an ionic compound that is result of a neutralization reaction (acid + base). Solution of salt may be:

- neutral, if salt is formed by strong acid and strong base, for example:

$$NaCl \rightarrow Na^+ + Cl^-$$

$$Na^+ + Cl^- + H_2O \neq \text{ reaction is not possible, } pH = 7;$$

- acidic, if salt is formed by strong acid and weak base, for example:

$$NH_4Cl \rightarrow NH_4^+ + Cl^-$$

$$NH_4^+ + H_2O \rightleftarrows NH_4OH + \underline{\mathbf{H^+}} \Rightarrow pH < 7;$$

- basic, if salt is formed by weak acid and strong base, for example:

$$KNO_2 \rightarrow K^+ + NO_2^-$$

$$NO_2^- + H_2O \rightleftarrows HNO_2 + \underline{\mathbf{OH^-}} \Rightarrow pH > 7;$$

- if salt is formed by weak acid and weak base, compare K_a and K_b to determine pH, for example:

$$CH_3COONH_4 \rightarrow NH_4^+ + CH_3COO^-$$

$$NH_4^+ + CH_3COO^- + H_2O \rightleftarrows NH_4OH + CH_3COOH$$

$$K_b(NH_4OH) = 1,76 \cdot 10^{-5} \approx K_a(CH_3COOH) = 1,74 \cdot 10^{-5} \Rightarrow pH = 7.$$

Buffers

Performing the analytical reaction in the analysis one should keep the certain requirements; one of the important requirements to the analytical reactions is a necessary value of pH.

To ensure in the analysis of a pH buffer systems are widely used. In addition, buffer systems play an important part in regulating the activity of organisms, which must be stored constancy of pH of blood, lymph and other liquids.

Buffers are solutions in which the pH remains relatively constant, even when small amounts of acid or base are added. Buffer solution is made from a pair of chemicals:

- weak acid and one of its salts (for example, acetic acid and sodium acetate);
- weak base and one of its salts (for example, ammonia solution and ammonia chloride).

One chemical neutralizes any acid added, while the other chemical would neutralize any additional base.

Let's look at how the acetic acetate buffer works. You have solution that contains a large amount of both CH_3COOH and CH_3COONa.

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$$

$$CH_3COONa \rightarrow CH_3COO^- + Na^+$$

Suppose you add strong acid, for instance, hydrochloric acid, to the buffer:

$$HCl + CH_3COONa \rightarrow CH_3COOH + NaCl$$

$$H^+ + CH_3COO^- \rightleftharpoons CH_3COOH$$

The buffer neutralizes most of the H^+, and the pH change of the solution is relatively small because weak acetic acid is formed in place of strong hydrochloric acid.

Suppose you add a strong base, sodium hydroxide, for example, to the buffer:

$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$$

$$OH^- + H^+ \rightleftharpoons H_2O$$

The buffer neutralizes OH^-. Once again the pH change is much smaller than it would be if the solution was not a buffer.

The buffer capacity is the amount (mol) of acid or base that can be added to 1L of buffer solution before a significant (more than 1) change in pH

4. Control test and patterns of responses:

4.1. Calculate the hydrolysis constant and pH for the 0.1 M solution of ammonium chloride.

Answer:

1). NH_4Cl is strong electrolyte and is completely dissociated in aqueous solutions:

$$NH_4Cl \rightarrow NH_4^+ + Cl^- \qquad (1)$$

NH_4Cl is salt, which is formed by the cation of a weak base and anion of strong acid. Cations that are derived from weak bases react with water to increase the hydrogen-ion concentration; they form acidic solutions. The ammonium ion is derived from the weak base NH_4OH and it reacts with water as follows:

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+ \qquad (2)$$

$$K = \frac{[H^+]\cdot[NH_4OH]}{[NH_4^+]\cdot[H_2O]} \qquad (3)$$

$$K\cdot[H_2O] = \frac{[H^+]\cdot[NH_4OH]}{[NH_4^+]} = K_g \qquad (4)$$

Ion product of water

$$[H^+]\,[OH^-] = K_w(H_2O)$$

$$[H^+] = \frac{K_{H_2O}}{[OH^-]}$$

$$K_g = \frac{[NH_4OH]\cdot[H^+]\cdot[OH^-]}{[NH_4^+]\cdot[OH^-]} \qquad (5)$$

$$K_g = \frac{K_{H_2O}}{K_{NH_4OH}} \qquad (6)$$

$$K_g = \frac{K_{H_2O}}{K_{NH_4OH}} = \frac{10^{-14}}{1{,}76\cdot10^{-5}} = 5{,}68\cdot10^{-10}$$

$$\left(K_{NH_4OH} = 1{,}76\cdot10^{-5}\right)$$

2). According (1) $[NH_4^+] = C_{salt}$. According (2) $[NH_4OH] = [H^+]$:

$$K_g = \frac{[H^+]^2}{C_{salti}} \qquad (7)$$

$$\frac{K_{H_2O}}{K_b} = \frac{[H^+]^2}{C_{salt}} \qquad (8)$$

$$[H^+] = \sqrt{\frac{K_{H_2O}\cdot C_{salt}}{K_b}} \qquad (9)$$

$$[H^+] = \sqrt{\frac{K_{H_2O}\cdot C_{salt}}{K_b}} = \sqrt{\frac{10^{-14}\cdot 0{,}1}{1{,}76\cdot10^{-5}}} = 7{,}5\cdot10^{-6}(mol/l)$$

$$pH = -\lg[H^+]$$

$$pH = 7 + \frac{1}{2}\lg K_b - \frac{1}{2}\lg C_{salt}$$

$$pH = 5{,}12$$

4.2. What is the pH of buffer that is 0.120M in acetic acid, and 0.100M in sodium acetate? For acetic acid, $K_a = 1.8\cdot10^{-5}$.

Answer:

The pH of buffer solution is easy to calculate if you know the concentrations of acid and conjugate base used to make the buffer. Buffer solution contains both weak acid CH_3COOH and its conjugate base Na^+ (CH_3COONa). The K_a expression for CH_3COOH:

$$CH_3COOH \leftrightarrow CH_3COO^- + H^+$$

$$K_a = \frac{[CH_3COO^-]\cdot[H^+]}{[CH_3COOH]}$$

$$[H^+] = K_a \cdot \frac{[CH_3COOH]}{[CH_3COO^-]}$$

- assume that $[CH_3COOH]$ represents the concentration of the acid component of the buffer.
- assume that $[CH_3COO^-]$ represents the concentration of the salt component of the buffer:

$$CH_3COONa \rightarrow CH_3COO^- + Na^+$$

$$[H^+] = K_a \cdot \frac{C_{acid}}{C_{salt}}$$

As we are interested in pH, let's take the negative logarithm of both sides of equation and obtain:

$$-\lg[H^+] = -\lg K_a - \lg\frac{[CH_3COOH]}{[CH_3COO^-]}$$

Because $-\lg[H^+] = pH$ and $-\lg[K_a] = pK_a$, we have

$$pH = pK_a - \lg\frac{[CH_3COOH]}{[CH_3COO^-]}$$

and in general $$pH = pK_a - \lg\frac{C_{acid}}{C_{salt}}$$

$$pH = pK_a - \lg\frac{C_{acid}}{C_{salt}} = 4.74 - \lg\frac{0.120}{0.100} = 4.74 - 0.049 = 4.69$$

5. Tasks for individual work (write in a textbook for protocols):

5.1. What is the pH of solution; a) $NaCN$; b) NH_4CN; c) $NaNO_3$; d) NH_4NO_3? Write chemical reaction.

5.2. Buffer solution was prepared by dissolving 8.5g of NH_4OH and 107g of NH_4Cl in enough water to give 1.00L of solution. What is the pH of this buffer solution?

5.3. Calculate the pH and pOH of 0.03M aqueous solution of NH_4NO_3.

Topic 11
Chemistry of the Vth Group Cations
Analysis systematic course of the Vth analytical group cations

1. The main purpose of the topic:

Medical preparations that contain compounds of metals belonging to the analytical group Vth (bismuth nitrate basic - astringent and antiseptic to the gastro-intestinal diseases; salicylates Bismuth and others) – are widely used in medical *practice. - Various ointments, cosmetics, drugs, used to treat syphilis, magnesium oxide, magnesium carbonate basic - preparations for the treatment of elevated stomach acidity, magnesium sulfate - laxative, sedative, protysudorozhnyy, antispasmodic, restored iron and iron (II) sulfate - preparations in complex therapy hipohromnyh (iron) anemia, potassium permanganate - disinfectant, antimony organic compounds - chemotherapeutic preparations, etc.). Thus, the effect of antimony compounds on the body like arsenic action: compounds of antimony, which entered blood, acting as a "capillary poison" manganese compounds are among the strongest protoplazmatychnyh poisons acting on the central nervous system, causing it to organic changes, affecting kidneys, lungs, organs of hematopoiesis, etc. Magnesium sulfate, which is used for injections, should not contain impurities of manganese salts.*

Introduction to qualitative reactions of cations V^th^ analytical group will identify future specialists inorganic and organic medical preparations that contain atoms of these metals, and facilitate further study in related fields: pharmaceutical chemistry, pharmacognosy, technology, medicine, toxicological chemistry, and others.

2. Basic questions:

2.1. The fifth analytical group cations (acid – base classification), general characteristic.
2.2. Group reagent for the Vth analytical group cations.
2.3. Characteristic reactions of Mg^{2+}.
2.4. Characteristic reactions of Fe^{3+}.
2.5. Characteristic reactions of Fe^{2+}.
2.6. Characteristic reactions of Mn^{2+}.
2.7. Characteristic reactions of Sb(III) and Sb(V).
2.8. Characteristic reactions of Bi^{3+}.
2.9. The analysis of a mix of the Vth analytical group cations.

3. Brief exposition of theoretical material:

General characteristic of the Vth analytical group cations
Mg^{2+}, Fe^{3+}, Fe^{2+}, Mn^{2+}, Sb(III) and Sb(V), Bi^{3+}

The cations of s-elements - Mg^{2+}, p-elements - Sb (III), Sb (V), Bi^{3+} and d-elements - Fe^{2+}, Fe^{3+}, Mn^{2+}, are referred to the Vth analytical group. Due to the strong polarizing activity of the Vth analytical group cations many of their compounds: hydroxides, sulphides, phosphates) are insoluble in water. But their chlorides, bromides, nitrites, nitrates, acetates, sulfates are soluble in water.

Strong ammonia solution is a group reagent, which precipitates the Vth analytical group cations as hydroxides, insoluble in reagent excess.

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

The compounds of Fe^{3+} are yellow - brown, Fe^{2+} compounds are light-green; the solution of other cations compounds are colourless.

4. Control test and patterns of responses:

4.1. Solution of potassium hydroxide was added to solution containing cation of the fifth analytical group. It resulted in generation of white precipitate, which is soluble in mineral acids and in excess of KOH. What cation is present in solution? Write the corresponding reactions.

Answer:

Cations of the fifth analytical group are formed with alkalis (NaOH or KOH) amorphous precipitates of hydroxides: white – with cations of magnesium, bismuth and antimony; green – iron (II) hydroxide and reddish-brown – iron (III) hydroxide:

$$Mg^{2+}\ 2OH^{-} \rightleftarrows Mg(OH)_2\downarrow$$

$$Mn^{2+}\ 2OH^{-} \rightleftarrows Mn\ (OH)_2\downarrow$$

$$Fe^{2+}\ 2OH^{-} \rightleftarrows Fe(OH)_2\downarrow$$

$$Fe^{3+}\ 3OH^{-} \rightleftarrows Fe(OH)_3\downarrow$$

$$Bi^{3+} + 3OH^{-} \rightleftarrows Bi(OH)_3\downarrow$$

$$\mathrm{X}SbCl_6\mathrm{Z}^{3-} + 3OH^{-} \rightleftarrows Sb(OH)_3\downarrow + 6Cl^{-}$$

$$\mathrm{X}SbCl_6\mathrm{Z}^{-} + 5OH^{-} \rightleftarrows Sb(OH)_5\downarrow + 6Cl^{-}$$

$$Sb(OH)_5\downarrow \rightarrow HSbO_3\downarrow + 2H_2O$$

All hydroxides of cations fifth analytical group are dissolved in acids, for example:

$$Fe(OH)_3\downarrow + 3H^{+}\ \text{ì}\ Fe^{3+} + 3H_2O$$

Hydroxides of Sb (III) and Sb (V) are dissolved in excess alkali by amphoteric properties:

$$Sb(OH)_3\downarrow + 3OH^{-} \rightarrow \mathrm{X}Sb(OH)_6\mathrm{Z}^{3-}$$

$$Sb(OH)_5\downarrow + OH^{-} \rightarrow \mathrm{X}Sb(OH)_6\mathrm{Z}^{-}$$

Hydroxide Sb (III) and Sb (V) are dissolved in acids:

$$Sb(OH)_3\downarrow + 6HCl \rightarrow \mathrm{X}SbCl_6\mathrm{Z}^{3-} + 3H^{+} + 3H_2O$$

$$Sb(OH)_5\downarrow + 6HCl \rightarrow \mathrm{X}SbCl_6\mathrm{Z}^{-} + 3H^{+} + 3H_2O$$

The described analytical effect indicates the presence of antimony ions in solution.

5. Tasks for individual work (write in a textbook for protocols):

5.1. What can cations of the V^th analytical group be detected by fractional method? Give the equation corresponding reactions.

5.2. Solution of alkali added into the solution that contains magnesium cations (II) and manganese (II), then H_2O_2 is added and warmed. What is observing? Write the appropriate reactions.

5.3. How to separate the magnesium hydroxide from other hydroxides of the V^th analytical group in the course of systematic analysis of mixtures of cations of this group?

5.4. Suggest the systematic analysis of solution which contains ions:

- Mg^{2+}, Fe^{3+}, Mn^{2+};

- Sb (V), Bi^{3+}, Fe^{2+};
- Fe^{3+}, Bi^{3+}.

The situation tasks are solved according to the systematic analysis of the Vth analytical group cations mixture.

6. *Laboratory experiment*

Laboratory experiment 11.1.

Characteristic reactions of the Vth analytical group cations and condition of their detection.

1. *Reaction with sodium hydroxide NaOH*

All cations of group Vth can be precipitated by addition of the reagent sodium hydroxide:

$Mg^{2+} + 2OH^- \leftrightarrow Mg(OH)_2\downarrow$ white
$Mn^{2+} + 2OH^- \leftrightarrow Mn(OH)_2\downarrow$ tan
$Fe^{3+} + 3OH^- \leftrightarrow Fe(OH)_3\downarrow$ red-brown
$Fe^{2+} + 2OH^- \leftrightarrow Fe(OH)_2\downarrow$ green
$Bi^{3+} + 3OH^- \leftrightarrow Bi(OH)_3\downarrow$ white
$\mathrm{x}SbCl_6\mathrm{z}^{3-} + 3OH^- \rightleftarrows Sb(OH)_3\downarrow + 6Cl^-$ white
$\mathrm{x}SbCl_6\mathrm{z}^{-} + 5OH^- \rightleftarrows Sb(OH)_5\downarrow + 6Cl^-$ white

All hydroxides dissolve in strong acids:

$Mg(OH)_2\downarrow + 2H^+ \rightarrow Mg^{2+} + 2H_2O$ $Fe(OH)_2\downarrow + 2H^+ \rightarrow Fe^{2+} + 2H_2O$
$Mn(OH)_2\downarrow + 2H^+ \rightarrow Mn^{2+} + 2H_2O$ $Fe(OH)_3\downarrow + 3H^+ \rightarrow Fe^{3+} + 3H_2O$
$Bi(OH)_3\downarrow + 3H^+ \rightarrow Bi^{3+} + 3H_2O$

Magnesium, manganese and iron (II) hydroxide are dissolved in saturated solution of NH_4Cl:

$$Mg(OH)_2\downarrow + 2NH_4^+ \rightarrow Mg^{2+} + 2NH_3{\cdot}H_2O$$
$$Mn(OH)_2\downarrow + 2NH_4^+ \rightarrow Mn^{2+} + 2NH_3{\cdot}H_2O$$
$$Fe(OH)_2\downarrow + 2NH_4^+ \rightarrow Mn^{2+} + 2NH_3{\cdot}H_2O$$

This reaction is used for magnesium cations separation from other cations of the Vth analytical group in analysis systematic course.

Procedure: Pour 3-5 drops of the magnesium, manganese, iron (II, III) and bismuth salts in small test tubes, add 2 drops of sodium hydroxide. Dissolve all the precipitates in strong acid and in saturated solution of NH_4Cl.

2. *Reaction with precipitating agent 25% NH_4OH*

All cations of group Vth may be precipitated and separated from the cations of another groups by adding 25% NH_4OH:

$Mg^{2+} + 2NH_3{\cdot}H_2O \leftrightarrow Mg(OH)_2\downarrow + 2NH_4^+$ white
$Mn^{2+} + 2NH_3{\cdot}H_2O \leftrightarrow Mn(OH)_2\downarrow + 2NH_4^+$ tan
$Fe^{2+} + 2NH_3{\cdot}H_2O \leftrightarrow Fe(OH)_2\downarrow + 2NH_4^+$ green
$Fe^{3+} + 3NH_3{\cdot}H_2O \leftrightarrow Fe(OH)_3\downarrow + 3NH_4^+$ red-brown
$Bi^{3+} + 2NH_3{\cdot}H_2O + Cl^- \rightarrow Bi(OH)_2Cl + 2NH_4^+$
$Bi(OH)_2Cl \rightarrow BiOCl\downarrow + H_2O$ white
$\mathrm{x}SbCl_6\mathrm{z}^{3-} + 3OH^- \rightleftarrows Sb(OH)_3\downarrow + 6Cl^-$ white

$[SbCl_6]^- + 5OH^- \rightleftarrows Sb(OH)_5\downarrow + 6Cl^-$ white

All hydroxides can be dissolved in strong acids and can not be dissolved in excess of precipitating agent.

Procedure: Pour 3-5 drops of the magnesium, manganese, iron (II, III) and bismuth salts in small test tubes, add 3 drops of 25% aqueous ammonia. Dissolve all precipitates in strong acid.

Magnesium (Mg^{2+}) ions reactions (colorless)

1. Reaction with sodium hydrophosphate Na_2HPO_4

Magnesium can be precipitated from aqueous solution as white precipitate by addition of the reagent Na_2HPO_4. Reaction at the presence of ammoniacal buffered solution:

$Mg^{2+} + HPO_4^{2-} + NH_3 \cdot H_2O \leftrightarrow MgNH_4PO_4\downarrow + H_2O$ white

Procedure: Pour 1-2 drops of the magnesium salt in a small test tube, add 2 drops of NH_4Cl and NH_4OH and 1 drop of Na_2HPO_4.

Iron (II) (Fe^{2+}) ions reactions (green)

1. Reaction with sodium sulfide Na_2S

Iron (II) cations can be precipitated from aqueous solution as black precipitate by adding sulfide – ions:

$Fe^{2+} + S^{2-} \leftrightarrow FeS\downarrow$ black

Procedure: Pour 3-4 drops of the iron (II) salt in a small test tube, add 2-3 drops of sodium sulfide.

2. Reaction with dimethylglyoxime ($HC_4H_7N_2O_2$)

Iron (II) cations can be precipitated from aqueous solution as red precipitate $[Fe(C_4H_7N_2O_2)_2]$ by adding the reagent dimethylglyoxime. Ni^{2+} cations interfere with this test for iron (II) ions.

Procedure: Pour 1 drop of the iron (II) salt in a small test tube, add 1 drop of the reagent dimethylglyoxime and aqueous ammonia.

3. Reaction with potassium hexacyanoferrate (III), $K_3[Fe(CN)_6]$

Iron (II) cations can be precipitated from aqueous solution as blue precipitate by adding the reagent potassium hexacyanoferrate (III), $K_3[Fe(CN)_6]$:

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

This reaction on Fe^{2+} cations is specific and allows to detect them by the fraction method. This precipitate can not be dissolved in strong acid but can be decomposed by adding sodium hydroxide:

$Fe_3[Fe(CN)_6]_2\downarrow + 6OH^- \rightarrow 3Fe(OH)_2 + 2[Fe(CN)_6]^{3-}$ green

Procedure: Pour 2-3 drops of the iron (II) salt into a small test tube, add 2 drops of the reagent potassium hexacyanoferrate (III), $K_3[Fe(CN)_6]$.

Iron (III) (Fe^{3+}) ions reactions (brown)

1. *Reaction with sodium sulfide Na_2S*

Iron (III) cations can be precipitated from aqueous solution as black precipitate by adding sulfide-ions:

$$2Fe^{3+} + 3S^{2-} \leftrightarrow Fe_2S_3 \quad \text{black}$$

<u>Procedure:</u> Pour 3-4 drops of the iron (III) salt into a small test tube, add 2-3 drops of sodium sulfide.

2. Reaction with thiocyanate ions, SCN^-

Iron (III) cations can be precipitated from aqueous solution as red precipitate by adding thiocyanate ions, SCN^-:

$$Fe^{3+} + 6SCN^- \rightarrow [Fe(SCN)_6]^{3-} \quad \text{red}$$

<u>Procedure:</u> Pour 3-4 drops of the iron (III) salt into a small test tube, add 2-3 drops of ammonium thiocyanate.

3. Reaction with potassium hexacyanoferrate (II), $K_4[Fe(CN)_6]$

Iron (III) cations can be precipitated from aqueous solution as dark blue precipitate (Prussian blue) by adding potassium hexacyanoferrate (II), $K_4[Fe(CN)_6]$:

$$4Fe^{3+} + 3[Fe(CN)_6]^{4-} \leftrightarrow Fe_4[Fe(CN)_6]_3 \quad \text{dark blue}$$

Reaction of Fe^{3+} with potassium hexacyanoferrate (II) is specific and allows to discover them by the fractional method. This precipitate is decomposed by adding sodium hydroxide:

$$Fe_4[Fe(CN)_6]_3 + 12OH^- \rightarrow 4Fe(OH)_3\downarrow + 3[Fe(CN)_6]^{4-} \quad \text{red-brown}$$

<u>Procedure:</u> Pour 2-3 drops of the iron (III) salt into a small test tube, add 2 drops of potassium hexacyanoferrate (II), $K_4[Fe(CN)_6]$, add some drops of sodium hydroxide.

Manganese (Mn^{2+}) ions reactions (colorless)

1. Reactions, taking place in the analysis systematic course at manganese (II) cations detection

Manganese (II) hydroxide is easily acidified by hydrogen peroxide. Dark-brown precipitate $H_2MnO_3(MnO_2{\cdot}mH_2O)$ is formed.

$$Mn(OH)_2\downarrow + H_2O_2 \rightarrow H_2MnO_3 + H_2O\downarrow$$

The manganese (IV) is also reduced up to manganese (II) in sulphate or nitrate medium by the action of H_2O_2:

$$H_2MnO_3\downarrow + H_2O_2 + 2H^+ \rightarrow Mn^{2+} + O_2\uparrow + 3H_2O$$

2. Reaction with ammonium persulphate $(NH_4)_2S_2O_8$

When solution of Mn^{2+} is acidified with HNO_3 and then treated with $(NH_4)_2S_2O_8$, Mn^{2+} is oxidized to MnO_4^-:

$$2Mn^{2+} + 5S_2O_8^{2-} + 8H_2O \rightarrow 2MnO_4^- + 16H^+ + 10SO_4^{2-} \quad \text{purple}$$

The reaction is carriend out at heating and at the presence of silver salts (catalytic agent). It is the reaction of manganese (II) ions detection

<u>Procedure:</u> Pour 4-5 drops of 2M nitric acid into a small test tube, add 2 drops of $AgNO_3$ and $(NH_4)_2S_2O_8$. Heat the test tube in a boiling-water bath for 3 minutes. Then add some drops of manganese salt.

3. Reaction with sodium sulfide Na_2S

Manganese cations can be precipitated from aqueous solution as salmon precipitate by adding sulfide-ions:

$$Mn^{2+} + S^{2-} \leftrightarrow MnS\downarrow \qquad \text{salmon}$$

$MnS\downarrow$ can be dissolved in strong acid:

$$MnS\downarrow + 2H^{+} \rightarrow Mn^{2+} + H_2S$$

<u>Procedure:</u> Pour 3-4 drops of the manganese salt into a small test tube, add 1-2 drops of sodium sulfide. Dissolve the precipitate in strong acid.

Bismuth (Bi^{3+}) ions reactions (colorless)

1. Reaction with sodium sulfide Na_2S

Bismuth cations can be precipitated from aqueous solution as brown precipitate by adding sulfide-ions:

$$2Bi^{3+} + 3S^{2-} \rightarrow Bi_2S_3 \qquad \text{brown}$$

<u>Procedure:</u> Pour 3-4 drops of the bismuth salt into a small test tube, add some drops of sodium sulfide.

2. Reaction with fresh prepared sodrium hexahydroxostannit(II) $Na_4[Sn(OH)_6]$

By blending of $SnCl_2$ solutions and NaOH excess solutions the hexahydroxostannit (II) ions $[Sn(OH)_6]_4$ are formed. Hexahydroxostannit(II) ions give with Bi^{3+} ions up to metalyc bismuth of black colour. $[Sn(OH)_6]^{4-}$ -ions are stable in alkaline solutions. In such conditions bismuth cations form white precipitate $Bi(OH)_3$:

$$Sn^{2+} + 2OH^{-} \rightarrow Sn(OH)_2\downarrow$$

$$Sn(OH)_2\downarrow + 4OH^{-} \rightarrow [Sn(OH)_6]^{4-}$$

$$Bi^{3+} + 3OH^{-} \rightarrow Bi(OH)_3\downarrow$$

$$2Bi(OH)_3\downarrow + 3[Sn(OH)_6]^{4-} \rightarrow 3[Sn(OH)_6]^{2-} + 2Bi\downarrow + 6OH^{-} \qquad \text{black}$$

<u>Procedure:</u> Pour 5 drops of the bismuth salt into a small test tube, add some drops of fresh prepared sodrium hexahydroxostannit(II).

3. Reaction with potassium iodide KI

Bismuth cations can be precipitated from aqueous solution as black precipitate by adding the reagent potassium iodide:

$$Bi^{3+} + 3I^{-} \leftrightarrow BiI_3\downarrow \qquad \text{black}$$

$BiI_3\downarrow$ can be dissolved in excess potassium iodide:

$$BiI_3\downarrow + I^{-} \rightarrow [BiI_4]^{-} \qquad \text{yellow-orange}$$

<u>Procedure:</u> Pour 5 drops of the bismuth salt into a small test tube, add some drops of potassium iodide.

Table 8

The action of some reagents on Vth analytical group cations

Reagent	Cations						
	Fe^{3+}	Fe^{2+}	Mg^{2+}	Mn^{2+}	Bi^{3+}	$[SbCl_6]^{3-}$	$[SbCl_6]^-$
NaOH; KOH	$Fe(OH)_3$ - red-brown precipitate not dissolved in NH_4CI	$Fe(OH)_2$ - green precipitate	$Mg(OH)_2$ - white precipitate	$Mn(OH)_2$ - white precipitate, which becomes brown in the air as a result of $MnO_2{\cdot}nH_2O$ formation	$Bi(OH)_3$ - white precipitate	$Sb(OH)_3$ - white precipitate	$HSbO_3$ - white precipitate
		Precipitates are dissolved in NH_4Cl solution			Precipitates are dissolved in HCI and alkalies		
	Precipitates are dissolved in acids						
NH_4OH	$Fe(OH)_3$- red-brown precipitate	$Fe(OH)_2$ - green precipitate	$Mg(OH)_2$ - white precipitate	$Mn(OH)_2$ - white precipitate, which becomes brown in the air as a result of MnO_2-nH_2O formation	BiOCl or $BiONO_3$, white precipitate dissolved in acids	$Sb(OH)_3$ - white precipitate	$HSbO_3$ - white precipitate
					Precipitates are dissolved in HCI and alkalis		
Na_2HPO_4 + NH_4OH	$FePO_4$	$Fe_3(PO_4)_2$	$MgNH_4PO_4$	$Mn_3(PO_4)_2$	$BiPO_4$ - white precipitate is not dissolved in the acetic and dilute nitric acid	White precipitates of the basic salts a transient composition	-
	White precipitates are dissolved in mineral acids and are not dissolved in acetic acid						
HNO_3, H_2O_2	-	-	-	-	-	-	$HSbO_3$ - white precipitate is dissolved in HCI and alkalis

Analysis systematic course of the Vth analytical cations group mixture

1. *Preliminary tests and observation (see page 23)*
2. *Cations detection by a fractional method*

2.1. Identification of Fe^{2+}

Measure out 5 drops of the test solution into a small test tube. Add 5 drops of potassium hexacyanoferrate (III), $K_3[Fe(CN)_6]$. The formation of blue precipitate indicates the presence of iron (II) cations.

2.2. Identification of Fe^{3+}

Measure out 5 drops of the test solution into a small test tube. Add 5 drops of potassium hexacyanoferrate (II), $K_4[Fe(CN)_6]$. The formation of dark blue precipitate indicates the presence of iron (III) cations.

2.3. Antimony cations separation and detection

Measure out 20-25 drops of the tested mixture (with or without a precipitate) 15-20 drops 1M nitric acid, 10 drops of 3 % peroxide hydrogen solution are added and heated in the water bath till full H_2O_2 decomposition. The mixture is centrifuged. Analytical group cations are in the centrifuge, $HSbO_3$ is in the precipitate.

The precipitate obtained according to point 3 is dissolved in 8-10 drops of concentrated chlorohydrogen acid. 1-2 drops of the obtained solution are poured on the nickel plate and a zinc granule is added.

3. Precipitation of the Group Vth cations

To the centrifugate, obtained according to Procedure №2, add 20-25 drops of 25% aqueous ammonia and some drops of hydrogen peroxide. The precipitate contains: hydroxides and basic analytical group Vth cations salts are separated by centrifugation. The centrifugate is rejected.

4. Separation of Mg^{2+}

Measure out the precipitate from Procedure №3 into a small test tube. Add the saturated solution of ammonium chloride and 5 drops of 3% hydrogen peroxide. Heat the test tube in a boiling-water bath for some minutes. The magnesium ions are in the centrifugate.

5. Identification of Mg^{2+}

Add 2 drops of Na_2HPO_4, 2 drops of ammonium chloride and aqueous ammonia to the supernate from Procedure№4. The formation of white precipitate indicates the presence of Mg^{2+}.

6. Separation of Mn^{2+}

Add 10-15drops of 2M HNO_3 to the precipitate from Procedure№4. Centrifuge and decant the supernate into a clean test tube. The obtained mixture is centrifugated Fe^{3+}, Bi^{3+} are in the centrifugate, H_2MnO_2 ($MnO_2 \cdot nH_2O$) is in the precipitate. Dissolve the precipitate in nitric acid, add 2-3 drops of hydrogen peroxide. Heat the test tube in a boiling-water bath for some minutes.

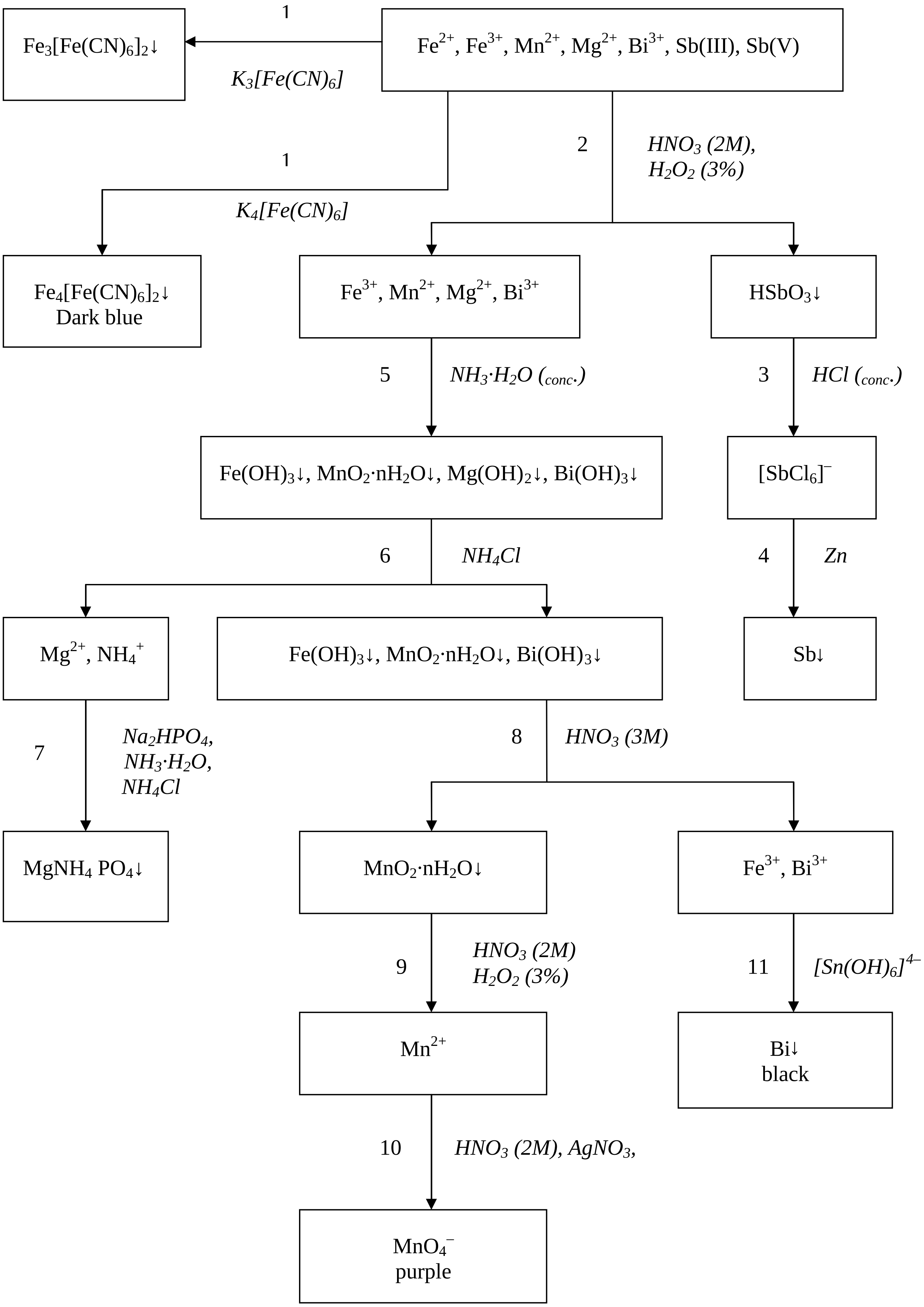
7. Identification of Mn^{2+}

Measure out 3-4 drops of 2M HNO_3 into a small test tube. Add 2 drops of $AgNO_3$ and $(NH_4)_2S_2O_8$. Heat the test tube in a boiling-water bath for 3 minutes. Add the solution from Procedure№6. The formation of purple solution indicates the presence of Mn^{2+}.

8. Identification of Bi^{3+}

Add 2 drops of the reagent potassium iodide into a small teat tube. Add some drops of the supernate from Procedure№6. The formation of black precipitate indicates the presence of Bi^{3+}.

SCHEME OF ANALYSIS SYSTEMATIC COURSE THE Vth ANALYTICAL GROUP *Scheme 6*



Topic 12
Oxidation – Reduction Equilibrium

1. The main purpose of the topic:

Oxidation-reduction reactions are widely used in qualitative analysis for detection of ions. Use different group redox reactions in order to identify drugs, products which have a characteristic colour or other analytical features. In the quantitative analysis reactions oxidation-reduction is the basis of redox processes.

Oxidation-reduction reactions are of great importance in biological systems. Photosynthesis, breathing, digestion—all these are chains of oxidation-reduction reactions. In engineering, the significance of redox reactions is also very great. For example, the entire metallurgical industry is based on oxidation-reduction processes during which metals are recovered from natural compounds.

2. Basic questions:

2.1. Oxidation – Reduction Reactions. Redox couple.

2.2. Electrode potential: standard electrode potential and real (equilibrium) redox potential. Nernst equation.

2.3. Electromotive force. Direction of redox reactions.

3. Brief exposition of theoretical material:

Reactions as a result of which the oxidation numbers of elements change are called oxidation-reduction (redox) reactions.

Redox reaction - an electron-transfer reaction.

As a result of this electron transfer, some of the elements involved in the reaction undergo a change in oxidation state.

$$\underset{\substack{\text{oxidizing}\\\text{form}}}{\text{Ox}} + \text{ne} \rightarrow \underset{\substack{\text{reducing}\\\text{form}}}{\text{Red}}$$

The pair of an oxidizing and reducing agent that are involved in a particular reaction is called a **redox pair**.

Equation **Ox + n $\leftrightarrow$ Red** describes the reduction-oxidation half-reaction.

Redox pair – is the system of oxidizing and reducing forms of substance, in which oxidizing form (oxidizer) is an electron acceptor and is itself reduced when it accepts electrons, reducing form (reducer) is electron donor and is oxidized itself when it gives up electrons.

The most important oxidizing agents:

1. $(NH_4)_2S_2O_8$, $KMnO_4$, $K_2Cr_2O_7$, K_2CrO_4, $KBrO_3$, $KClO_3$, KJO_3
2. Cl_2, Br_2, J_2, JCl, JBr, NaClO, NaBrO, $CaOCl_2$
3. H_2O_2, HNO_3, H_2SO_4 (concentrated), MgO_2, Na_2O_2, HCl + HNO_3, H_2O_2 + HCl (Komarovsky's mixture)
4. Cu^{2+}, Fe^{3+}, Hg^{2+}

The most important reduction agents:

1. Zn, Fe, Mg, Al, alkali and alkali-earth metals
2. Sn^{2+}, Mn^{2+}, Fe^{2+}

3. S^{2-}, SO_3^{2-}, $S_2O_3^{2-}$, J^-, Br^-, $C_2O_4^{2-}$

Devices used for the direct conversion of the energy of a chemical reaction into electrical energy are called galvanic (or voltaic) cells. They are also known as chemical sources of electrical energy or chemical sources of current.

Functioning of any galvanic cell is based on the proceeding of the redox reaction in it. The simplest galvanic cell consists of two plates or rods made from different metals and immersed in a solution of an electrolyte. Thus, in the operation of a galvanic cell, the electrons from the reducing agent are passe to the oxidizing agent through the external circuit, electrochemical processes take place at the electrodes, and the directed motion of the ions is observed in the solution.

The net equation of the reaction proceeding in the cell is obtained when the equations of the two half-reactions are summated. Thus, in the operation of a galvanic cell, the electrons from the reducing agent pass to the oxidizing agent through the external circuit, electrochemical processes take place at the electrodes, and the directed motion of the ions is observed in the solution. The electrode at which oxidation takes place is called the anode. The one at which reduction takes place is called the cathode.

The maximum value of the voltage of a galvanic cell corresponding to the reversible proceeding of the reaction is called the **electromotive force (e.m.f.)** of the given cell.

If the concentrations of the substances participating in a reaction equal unity, i.e. if standard conditions are observed, the e.m.f. of a cell is called its **standard electromotive force** and is marked by the symbol E^0.

The **standard (normal) oxidation-reduction potential** of pairs which are soluble forms, is a difference of potentials, which arises between the standard hydrogen and inactive (platinum) electrode dipped into the solution, which contains the oxidizing and reducing forms of one redox-pairs (25 °C, activity of components of pair equal 1 mol/L).

The **standard hydrogen electrode (S.H.E.)** It consists of a platinum electrode in contact with H_2 gas and aqueous H^+ ions at standard-state conditions [1 mol/L (C_N or N) H_2SO_4 or 1,25 mol/L HCl, 1 atm H_2, 25°C]. The corresponding half-reaction is assigned an arbitrary potential of exactly 0 V:

$$2H^+ + 2e \leftrightarrow H_2\uparrow$$

Nernst equation - an equation relating electrochemical potential to the concentrations of products and reactants**:**

$$E = E^0 + \frac{RT}{nF}\ln\frac{a_{Ox}}{a_{\mathrm{Re}d}}.$$

R - is the molar gas constant

T - is the absolute temperature

F - is the Faraday constant

[Ox] – oxidized form

[Red] – reduced form

n - number of electrons participating in the process

Substituting appropriate values for R and F, assuming a temperature of 25 °C (298 K), and switching from ln to log gives the potential in volts as

$$E = E^0 + \frac{0{,}059}{n}\lg\frac{a_{Ox}}{a_{\mathrm{Re}d}}.$$

In the standard conditions: **a(Ox) = a(Red) = 1 mol/L** and **$E=E^0$.**

In the nonstandard conditions:

$$E = E^0 + \frac{0{,}059}{n}\lg\frac{[Ox]}{[\mathrm{Re}d]}.$$

Real redox potential – it is potential of the redox pair than components of reaction are in real condition, not standard.

Formal redox potential – it is potential of redox pair when concentration of reaction components is formal (concentration of reagents is equal 1 mol/L, but concentrations of other compounds in solution are certain).

1. As more oxidation-reduction potential of redox-pair as stronger oxidizer is oxidizing form this redox-pair.
2. As less oxidation-reduction potential of redox-pair as stronger reducer is reducing form this redox-pair.

The direction of passage of reaction depends on value of **electromotive force** (EMF), which is called **potential of reaction E**

$$\text{EMF} = E = E^0(\text{Ox}) - E^0(\text{Red}).$$

EMF (E) > 0, than passes direct reaction

EMF (E) < 0, than passes return reaction

EMF (E) = 0 condition of equilibrium

Equilibrium constant of Reduction-oxidation reactions:

$$\frac{(E_1^0 - E_2^0)\cdot n}{0{,}059} = lg\, K_{eq}$$

Reactions which are passed completely, should have a equilibrium constant more than 10^8 (when 99,99 % starting compounds should pass), so:

$$\frac{(E_1^0 - E_2^0)n}{0{,}059} \geq 8$$

$E^0 \geq + 0{,}4$ V (n=1)

$E^0 \geq + 0{,}2$ V (n=2)

4. Control test and patterns of responses:

4.1. Find out the direction in which the following reaction can be proceeded:

$$2KBr + PbO_2 + 4HNO_3 = Pb(NO_3)_2 + Br_2 + 2KNO_3 + 2H_2O$$

Answer:

We have to detect what elements can change oxidation number and write the equation of the reaction in the net ionic form :

$$2Br^- + PbO_2 + 4H^+ = Pb^{2+} + Br_2 + 2H_2O$$

In the Table, we find out the standard electrode potentials for the electrochemical systems participating in the reaction:

$Br_2 + 2\bar{e} = 2Br^-$ E_1^0=1.065 V

$PbO_2 + 4H^+ + 2\bar{e} = Pb^{2+} + 4H_2O$ E_2^0=1.449 V

The substance (redox couple) with more positive E^0 is oxidizing agent.

$$E_2^0 > E_1^0 \ (1.449V > 1.065V)$$

Therefore, bromide ion will be the reducing agent and will be oxidized by the lead dioxide: the reaction will be proceeded spontaneously from left to right.

5. Tasks for individual work (write in a textbook for protocols):

5.1. Find out the direction in which the following reaction can proceed:

$2Cr^{3+} + S_2O_8^{2-} + H_2O = CrO_4^{2-} + SO_4^{2-} + H^+$

$Cr_2O_7^{2-} + 6I^- + 14H^+ = 2Cr^{3+} + 3I_2 + 7H_2O$

$2Cr^{3+} + 6Fe^{3+} + 7H_2O = Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+$

$2HNO_2 + 2I^- + 2H^+ = 2NO + I_2 + 2H_2O$

$Sn^{2+} + 2Fe^{3+} = Sn^{4+} + 2Fe^{2+}$

Topic 13
Chemistry of the VIth Group Cations
Analysis systematic course of the VIth analytical group cations

1. The main purpose of the topic:

Medicines, which contain compounds of copper (II), mercury (II) cations are used in medical practice.

Copper (II) sulphate is applied as an antiseptic, astringent or cauterizing as solutions (w=0.25%) in eye practice and urology.

Mercury (II) oxide is applied in ophthalmology and dermatology as oinments. Mercury (II) chloride (sublimate) in the concentration 1:1000 is used for disinfection. It should be remembered that mercury and its salts are very toxic!

The ratio-active cobalt of ^{60}Co *is applied in medicine for treating malignant tumours. Cobalt as the vitamin* B_{12} *takes part in the synthesis of hemoglobin. Nickel as microelement also takes part in very important biological processes in the human's organism.*

But in the large doses of the compounds of all these metals are very poisonous.

Comprehension of the characteristic reactions of cations of these metals and conditions of their performance is making for students the theoretical base of chemical analysis, practical skills and experience of making it and also bases the subsequent study of such core of disciplines as pharmaceutical chemistry, pharmacognosicy, forensic chemistry, technology of drugs, etc. for future specialists in pharmacy.

2. Basic questions:

2.1. Cations of the VIth analytical group (acid–base classification), their general characteristic.

2.2. Group reagent for the VIth analytical group cations and condition of their application.

2.3. Characteristic reactions of Cu^{2+} cation.

2.4. Characteristic reactions of Hg^{2+} cation.

2.5. Characteristic reactions of Co^{2+} cation.

2.6. Characteristic reactions of Ni^{2+} cation.
2.8. Analysis systematic course of the VIth analytical group cations.

3. Brief exposition of theoretical material:

General characteristic of the VIth analytical group cations
Cu^{2+}, Hg^{2+}, Co^{2+}, Ni^{2+}

To the VIth analytical group belong the cations of d-elements - Cu^{2+}, Hg^{2+}, Co^{2+}, Ni^{2+} . Their electronic structure is characterized by free d-orbitals presence. Therefore for the VIth analytical group cations the reactions of complex forming are characteristic. The majority of compounds (sulphates, chlorides, nitrates, acetates) are well soluble in water, but hydroxides, carbonates, phosphates are insoluble in water.

Group reagent of the VIth analytical group is ammonia concentrated solution, forming with the VIth analytical group cations soluble ammoniac complexes. The further analysis course is based on the destruction of these complexes by the action of 6M solution of sulfuric acid, and on precipitation of Cu(I) and Hg^{2+} sulphides by action of crystalline sodium thiosulfate and their different dissolubility in nitric acid and bromine water. Determination of the VIth analytical group cations is based on the usage of complexing and oxidizing-reduction reactions. All cations of the VIth analytical group (except Hg^{2+}-cations) are coloured and they form coloured compounds.

4. Control test and patterns of responses:

4.1. Just prepared tin (II) chloride solution was added to solution containing cations of the VIth analytical group. It resulted in generation of white precipitate, which turns black. What cations are contained in the solution? Write the equations of the conforming reactions.

<u>Answer:</u>

The described analytical effect indicates the presence Hg^{2+} cations in the solution. After adding of tin (II) chloride solution to solution containing Hg^{2+} cations formation of white precipitate Hg_2Cl_2 is observed:

$$2Hg^{2+} + 2Cl^{-} + 2e \rightleftarrows Hg_2Cl_2\downarrow \qquad | \ 1$$
$$Sn^{2+} + 6Cl^{-} - 2e \rightleftarrows [SnCl_6]^{2-} \qquad | \ 1$$

$$2Hg^{2+} + 8Cl^{-} + Sn^{2+} \rightleftarrows Hg_2Cl_2\downarrow + [SnCl_6]^{2-}$$

Precipitate Hg_2Cl_2 gradually turns black due to the formation of finely dispersed metallic mercury:

$$Hg_2Cl_2\downarrow + 2e \rightleftarrows 2Hg\downarrow + 2Cl^{-} \qquad | \ 1$$
$$Sn^{2+} + 6Cl^{-} - 2e \rightleftarrows [SnCl_6]^{2-} \qquad | \ 1$$

$$Hg_2Cl_2\downarrow + Sn^{2+} + 4Cl^{-} \rightleftarrows 2Hg\downarrow + [SnCl_6]^{2-}$$

5. Tasks for individual work (write in a textbook for protocols):

5.1. What cations of IV^th analytical group can be identified by action of group reagent of this analytical group cations? Write the equations of the conforming reactions and explain the analytical effects.

5.2. What cations of the VI^th analytical group form red precipitate with potassium iodide, which is soluble in the reagent excess? Write the equations of the conforming reactions.

5.3. There are Cu^{2+} and Hg^{2+} cations in aqueous solution. What will happen, if we add $Na_2S_2O_3$ and hot nitric acid? Write the equations of the conforming reactions and explain the analytical effects.

5.4. Suggest the systematic analysis of solution which contains ions:

- Cu^{2+}, Co^{2+}, Ni^{2+};
- Hg^{2+}, Ni^{2+};
- Co^{2+}, Hg^{2+}, Cu^{2+}.

The situation problems are solved according to the analysis systematic course of the VI^th analytical group cations mixture.

6. Laboratory experiment

Laboratory experiment 13.1

Characteristic reactions of the VI^th analytical group cations and condition of their detection

1. Reaction with sodium hydroxide solution (NaOH)

All cations of VI^th group can be precipitated by addition of the reagent sodium hydroxide:

$Cu^{2+} + 2OH^- \leftrightarrow Cu(OH)_2\downarrow$ blue

$Hg^{2+} + 2OH^- \leftrightarrow Hg(OH)_2\downarrow$ white

$Hg(OH)_2\downarrow \rightarrow HgO\downarrow + H_2O$ yellow

$Co^{2+} + 2OH^- + NO_3^- \leftrightarrow Co(OH)Cl\downarrow$ blue

$Co(OH)Cl\downarrow + OH^- \leftrightarrow Co(OH)_2\downarrow + Cl^-$ pink

$Ni^{2+} + 2OH^- \leftrightarrow Ni(OH)_2\downarrow$ green

All hydroxides are dissolved in strong acids, for instanse:

$$Cu(OH)_2\downarrow + 2H^+ \rightarrow Cu^{2+} + 2H_2O$$

$$Ni(OH)_2\downarrow + 2H^+ \rightarrow Ni^{2+} + 2H_2O$$

Hydroxides of group VI^th cations can not be dissolved in excess of sodium hydroxide.

Procedure: Pour 3-5 drops of the copper, mercury, cobalt and nickel salts into small test tubes, add 5 drops of sodium hydroxide. Dissolve all precipitates in strong acid.

2. Reaction with precipitating agent (25% NH_4OH)

All cations of group VI may be precipitated and separated from the cations of another groups by adding 25% NH_4OH:

$2CuSO_4 + 2NH_4OH \rightarrow (CuOH)_2SO_4\downarrow + (NH_4)_2SO_4$ green

$Hg^{2+} + 2NH_3{\cdot}H_2O + Cl^- \rightleftharpoons [NH_2Hg]Cl\downarrow + NH_4^+ + H_2O$ white

$$Co^{2+} + NH_3{\cdot}H_2O + Cl^{-} \rightleftarrows Co(OH)Cl\downarrow + NH_4^{+} \qquad \text{blue}$$

$$Ni^{2+} + 2NH_3{\cdot}H_2O + SO_4^{2-} \rightleftarrows (NiOH)_2SO_4\downarrow + 2NH_4^{+} \qquad \text{green}$$

All precipitates can be dissolved in excess of precipitating agent:

$$(CuOH)_2SO_4\downarrow + 8NH_3{\cdot}H_2O \rightleftarrows [Cu(NH_3)_4]^{2+} + SO_4^{2-} + 2OH^{-} + 8H_2O$$

intensive-blue

$$[NH_2Hg]Cl\downarrow + 3NH_3{\cdot}H_2O \rightleftarrows [Hg(NH_3)_4]^{2+} + Cl^{-} + OH^{-} + 2H_2O$$

colouorless

$$(NiOH)_2SO_4\downarrow + 12NH_3{\cdot}H_2O \rightleftarrows 2[Ni(NH_3)_6]^{2+} + SO_4^{2-} + 2OH^{-} + 12H_2O$$

lilic

$$Co(OH)Cl\downarrow + 6NH_3{\cdot}H_2O \rightleftarrows 2[Co(NH_3)_6]^{2+} + Cl^{-} + OH^{-} + 6H_2O$$

brown

Procedure: Pour 3-5 drops of copper, mercury, cobalt and nickel salts into small test tubes, add 5 drops of 25% aqueous ammonia. Dissolve all precipitates in excess of precipitating agent.

3. Reaction with $Na_2S_2O_3$

Copper and mercury cations can be precipitated from aqueous solution as black precipitates by adding the reagent $Na_2S_2O_3$:

$$2Cu^{2+} + 2S_2O_3^{2-} + 2H_2O \rightarrow Cu_2S\downarrow + S\downarrow + 2SO_4^{2-} + 4H^{+} \qquad \text{black}$$

$$Hg^{2+} + S_2O_3^{2-} + H_2O \rightarrow HgS\downarrow + SO_4^{2-} + 2H^{+} \qquad \text{black}$$

Copper (I) sulfide can be dissolved in hot nitric acid and mercury (II) sulfide in bromine water:

$$2Cu_2S\downarrow + 4NO_3^{-} + 16H^{+} \rightarrow 6Cu^{2+} + 3S\downarrow + 4NO + 8H_2O$$

$$HgS\downarrow + Br_2 + 2Cl^{-} \rightarrow [HgCl_2] + 2Br^{-} + S\downarrow$$

Procedure: Pour 2-3 drops of the copper, mercury, cobalt and nickel salts into small test tubes, add $Na_2S_2O_3$. Dissolve copper (II) sulfide in hot nitric acid.

Cobalt (Co^{2+}) ions reactions (pink)

4. Reaction with sulfide-ions

Cobalt cations can be precipitated from aqueous solution as black precipitate by adding sulfide – ions:

$$Co^{2+} + S^{2-} \leftrightarrow CoS\downarrow \qquad \text{black}$$

Procedure: Pour 2-3 drops of the cobalt salt in a small test tube, add 2-3 drops of sodium sulfide.

5. Reaction with thiocyanate ions, SCN^{-}

$$Co^{2+} + 4SCN^{-} \leftrightarrow [Co(SCN)_4]^{2-} \qquad \text{blue}$$

Procedure: Place 2-3 drops of the cobalt salt solution into a small test tube, add a few crystals of ammonium thiocyanate and 5-6 drops of amil alcohol.

Mercury (Hg^{2+}) ions reactions (colorless)

1. Reaction with sulfide-ions

Mercury cations can be precipitated from aqueous solution as black–brown precipitate by addition sulfide – ions:

$$Hg^{2+} + S^{2-} \leftrightarrow HgS\downarrow \qquad \text{black–brown}$$

Procedure: Pour 2-3 drops of the mercury salt into a small test tube, add 5-6 drops of sodium sulfide.

2. Reaction with potassium iodide

Mercury (II) cations can be precipitated from aqueous solution as red precipitate by adding the reagent potassium iodide:

$$Hg^{2+} + 2I^{-} \leftrightarrow HgI_2\downarrow \qquad \text{red}$$

$HgI_2\downarrow$ can be dissolved in excess potassium iodide:

$$HgI_2\downarrow + 2I^{-} \rightarrow [HgI_4]^{2-} \qquad \text{colorless}$$

Pb^{2+}, Cu^{2+}, Ag^{+} and Bi^{3+} cations interfere with this test for mercury (II) cations.

Procedure: Pour 2-3 drops of the mercury salt into a small test tube, add 1 drop of potassium iodide. Dissolve the precipitate in excess of potassium iodide.

Nickel (Ni^{2+}) ions reactions (green)

Reaction with sulfide-ions

Nickel cations can be precipitated from aqueous solution as black precipitate by addition sulfide – ions:

$$Ni^{2+} + S^{2-} \leftrightarrow NiS\downarrow \qquad \text{black}$$

Procedure: Pour 2-3 drops of the nickel salt into a small test tube, add 5-6 drops of sodium sulfide.

2. Reaction with dimethylglyoxime ($HC_4H_7N_2O_2$)

The presence of Ni^{2+} is confirmed by the formation of bright red precipitate when an organic compound dimethylglyoxime called Chugaev reagent is added to ammonia solution:

$$[Ni(NH_3)_6]^{2+} + 2HC_4H_7N_2O_2 \rightarrow Ni(C_4H_7N_2O_2)_2 + 4NH_3 + 2NH_4^{+} \qquad \text{strawberry red}$$

Procedure: Pour 5-6 drops of the nickel salt into a small test tube, add 2-3 drops of aqueous ammonia and ammonium chloride and some drops of dimethylglyoxime.

Table 9

Action of some reagents to the VIth analytical group cations

Reagent	Cations			
	Cu^{2+}	Hg^{2+}	Co^{2+}	Ni^{2+}
NaOH or KOH	$Cu(OH)_2$↓ - blue	$Hg(OH)_2$↓ - white, decomposes to HgO↓ yellow	Co(OH)Cl↓ - blue	$Ni(OH)_2$↓- green
	Precipitates are dissolved in acids and ammonium excess			
$NH_3\cdot H_20$ without excess	$(CuOH)_2SO_4$↓ and others - green	NH_2HgCl↓ - white	Co(OH)Cl↓ and others - blue	$(NiOH)_2SO_4$↓ and others - green
	Precipitates are dissolved in the excess of reagent with complex cations forming			
	$[Cu(NH_3)_4]^{2+}$ - dark-blue	$[Hg(NH_3)_4]^{2+}$ - colourless	$[Co(NH_3)_6]^{2+}$- brown	$[Ni(NH_3)_6]^{2+}$ - lilac
	Are destroyed in acids			
$Na_2S_2O_3$	Cu_2S↓ black + S↓ dissolved in HNO_3	HgS↓ black, dissolved in bromine water	—	—
KI	CuI↓ "body colour" + I_2 brown	HgI_2↓ orange-red, disslved in the excess of the reagent forming $[HgI_4]^{2-}$ colourless	—	—
NH_4NCS	$Cu(NCS)_2$↓black, is gradually turning into CuNCS↓ white	$Hg(NCS)_2$↓ white, dissolved in the excess of the reagent forming $[Hg((NCS)_4]^{2-}$ colourless	$[Co(NCS)_4]^{2-}$ - blue solution	—
$SnCl_2$	Cu↓ - black	Hg↓ - black	—	—

Analysis systematic course of a mixture of the VIth analytical group cations

1. Preliminary observations and testing (see page 23)

2. Action of group reagent

Measure out 10-15 drops of the solution into a small test tube. Add 30 drops of 25% aqueous ammonia.

3. Destruction of ammonia complex compounds

Add 6M H_2SO_4 solution to the solution from point *2* to acidic medium (indicator paper is used).

4. Extraction of Cu^{2+} and Hg^{2+}

Add $Na_2S_2O_3$ to the solution from point *3*. Heat the test tube in a boiling water bath for some minutes. Separate the precipitate by centrifuge.

5. Separation Cu_2S from HgS

Measure out the precipitate from point *4* into a small test tube. Add 5-7 drops of 2M HNO_3. Heat the test tube in a boiling water bath for some minutes. Separate the precipitate by centrifuge.

6. Identification of Cu^{2+}

Add 8-10 drops of the reagent 25% aqueous ammonia into a small test tube. Add some drops of the supernate from point *5*. The formation blue solution indicates the presence of Cu^{2+}.

7. Identification of Hg^{2+}

Measure out the precipitate from point *6* into a small test tube. Add 6-8 drops of bromine water. Heat the test tube in a boiling water bath for some minutes. Separate the precipitate by centrifuge.

Add 1 drop of iodide to the supernate. The formation of red precipitate, which is soluble in the reagent excess, indicates the presence of Hg^{2+} cations.

8. Identification of Co^{2+}

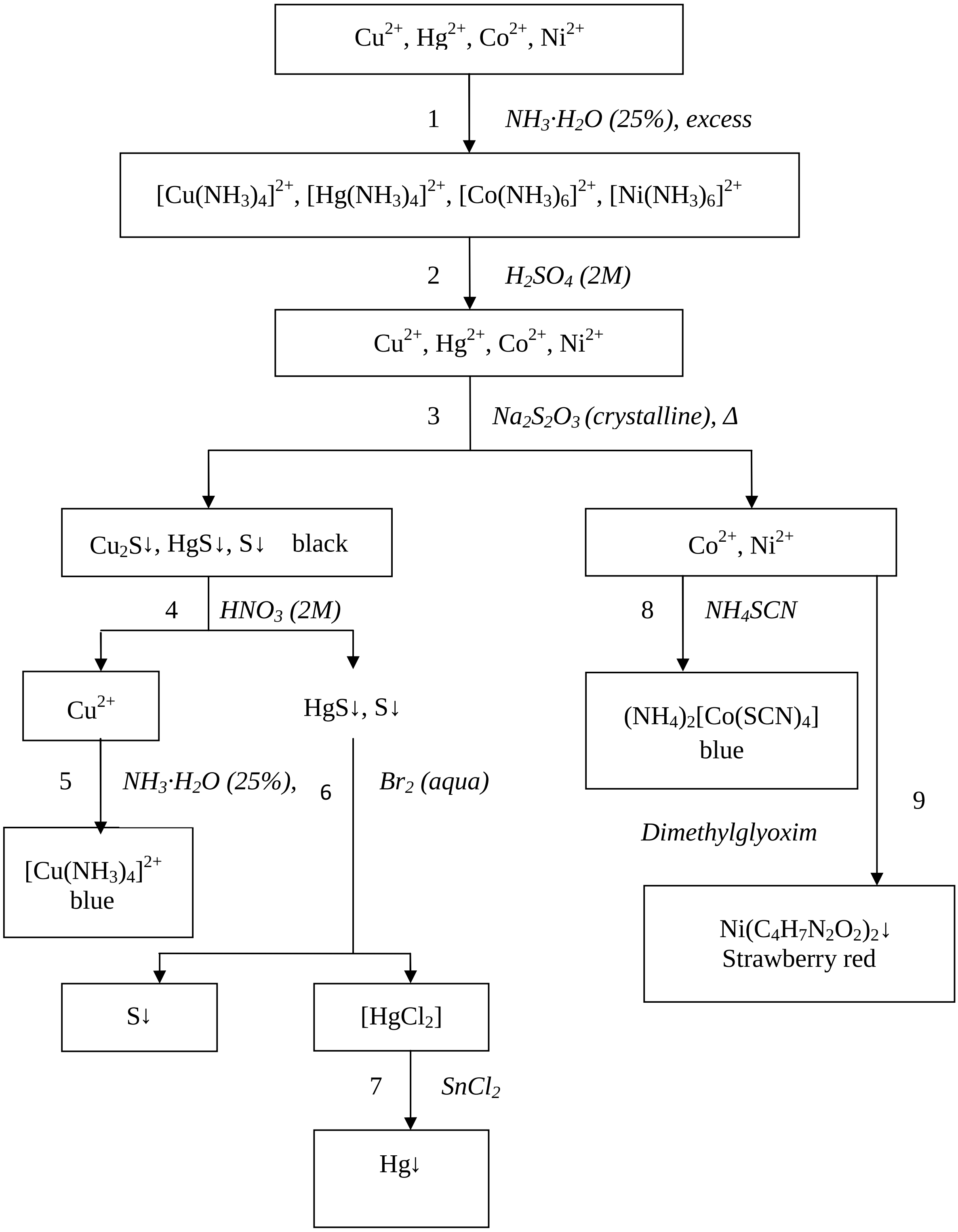
Add a few crystals of ammonium thiocyanate and amil alcohol to the supernate from point *4*. The formation of a blue organic layer indicates the presence of Co^{2+} cations.

9. Identification of Ni^{2+}

Add some drops of 25% aqueous ammonia and dimethylglyoxime to the supernate from point *4*. The formation of strawberry red precipitate indicates the presence of Ni^{2+} cations.

SCHEME OF ANALYSIS SYSTEMATIC COURSE THE VIth ANALYTICAL GROUP

Scheme 7



Topic 14
Complex Ion Equilibrium

1. The main purpose of the topic:

Complex compounds are widely used as reagents in qualitative analysis for of a number of cations and anions. The process of complex formation is more widely used, which occurs with both inorganic and organic reagents. Reactions of complex formation are used for identification of many drugs: vitamins, antibiotics, alkaloids, etc.

Comprehension of the theoretical bases of complex formation processes creates for students the theoretical base of both theoretical and practical principles of qualitative and quantitative analysis and also bases the subsequent study of such core of disciplines as pharmaceutical chemistry, pharmacognosicy, forensic chemistry, technology of drugs, etc. for future specialists in pharmacy.

2. Basic questions:

2.1. The structure of complex compounds.
2.2. Equilibrium in solutions of complex compounds. Dissociation of complex ions. Constant of instability. Calculation of ions concentrations in the solution of complex compound.
2.3. Conditions of formation and destruction of complex compounds.
2.4. Application of complex compounds with organic and inorganic ligands in the analysis.

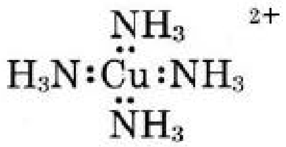
3. Brief exposition of theoretical material:

Coordination Compounds

A characteristic feature of the transition metals is their ability to form a group of compounds called **coordination compounds, complex compounds**, or sometimes simply **complexes**. A typical coordination compound $Cu(NH_3)_4SO_4$ is intensely blue solid substance which can be crystallized from solutions of $CuSO_4$ to which very large excess of concentrated NH_3 has been added. These crystals contain two polyatomic ions, one of which is the sulfate ion, SO_4^{2-}, and the other is the **complex ion** $Cu(NH_3)_4^{2+}$ which is responsible for blue color.

$$Cu^{2+} + 4NH_3 \rightleftarrows [Cu(NH_3)_4]^{2+}$$

We can regard a complex ion such as $Cu(NH_3)_4^{2+}$ as being the result of interaction of **:**NH_3 acting as Lewis base with the Cu^{2+} ion acting as a Lewis acid. Each NH_3molecule can be considered as donating a pair of electrons to a central Cu^{2+}, thus forming four coordinate covalent bonds to it:



$$\begin{array}{c} NH_3 \\ H_3N:\overset{..}{\underset{..}{Cu}}:NH_3 \\ NH_3 \end{array}^{2+}$$

Most coordination compounds contain a complex ion similar to $Cu(NH_3)_4^{2+}$. This ion can be either positively charged like $Cr(H_3O)_6^{3+}$, or it can be negatively charged like $CoCl_6^{3-}$. Neutral complexes like $Pt(NH_3)_2Cl_2$ are also known. All these species contain a central metal ion attached by coordinate covalent bonds to several **ligands**. These ligands are invariably Lewis bases. Some typical examples of ligands are H_2O, NH_3, Cl^-, OH^-, CN^-, Br^-, and SCN^-. The number of ligands attached to the central metal ionis said to be its **coordination number** and is usually 2, 4, or 6. The group of ligands bonded to the metal taken collectively is said to constitute the metal's **coordination sphere**.

When writing the formula of a coordination compound containing complex ions, square brackets are usually used to enclose the coordination sphere:

$[Cu(NH_3)_4]SO_4$ – tetraamminecopper (II) sulphate

The formation reaction of a complex ion is **reversible**, and the equilibrium state in the reaction is described through an equilibrium constant called a formation constant, represented by the symbol K_f. The K_a expression is for $[Cu(NH_3)_4]^{2+}$:

$$K_f = \frac{\left[\left[Cu(NH_3)_2\right]^{2+}\right]}{\left[Cu^{2+}\right]\cdot\left[NH_3\right]^4}$$

Complex compounds are electrolytes. The **primary** dissociation in aqua solutions proceeds almost to the end like the dissociation of strong electrolytes:

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

The **secondary** dissociation **(**ionization of complex ion) proceeds partly like the dissociation of weak electrolytes:

$$[Cu(NH_3)_4]^{2+} \rightleftarrows Cu^{2+} + 4NH_3$$

Ionization of complex ion can be characterized by the relevant equilibrium constant, known as the **constant of instability** of the complex ion:

$$K_{inst.} = \frac{\left[Cui^{2+}\right]\cdot\left[NH_3\right]^4}{\left[\left[Cui(NH_3)_4\right]^{2+}\right]}$$

$$K_{inst.} = \frac{1}{K_f}$$

The coordination compounds are of great importance. These compounds are widely present in the mineral, plant and animal worlds and are known to play many important functions in the area of analytical chemistry, industry and medicine.

4. Control test and patterns of responses:

4.1. Calculate the concentration of ions in 1M solution of $[Ag(NH_3)_2]^+$.

Answer:

The dissociation of the complex $[Ag(NH_3)_2]CI$ can be written as follows:

primary dissociation

$$[Ag(NH_3)_2]Cl \rightarrow [Ag(NH_3)_2]^+ + Cl^- \quad (1)$$

secondary dissociation

$$[Ag(NH_3)_2]^+ \leftrightarrow Ag^+ + 2NH_3 \qquad (2)$$

In accordance with (1) we can write:

$$[[Ag(NH_3)_2]^+] = C([Ag(NH_3)_2]Cl) = 1\ mol/l$$

In accordance with (2) we can write:

$$[Ag^+] = x\ mol/l;\ [NH_3] = 2x\ mol/l;\ [Ag(NH_3)_2]^+ = (1–x)\ mol/l$$

Next, enter the known and unknown concentrations into the K_{inst} expression and solve for *x:*

$$K_{inst} = \frac{[Ag^+]\cdot[NH_3]^2}{[Ag(NH_3)_2]^+} = \frac{x\cdot(2x)^2}{1-x} = 6.8\cdot 10^{-8}$$

1.0 » 6.8 · 10^{-8}. This means that you can use 1.0 M for $[Ag(NH_3)_2]^+$ in the K_{inst} expression.

$$4x^3 = 6.8\cdot 10^{-8}$$

$$x = [Ag^+] = \sqrt[3]{\frac{6.8\cdot 10^{-8}}{4}} = 2.4\cdot 10^{-3}\, mol/L$$

$$[NH_3] = 2x = 4.8\cdot 10^{-3}\, mol/L$$

5. Tasks for individual work (write in a textbook for protocols)*:*

5.1. Calculate the concentration of $[Hg^{2+}]$, $[I^-]$ and $[K^+]$ in 0,05M solution of $K_2[HgI_4]$. ($K_{inst.} = 1{,}48\cdot 10^{-30}$)

5.2. Will Ag_3PO_4 precipitate upon after mixing 10mL of 0,01M $[Ag(NH_3)_2]Cl$ with 10mL of 0,01M K_3PO_4? ($K_{SP}(Ag_3PO_4) = 1{,}3\cdot 10^{-20}$)

5.3. In which cases is the interaction between solutions of electrolytes possible?

$$[Ag(NH_3)_2]\ Cl + NaCN =$$

$$[Ag(NH_3)_2]\ NO_3 + NaNO_2 =$$

Explain. Write the equations of the conforming reactions.

Topic 15

Analysis systematic course of a mixture of the IV^th^ –VI^th^ analytical group cations

1. The main purpose of the topic:

Inorganic drugs, which contain more than one cation, but several are widely used in medical practice. And a lot of cations with the same reagents give similar analytical effects. The analysis of a mix of the IVth *–VI*th *analytical group cations is based on the knowledge of the characteristic reactions of metal cations of the IV*th *–VI*th *analytical groups, the conditions for their implementation, the properties of compounds that contain cations of these metals. But it is impossible to identify individual ions using analytical reactions ina randomly selected order. Therefore a systematic course of analysis of cations mixtures is often used in practice.*

Comprehension of a systematic course of analysis of mixtures of IVth *–VI*th *analytical group cations gives the students the theoretical base of chemical analysis, practical skills and experience of making.*

2. Basic questions:

2.1. Characteristic reactions of the IVth analytical group cations (acid – base classification). The analysis of a mix of the IVth analytical group cations.

2.2. Characteristic reactions of the fifth analytical group cations. The analysis of a mix of the fifth analytical group cations.

2.3. Characteristic reactions of the sixth analytical group cations. The analysis of a mix of the sixth analytical group cations.

3. Brief exposition of theoretical material:

Analysis systematic course of a mixture of the IVth –VIth analytical group cations

Mixture analysis should begin from trial tests and observations: colour, odour flame colouring, relation to water, acetic and inorganic acids, heating, definition; environment pH etc. It allows to make preliminary conclutions about availability of some cations in a mixture. The low values of pH indicate possible presence in solution of free acids or cations, which strongly hydrolyze, for example Bi^{3+}. Alkaline environment of the solution indicates presence of cations in mixture, for example Cu^{2+}, Co^{2+} etc., which form oxyhydroxides insoluble in water. After carrying out the trial tests and observations the systematic analysis is made.

Fe^{2+}, Fe^{3+} cations are found out by fractional reactions in separate portions of the analysed solution by action of solutions at, $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$ correspondingly.

From the analyzed solution, containing the IVth-VIth analytical groups cations, the cations of the IVth analytical group are separated from cations of the Vth, VIth calytical groups by the action of group reagent (6M NaOH excess, 3% solution of H_2O_2). The IVth analytical group cations still remain in the solution as hydrocomplexes and oxoanions, and the Vth and VIth analytical groups cations form precipitates of corresponding oxides, hydroxides and basic salts. The precipitate is separated by centrifuging. The centrifugate is analysed according to analysis systematic course of the mixture of the IVth analytical group cations.

For Sb(V) ions separation from other cations of the Vth and VIth analytical groups the precipitate is processed by 2M solution of HNO_3 and 3% solution of H_2O_2. During this process precipitates of other cations of Vth and VIth analytical groups are dissolved. $MnO_2 \cdot nH_2O$ and $Co(OH)_3$ are reduced up to Mn^{2+} and Co^{2+}, and Sb (V) remains as precipitate of $HSbO_3$, which is separated by centrifuging and analysed according to analysis systematic course of a mixture of the Vth analytical group cations.

For the Vth and VIth analytical groups cations separation to centrifugate the excess of concentrated solution of $NH_3 \cdot H_20$ is added. During this reaction, the cations of the Vth analytical group form precipitates of corresponding hydroxides and basic salts, but the VIth analytical group cations remain in the solution as metallamine. Subsequent precipitate and solution analysis is carried out according to the scheme of analysis of mixture of the Vth and VIth analytical groups cations correspondingly.

4. Tasks for individual work (write in a textbook for protocols):

4.1. The group reagent for the IVth analytical group added to a solution containing cations IVth –VIth groups of cations. What is observed? Write the equations of the conforming reactions.

4.2. The group reagent for the sixth analytical group is added to a solution containing cations IVth –VIth groups of cations. What is observed? Write the equations of the conforming reactions.

4.3. The solution of $K_4[Fe(CN)_6]$ is added to a solution containing cations IVth –VIth groups of cations. What is observed? Write the equations of the conforming reactions.

4.4. Suggest the systematic analysis of solution which contains ions:

- Cu^{2+}, Bi^{3+}, Zn^{2+};
- Ni^{2+}, Mn^{2+}, Al^{3+};
- Hg^{2+}, Cr^{3+}, Mg^{2+}.

The situation problems are solved according to the analysis systematic course of the IVth –VIth analytical group cations mixture.

5. Laboratory experiment

Laboratory experiment 15.1.

Analysis systematic course of a mixture of the IVth –VIth analytical group cations (without precipitate)

1. *Preliminary observations and testing (see page 26)*
2. *Detection of cations by separate method in analyzable solution*

2.1. Identification of Fe^{2+}

Measure out 5 drops of test solution into a small test tube. Add 5 drops of potassium hexacyanoferrate (III), $K_3[Fe(CN)_6]$. The formation of blue precipitate indicates the presence of iron (II) cations.

2.2. Identification of Fe^{3+}

Measure out 5 drops of the test solution into a small test tube. Add 5 drops of potassium hexacyanoferrate (II), $K_4[Fe(CN)_6]$. The formation of dark blue precipitate indicates the presence of iron (III) cations.

3. Separation of IVth analytical group cations from Vth and VIthanalyticasl groups cations

Measure out 20-25 drops of the solution into a small test tube. Add 1mL of 4M NaOH and 5 drops of 3% hydrogen peroxide. Heat the test tube in a boiling-water bath until hydrogen peroxide troyed full. (You will see: secretion of oxygen bubbles will be finished). The formation of yellow solution indicates the presence of chromium cations. Hydroxo- and oxoanions of IVth analytical group are centrifugate. The oxides, hydroxides and base salts of Vth-VIth analytical group cations are precipitate.

3.1. Analysis of IVthanalytical group cations

Add ammonium chloride to the solution from Procedure №3 and place the test tube in a hot-water bath. The formation of precipitate indicates the presence of $Al(OH)_3$. Centrifuge and decant the supernate into a clean test tube.

3.2. Identification of Al^{3+}

Add some drops of 2M HCl to the precipitate from Procedure №3.1. Add 3 drops of aqueous ammonia and Aluminon reagent. The formation of red precipitate indicates the presence of aluminum.

3.3. Identification of Zn^{2+}

Add some drops of the reagent potassium hexacyanoferrate (II), $K_4[Fe(CN)_6]$ to the supernate from Procedure №3.1. Heat the test tube in a boiling-water bath for 3 min. The formation of white precipitate indicates the presence of zinc.

4. Separation of antimony cations

The precipitate which was obtained from Procedure №3, 20-30 drops of 2M nitric acid, 10- 15 drops of 3 % peroxide hydrogen solution are added and heated in the water both till full H_2O_2 decomposition. The mixture is centrifuged.

The Vth-VIth analytical group cations are in the centrifuge, $HSbO_3$ is in the precipitate.

4.1. Detection of antimony cations

The precipitate obtained from Procedure №4 is dissolved in 10-15 drops of concentrate chlorohydrogen acid. 1-2 drops of the obtained solution are placed on the nickel plate and a zinc granule is added.

5. Separation of the Vth-VIth analytical group cations

Measure out 10-15 drops of the solution from Procedure№4 into a small test tube. Add 30 drops of 25% aqueous ammonia and saturated solution of NH_4Cl, centrifuge. The mixture is centrifuged. The amnionic complexes of VIth analytical group cations and Mg^{2+}cation are in the centrifuge, hydroxides of Vth analytical group cations are the precipitate.

6. Analysis of Vth analytical group cations

Add 10-15drops of 2M HC1 to the precipitate from Procedure№5 and heating carefully. Centrifuge and decant the supernate into a clean test tube.

6.1. Identification of Mn^{2+}

Measure out 3-4 drops of 2M HNO_3 into a small test tube. Add 2 drops of $AgNO_3$ and $(NH_4)_2S_2O_8$. Heat the test tube in a boiling-water bath for 3 minutes. Add the solution from Procedure№6. The formation of purple solution indicates the presence of Mn^{2+}.

6.2. Identification of Bi^{3+}

Add 2 drops of the reagent potassium iodide into a small test tube. Add some drops of the supernate from Procedure№6. The formation of black precipitate indicates the presence of Bi^{3+}.

7. Analysis of VIth analytical group cations and Mg^{2+}

7.1. Identification of Mg^{2+}

Add 2 drops of Na_2HPO_4, 2 drops of ammonium chloride and aqueous ammonia to the supernate from Procedure№5. The formation of white precipitate indicates the presence of Mg^{2+}.

7.2. Reaction with 6M sulfuric acid

Add some drops of 6M H_2SO_4 to the solution from Procedure №5.

7.3. Separation of the Cu^{2+} *and* Hg^{2+}

Add $Na_2S_2O_3$ to the solution from Procedure №7.2. Heat the test tube in a boiling-water bath for some minutes. Centrifuge it.

7.4. Separation Cu_2S *from HgS*

Measure out the precipitate from Procedure №7.3 into a small test tube. Add 5-7 drops of 2M HNO_3. Heat the test tube in a boiling-water bath for some minutes. Centrifuge it.

7.5. Identification of Cu^{2+}

Add 8-10 drops of the reagent 25% aqueous ammonia into a small test tube. Add some drops of the supernate from Procedure №7.4. The formation of blue solution indicates the presence of Cu^{2+}.

7.6. Identification of Hg^{2+}

Measure out the precipitate from Procedure №7.3 into a small test tube. Add 6-8 drops of brome water. Heat the test tube in a boiling-water bath for some minutes. Centrifuge it.

Add 1 drop of potassium iodide to the supernate. The formation of red precipitate indicates the presence of mercury.

7.7. Identification of Co^{2+}

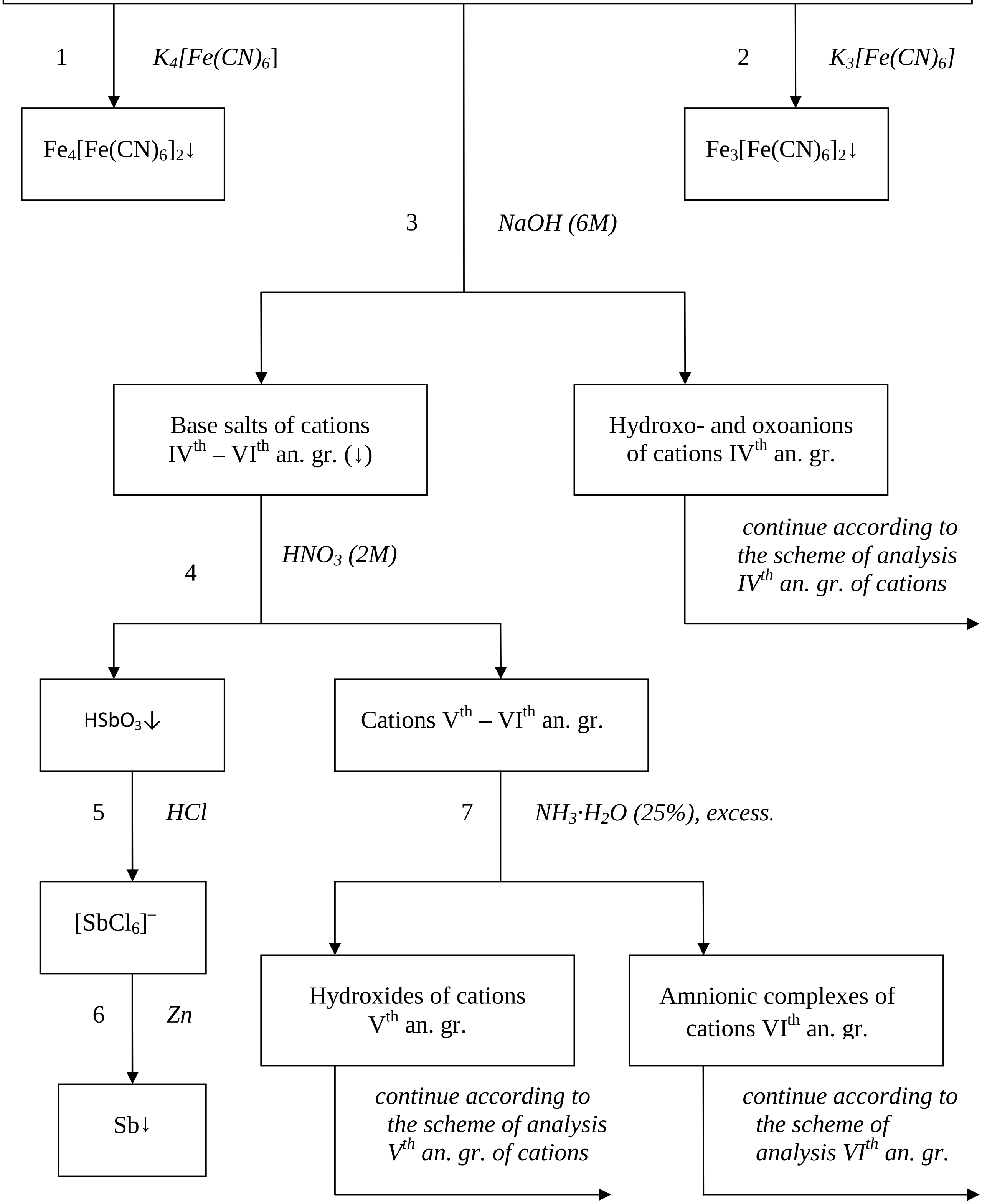
Add some drops of saturated solution of ammonium thiocyanate and chloroform to the supernate from Procedure №7.4. The formation of blue solution indicates the presence of cobalt cations.

7.8. Identification of Ni^{2+}

Add some drops of 25% aqueous ammonia and dimethylglyoxime to the supernate from Procedure №7.4. The formation of strawberry red precipitate indicates the presence of nickel.

SCHEME OF ANALYSIS SYSTEMATIC COURSE THE IVth –VIth ANALYTICAL GROUP

Scheme 8



Topic 16
Analysis systematic course of a mixture of the IVth – VIth analytical groups cations
Experimental control problem

Objective: identifying cations of the IVth – VIth analytical groups in the mixture, using analysis systematic course of a mixture of the IVth – VIth analytical groups cations.

Laboratory experiment 16.1.

Each student receives solution from the teacher and applying systematic analysis of a mix of the IVth – VIth analytical group cations detects what cations are present in it. In writing describe procedure of the analysis, the reactions, observations and conclusions in the laboratory copybook.

Thematic Module 2

Objective: checking the students comprehension which they got at the lectures and practical lessons in the following sections:

1. Characteristic reactions of the IVth analytical group cations. Analysis systematic course of the IVth analytical group cations (topic 9).
2. Acid – base equilibrium (topic 10).
3. Characteristic reactions of the Vth analytical group cations. Analysis systematic course of the Vth analytical group cations (topic 11).
4. Oxidation – reduction equilibrium (topic 12).
5. Characteristic reactions of the VIth analytical group cations. Analysis systematic course of the VIth analytical group cations (topic 13).
6. Complex ion equilibrium (topic 14).
7. Analysis systematic course of a mixture of the IVth – VIth analytical group cations (topic 15).

Control card of thematic module 2 includes the tasks:

- 8 tests. You must select the correct answer and give a brief explanation, write the corresponding equations of chemical reactions;
- 4 calculation problems. You must write the corresponding equations of chemical reactions, write the formula that used in the course of solving the problem, and perform the necessary calculations to indicate the unit of measurement calculated parameters.

Theory and practice analysis of anions and unknown sample

Objectives:

Classifying anions. Applying the group reagents in the analysis of anions. Carrying out and explaining the conditions of the reactions of anions: SO_4^{2-}, SO_3^{2-}, $S_2O_3^{2-}$, CrO_4^{2-} ($Cr_2O_7^{2-}$), BO_2^- ($B_4O_7^{2-}$), CO_3^{2-}, AsO_4^{3-}, AsO_3^{3-}, CO_3^{2-}, $C_2O_4^{2-}$, PO_4^{3-}, Cl^-, Br^-, I^-, S^{2-}, NO_3^-, NO_2^-, CH_3COO^-, BrO_3^- , anions of organic acids.

Carrying out fractional and systematic course of the analysis mixture of anions. Explaining the features of the analysis of mixtures of substances of known and unknown composition.

Learning the methods of separation and concentration. Explaining the essence of extraction. Applying the methods of separation and concentration in qualitative analysis. Learning qualitative elemental and functional analysis.

THE ANALYSIS OF ANIONS

Anions, unlike cations, may be found out in separate portions of solution fractional reactions in any consequence. But for analysis simplification they are divided into some groups. There is no common principle of anions separation into these groups. In most cases anions classification is based on the difference in solubility barium and silver salts of corresponding anions.

According to this classification to the I^st^ analytical group the following anions are reffered: SO_4^{2-}, SO_3^{2-}, CO_3^{2-}, $S_2O_3^{2-}$, $C_2O_4^{2-}$, BO_2^- ($B_4O_7^{2-}$), PO_4^{3-}, AsO_4^{3-}, AsO_3^{3-}, F^-,CrO_4^{2-}($Cr_2O_7^{2-}$),etc.

To the II^nd^ analytical group such anions are reffered: Cl^-, Br^-, I^-, S^{2-} etc.

To the III^d^ analytical group: NO_2^-, NO_3^-, CH_3COO^- etc.

Group reagent on I analytical group anions are the solutions of barium chloride or nitrate in neutral or alkalescent medium (pH ~ 7-9). In such conditions they form salts with Ba^{2+} ions, which are hardly soluble in water, but are soluble in diluted HCl except $BaSO_4$.

Group reagent on II^nd^ analytical group anions is the solution of silver nitrate, acidulous by 2M solution of nitric acid. The II^nd^ analytical group anions form precipitations with Ag^+ cations, insoluble in diluted nitric acid. At II^nd^ analytical group anions determination by action of $AgNO_3$ solution the group reagent is acidified but not the analysed solution, because at acidifying of analysed solution by nitric acid S^{2-} -ions acidify up to S or SO^{2-} or will be lost.

The III^d^ analytical group anions with the most of cations form salts, which are well dissolved in water, therefore they have no group reagent.

Group reagents in the analysis of anions have another purpose, than in the analysis of cations. They are used not for groups separation, but only for their detection. Along with group reagents action the series of group samples is carried out for simplification of anions analysis. Such samples allow to reveal availability of particular groups of anions:

- sample on oxidizing anions ($Cr_2O_7^{2-}$, AsO_4^{3-}, NO_3^-) - oxidizing anions are found out by action of KI solution in acidic medium at the presence of chloroform, which in case of their presence tinctures in red-violet;

- sample on reducing anions ($C_2O_4^{2-}$ $S_2O_3^{2-}$, S^{2-}, SO_3^{2-}, AsO_3^{3-}, I^-, NO_2^-) - reducing anions are found out by decolorization of iodine solution in subacid medium, except AsO_3^{3-}-ions , which are found out in alkalescent medium;
- sample on anions of nonresistant acids (H_2SO_3, $H_2S_2O_3$, H_2CO_3 etc.) is carried out by action of HCl, owing to which gaseous products (SO_2, CO_2, H_2S etc.) are formed;
- sample on anions (Cl^-, Br^-, I^-, $C_2O_4^{2-}$, NO_3^-, SO_3^{2-}, $S_2O_3^{2-}$ etc.) is carried out by action of concentrated H_2SO_4 on their salt, owing to which gaseous products (Cl_2, I_2, CO_2 etc.) are formed.

Classification of anions based on the formation of insoluble salts of barium and silver

Table 10

Group	Anions	Precipitating agents
I	SO_4^{2-}, SO_3^{2-}, CO_3^{2-}, $S_2O_3^{2-}$, $C_2O_4^{2-}$, BO_2^- ($B_4O_7^{2-}$), PO_4^{3-}, AsO_4^{3-}, AsO_3^{3-}, F^-	Solution of barium chloride in a neutral or slightly alkaline environment
II	Cl^-, Br^-, I^-, S^{2-}, NCS^-, CN^-, BrO_3^-	Solution of silver nitrate in 2M nitric acid solution
III	NO_2^-, NO_3^-, CH_3COO^-	No group reagent

Classification of anions based on the redox properties

Table 11

Group	Anions	Group reagent
I Oxidizers	BrO_3^-, AsO_4^{3-}, NO_3^-, NO_2^-	KI solution in sulfuric acid
II Reducers	SO_3^{2-}, S^{2-}, $S_2O_3^{2-}$, AsO_3^{3-}	Solution I_2 in KI
	SO_3^{2-}, S^{2-}, $S_2O_3^{2-}$, AsO_3^{3-}, NO_2^-, $C_2O_4^{2-}$, Cl^-, Br^-, I^-, CN^-, NCS^-	Solution $KMnO_4$ in sulfuric acid
III Indifferent	SO_4^{2-}, CO_3^{2-}, PO_4^{3-}, $B_4O_7^{2-}$, (BO_2^-), CH_3COO^-	No group reagent

In the analytical classification of anions, based on their redox properties, anions are divided into three groups: anions-oxidants, anions-reducings and indifferent anions, those who do not have oxidation-reduction properties under normal conditions.

Topic 17
Chemistry of the Group Ist anions (classification based on the formation of insoluble salts of barium and silver)

1. The main purpose of the topic:

A systematic scheme based on the kinds of principles involved in cation analysis can be designed for the analysis of anions. This would involve the separation of the anions followed by their identification. However, it is generally easier to take another approach to the identification of anions. An effort is made either to eliminate or verify the presence of certain anions on the basis of the colour and solubility of the samples; then the material being analyzed is subjected to a series of preliminary tests. From the results of the preliminary tests and observations, certain anions may definitely be shown to be present or absent; then specific tests are performed for those anions not definitely eliminated in the preliminary tests and observations. The preliminary tests include treating the solid with concentrated sulfuric acid and using silver nitrate and $BaCl_2$ *precipitating agents.*

The colour of substance offers a clue to its constituents. By contrast, only a few anions are coloured, and these contain transition metals as well. The coloured anions are chromate, CrO_4^{2-}*, yellow; dichromate,* $Cr_2O_7^{2-}$*, orange-red; and permanganate,* MnO_4^-*, violet-purple. Hence, the colour of the solid may be used as a very good indicator of the presence of these ions. Observe the colour of your unknown and note it on the report sheet.*

There are different classifications of anions. Below there are the classifications based on the ability of anions to form insoluble compounds with cations of barium and silver, and on the redox properties of anions in aqueous solutions.

2. Basic questions:

2.1. Ist analytical group anions (classification based on the formation of insoluble salts of barium and silver), general characteristic, characteristic reactions of Ist group anions.
2.2. The group reagent, conditions for it application.
2.3. Characteristic reactions of SO_4^{2-} anions.
2.4. Characteristic reactions of SO_3^{2-} anions.
2.5. Characteristic reactions of $S_2O_3^{2-}$ anions.
2.6. Characteristic reactions of CO_3^{2-} anions.
2.7. Characteristic reactions of PO_4^{3-} anions.
2.8. Characteristic reactions of AsO_4^{3-} anions.
2.9. Characteristic reactions of AsO_3^{3-} anions.
2.10. Characteristic reactions of BO_2^- ($B_4O_7^{2-}$) anions.
2.11. Characteristic reactions of CrO_4^{2-}($Cr_2O_7^{2-}$) anions.
2.12. Characteristic reactions of F^- anions.
2.13. The analysis of a mix of the Ist analytical group anions.

3. Brief exposition of theoretical material:

General characteristic of the Ist analytical group anions

Group reagent on Ist analytical group anions are the solutions of barium chloride or nitrate in neutral or alkalescent medium (pH ~ 7-9). In such conditions they form salts with Ba^{2+} ions, which are hardly soluble in water, but are soluble in diluted HCl except $BaSO_4$. Precipitates barium salts are soluble in mineral acids, except barium sulfate $BaSO_4$. Carbonate $BaCO_3$, tetraborate BaB_4O_7, orthophosphate $Ba_3(PO_4)_2$ and arsenate $Ba_3(AsO_4)_2$ and are soluble in acetic acid.

The Ist analytical group anions (except F^-) are also precipitated by Ag^+ cations, but their precipitates are dissolved in nitric acid.

Anions of the first analytical group in aqueous solutions are colourless. The first group includes anions-oxidants (AsO_4^{3-}, sometimes CrO_4^{2-}, $Cr_2O_7^{2-}$), and anions-reducing (AsO_3^{3-}, $S_2O_3^{2-}$, $SO_3^{2-)}$. Anions of "volatile" acids ($SO_3^{2-,}$ $S_2O_3^{2-}$and CO_3^{2-}) are destroyed under the action of mineral acids with evolution of gaseous CO_2 or SO_2.

4. Control test and patterns of responses:

4.1. Name the anions unstable and volatile acids, which belong to the first analytical group (classification based on the formation of insoluble salts of barium and silver (I)). Write their relation to hydrochloric acid. Write the corresponding reactions.

Answer:

Anions volatile acids are decomposed in contact with mineral acids with evolution of gaseous products.

The first group of anions (classification based on the formation of insoluble salts of barium and silver (I)) include of anions volatile acids: sulfite - SO_3^{2-}, thiosulfate - $S_2O_3^{2-}$, carbonate - CO_3^{2-}.

All sulfites decomposed mineral acids with evolution of gaseous sulfur dioxide SO_2:

$$SO_3^{2-} + 2H^+ \rightarrow SO_2\uparrow + H_2O$$

Sulfur dioxide is found out by a characteristic odour and discoloration by water solution of iodine or potassium permanganate:

$$SO_2\uparrow + I_2 + 2H_2O \rightarrow H_2SO_4 + 2HI$$

$$5SO_2\uparrow + 2KMnO_4 + 2H_2O \rightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4$$

The action of mineral acids to thiosulfates at first formed unstable acid $H_2S_2O_3$, which is quickly decomposed with evolution of gaseous sulfur dioxide SO_2 and elemental sulfur S, that causes turbidity of the solution:

$$S_2O_3^{2-} + 2H^+ \rightarrow H_2S_2O_3$$

$$H_2S_2O_3 \rightarrow S\downarrow + SO_2\uparrow + H_2O$$

Gaseous sulfur dioxide, that is given off, is found by a characteristic odour, or discoloration of solution of potassium permanganate or iodine.

Carbonate ions and bicarbonate ions in the interaction with acids form weak unstable carbonic acid which is quickly decomposed in acidic medium with the release of gaseous carbon dioxide CO_2:

$$CO_3^{2-} + 2H_3O^+ \rightarrow H_2CO_3 + 2H_2O$$

$$HCO_3^- + H_3O^+ \rightarrow H_2CO_3 + H_2O$$

$$H_2CO_3 \rightarrow CO_2\uparrow + H_2O$$

Carbon dioxide, that is given off, is found out in the device to detect gases by turbidity lime water as a result the formation of soluble calcium (barium) carbonate:

$$Ca^{2+} + 2OH^- + CO_2\uparrow \rightarrow CaCO_3\downarrow + H_2O$$

5. Tasks for homework (write in a textbook for protocols):

5.1. Which reaction must you separate AsO_3^{3-} and AsO_4^{3-} ions?

5.2. Write the scheme for separation and identification ions in the following sample solutions that contains:

- $Cr_2O_7^{2-}$, $S_2O_3^{2-}$;
- PO_4^{3-}, SO_3^{2-};
- SO_4^{2-}, CO_3^{2-}.

The situation tasks are solved according to the systematic analysis of the Ist analytical group anions mixture.

6. Laboratory experiment

Laboratory experiment 17.1.

Characteristic reactions of the Ist analytical groups of anions

Sulfate (SO_4^{2-}) ions reactions

1. Reaction with precipitating agent BaCl$_2$

Sulfate anions can be precipitated from aqueous solution as white precipitate by addition $BaCl_2$:

$$Ba^{2+} + SO_4^{2-} \leftrightarrow BaSO_4\downarrow \qquad \text{white}$$

Barium sulfate can't be dissolved in strong acids and bases.

Procedure: Pour 10 drops of solution of the anion into a test tube, acidify it with 6M HC1, and add 1 drop of $BaCl_2$ solution. White precipitate of $BaSO_4$ confirms SO_4^{2-} ions.

2. Reaction with Lead (II) cations Pb^{2+}

Sulfate anions can be precipitated from aqueous solution as white precipitate by addition Pb^{2+}:

$$Pb^{2+} + SO_4^{2-} \leftrightarrow PbSO_4\downarrow \qquad \text{white}$$

$PbSO_4\downarrow$ can be dissolved in strong bases and ammonium acetate at heating:

$$PbSO_4\downarrow + 4NaOH \rightarrow Na_2[Pb(OH)_4] + Na_2SO_4$$

$$2PbSO_4\downarrow + 2CH_3COO^- \rightarrow [Pb(CH_3COO)_2PbSO_4] + SO_4^{2-}$$

Procedure: Pour 3-4 drops of solution of the anion into a test tube, add 2-3 drops of $Pb(NO_3)_2$ solution. Dissolve the precipitate in strong base.

Sulfite (SO_3^{2--}) ions reactions

1. Reaction with precipitating agent BaCl$_2$

Sulfite anions can be precipitated from aqueous solution as white precipitate by addition $BaCl_2$:

$$Ba^{2+} + SO_3^{2-} \leftrightarrow BaSO_3\downarrow \quad \text{white}$$

$BaSO_3$ can be dissolved in strong acids (HCI or HNO_3)

$$BaSO_3 + 2HCl \rightarrow SO_2\uparrow + BaCl_2 + H_2O$$

Procedure: Pour 10 drops of a solution of the anion into a test tube, acidify it with 6M HCI and add 2-3 drops of $BaCl_2$.

2. Reaction with strong inorganic acids

When sulfite anions react with strong acids a colorless gas is formed:

$$SO_3^{2-} + 2H^+ \rightarrow SO_2\uparrow + H_2O$$

Sulfur dioxide can react with iodine water and potassium permanganate:

$$SO_2 + I_2 + 2H_2O \rightarrow H_2SO_4 + 2HI \qquad \text{colorless}$$

$$5SO_2 + 2KMnO_4 + 2H_2O \rightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4 \qquad \text{colorless}$$

Procedure: Pour 6-8 drops of solution of the anion into a test tube, and add 6-8 drops of sulfuric acid.

3. Reaction with silver nitrate $AgNO_3$

Sulfite anions can be precipitated from aqueous solution as white precipitate by addition $AgNO_3$:

$$2Ag^+ + SO_3^{2-} \rightarrow Ag_2SO_3\downarrow \text{ white}$$

$$Ag_2SO_3 \rightarrow Ag_2O\downarrow + SO_2\uparrow \text{ brown-black}$$

Procedure: Pour 6-8 drops of a solution of the anion into a test tube, and add some drops of silver nitrate. Heat the test tube in a boiling water bath for some minutes.

4. Reaction with potassium permanganate $KMnO_4$

Sulfite anions can be oxidized in acidic solution by adding potassium permanganate:

$$5SO_3^{2-} + 2MnO_4^- + 6H^+ \rightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O \text{ colorless}$$

Procedure: Pour 2-3 drops of solution of the anion in a test tube, and add 1 drop of sulfuric acid and some drops of $KMnO_4$.

5. Reaction with I_2

Sulfite anions can be oxidized in neutral solution by adding iodine solution:

$$SO_3^{2-} + I_2 + H_2O \rightarrow SO_4^{2-} + 2I^- + 2H^+ \text{ colorless}$$

Procedure: Pour 2-3 drops of solution of the anion into a test tube, and add 2-3 drops of acetic acid and iodine solution.

Thiosulfate ($S_2O_3^{2-}$) ions reactions

1. Reaction with precipitating agent $BaCl_2$

Thiosulfate anions can be precipitated from aqueous solution as white precipitate by addition $BaCl_2$:

$$Ba^{2+} + S_2O_3^{2-} \rightarrow Ba_2S_2O_3\downarrow \text{ white}$$

BaS_2O_3 is dissolved in strong acids:

$$Ba_2S_2O_3 + 2H^+ \rightarrow Ba^{2+} + S\downarrow + SO_2\uparrow + H_2O$$

Procedure: Pour 2-3 drops of solution of the anion into a test tube and add 2-3 drops of $BaCl_2$ solution.

2. Reaction with strong inorganic acids

When thiosulfate anions react with strong acids a colourless gas, sulphur dioxide SO_2, sulphur and precipitate of sulfur forms:

$$S_2O_3^{2-} + 2H^+ \rightarrow H_2S_2O_3$$

$$H_2S_2O_3 \rightarrow S\downarrow + SO_2\uparrow + H_2O \text{ white}$$

Procedure: Pour 3-4 drops of a solution of the anion into a test tube, and add some drops of HCI.

3. Reaction with I₂

Thiosulfate-ions are decolorized iodine solution:

$$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^- \quad \text{colorless}$$

Procedure: Pour 3-4 drops of a solution of I_2 into a test tube and add some drops of thiosulfate anions.

4. Reaction with silver nitrate AgNO₃

Thiosulfate anions can be precipitated from aqueous solution as white precipitate by adding $AgNO_3$:

$$2Ag^+ + S_2O_3^{2-} \rightarrow Ag_2S_2O_3\downarrow \qquad \text{white}$$

$Ag_2S_2O_3$ is decomposed with formation of black precipitate of a Ag_2S:

$$Ag_2S_2O_3 + H_2O \rightarrow Ag_2S\downarrow + H_2SO_4 \quad \text{brown-black}$$

Procedure: Pour 2-3 drops of solution of the anion into a test tube and add some drops of silver nitrate.

5. Reaction with copper (II) sulfate CuSO₄

Thiosulfate anions can be precipitated from aqueous solution as black precipitate cupper (I) sulfide Cu_2S by adding copper (II) sulfate:

$$2Cu^{2+} + 3S_2O_3^{2-} \rightarrow Cu_2S_2O_3 + S_4O_6^{2-}$$

$$Cu_2S_2O_3 + H_2O \rightarrow Cu_2S\downarrow + H_2SO_4 \quad \text{black}$$

Procedure: Pour 2-3 drops of solution of the anion into a test tube and add some drops of copper (II) sulfate.

Oxalate ($C_2O_4^{2-}$) ions reactions

1. Reaction with precipitating agent BaCl₂

Oxalate anions can be precipitated from aqueous solution as white precipitate by adding $BaCl_2$:

$$Ba^{2+} + C_2O_4^{2-} \rightarrow BaC_2O_4\downarrow \quad \text{white}$$

Barium oxalate can be dissolved in strong acids and hot acetic acid.

$$BaC_2O_4\downarrow + 2H^+ \rightarrow Ba^{2+} + H_2C_2O_4$$

Procedure: Pour 2-3 drops of the ammonium oxalate into a test tube and add 2-3 drops of $BaCl_2$.

2. Reaction with silver nitrate AgNO₃

Oxalate anions can be precipitated from aqueous solution as white precipitate by adding $AgNO_3$:

$$2Ag^+ + C_2O_4^{2-} \rightarrow Ag_2C_2O_4\downarrow \quad \text{white}$$

Silver oxalate can be dissolved in nitric acid and concentrated solution of aqueous ammonia.

Procedure: Pour 2-3 drops of the ammonium oxalate into a test tube and add 2-3 drops silver nitrate.

3. Reaction with potassium permanganate KMnO₄

Oxalate-ions decolorize potassium permanganate solution in acid environment:

$$5C_2O_4^{2-} + 2MnO_4^- + 16H^+ \rightarrow 10CO_2 + 2Mn^{2+} + 8H_2O \quad \text{colorless}$$

Procedure: Pour 2-3 drops of the ammonium oxalate into a test tube, and add 3-5 drops of sulfuric acid, heat the test tube in a boiling - water bath for some minutes, add some drops of potassium permanganate.

4. Reaction with calcium chloride solution $CaCl_2$

Oxalate-ions form white fine-grained precipitate CaC_2O_4 with calcium ions:

$$Ca^{2+} + C_2O_4^{2-} \rightarrow CaC_2O_4\downarrow$$

Precipitate is dissolved in inorganic acids and is not dissolved in acetic acid:

$$CaC_2O_4\downarrow + 2H^+ \rightarrow Ca^{2+} + H_2C_2O_4$$

Procedure: Pour 2-3 drops of the ammonium oxalate into a test tube and add 2-3 drops calcium chloride.

Carbonate (CO_3^{2-}) ions reactions

1. Reaction with precipitating agent $BaCl_2$

Carbonate anions can be precipitated from aqueous solution as white precipitate by adding $BaCI_2$:

$$Ba^{2+} + CO_3^{2-} \rightarrow BaCO_3\downarrow \quad \text{white}$$

$BaCO_3$ can be dissolved in strong acids (HCI and HNO_3) and in week acetic acid.

$$BaCO_3\downarrow + 2H^+ \rightarrow H_2CO_3 + Ba^{2+}$$

$$H_2CO_3 \rightarrow CO_2\uparrow + H_2O$$

Procedure: Pour 2-3 drops of carbonate anions into a test tube and add 2-3 drops of $BaCI_2$ solution.

2. Reaction with magnesium sulfate $MgSO_4$

Carbonate anions can be precipitated from aqueous solution as white precipitate by adding $MgSO_4$:

$$Mg^{2+} + CO_3^{2-} \rightarrow MgCO_3\downarrow \quad \text{white}$$

Hydrocarbonates give a similar precipitate only at boiling:

$$2HCO_3^- + Mg^{2+} \rightarrow MgCO_3\downarrow + CO_2\uparrow + H_2O$$

Procedure: Pour 3-5 drops of carbonate anions into a test tube and add 5 drops of $MgSO_4$.

3. Reaction with inorganic acids

Carbonate-ions are decomposed with formation of CO_2 and H_2O under action an acid:

$$CO_3^{2-} + 2H^+ \rightarrow H_2CO_3 \rightarrow CO_2\uparrow + H_2O$$

White precipitate of $CaCO_3$ is formed at passing CO_2 through lime water:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3\downarrow + H_2O$$

Procedure: Pour 3-5 drops of carbonate anions into a test tube and add 5 drops of HCl or H_2SO_4 and immediately close the test tube with a stopper free end which is quickly dipped in lime water, which is located in test tube receivers 2. In the first test-tube there is effervescence (CO_2), in the second test tube - clouding of the solution.

Phosphate (PO_4^{3-}) ions reactions

1. Reaction with precipitating agent $BaCl_2$

Phosphate anions can be precipitated from aqueous solution as white precipitate by adding $BaCl_2$:

$$2PO_4^{3-} + 3Ba^{2+} \rightarrow Ba_3(PO_4)_2\downarrow \text{ white}$$

Precipitate is dissolved in inorganic acids:

$$Ba_3(PO_4)_2\downarrow + 6H^+ \rightarrow 3Ba^{2+} + 2H_3PO_4$$

Procedure: Pour 2-3 drops of the phosphate anions into a test tube, add some drops of $BaCl_2$.

2. Reaction with silver nitrate $AgNO_3$

Phosphate anions can be precipitated from aqueous solution as yellow precipitate by adding $AgNO_3$:

$$PO_4^{3-} + 3Ag^+ \rightarrow Ag_3PO_4\downarrow \text{ yellow}$$
$$HPO_4^{2-} + 3Ag^+ \rightarrow Ag_3PO_4\downarrow + H^+$$

Precipitate is dissolved in nitric acid:

$$Ag_3PO_4\downarrow + 3H^+ \rightarrow 3Ag^+ + H_3PO_4$$

And in ammonia solution:

$$Ag_3PO_4\downarrow + 6NH_3 \rightarrow 3[Ag(NH_3)_2]^+ + PO_4^{3-}$$

Procedure: Pour 2-3 drops of the phosphate anions into a test tube, add 3 drops of silver nitrate.

3. Reaction with ammonium molybdate $(NH_4)_2MoO_4$

Phosphate ions with ammonium molybdate form yellow precipitate $(NH_4)_3[PO_4(MoO_3)_{12}]$:

$$PO_4^{3-} + 3NH_4^+ + 12MoO_4^{2-} + 24H^+ \rightarrow (NH_4)_3[PO_4(MoO_3)_{12}]\downarrow + 12H_2O$$

Procedure: Pour 4 or 5 drops of solution of the phosphate anion into a test tube, then add two drops of 6M HNO_3 and three or four drops of $(NH_4)_2MoO_4$ (ammonium molybdate). Mix them thoroughly and heat almost to boiling for 2 min. formation, sometimes very slow, of finely divided yellow precipitate confirms phosphate.

4. Reaction with magnesian blend

Phosphate-ions with a magnesian blend ($MgCl_2$; $NH_3 \cdot H_2O$, NH_4C1) form white crystalline precipitate of $MgNH_4PO_4$:

$$HPO_4^{2-} + NH_3 + Mg^{2+} \rightarrow MgNH_4PO_4\downarrow \text{ white}$$

Procedure: Pour 2-3 drops of the phosphate anions into a test tube, add 3 drops of magnesian blend.

Arsenate (AsO_4^{3-}) ions reactions

1. Reaction with precipitating agent $BaCl_2$

Arsenate-ions form white precipitate of $Ba_3(AsO_4)_2$ with barium ions:

$$2AsO_4^{3-} + 3Ba^{2+} \rightarrow Ba_3(AsO_4)_2\downarrow \text{ white}$$

Precipitate is dissolved in acids:

$$Ba_3(AsO_4)_2 + 6H^+ \rightarrow 2H_3AsO_4 + 3Ba^{2+}$$

Procedure: Pour 2-3 drops of the arsenate anions into a test tube, add 3 drops of $BaCl_2$.

2. Reaction with magnesian blend

Arsenate-ions form white crystalline precipitate of $MgNH_4AsO_4$ with magnesian blend ($MgCl_2$, $NH_3 \cdot H_2O$, NH_4CI):

$$AsO_4^{3-} + Mg^{2+} + NH_4^+ \rightarrow MgNH_4AsO_4\downarrow \text{ white}$$

Phosphate-ions prevented by reaction processing, because they also form white precipitate of $MgNH_4PO_4$ with magnesian blend. Arsenite-ions do not react at that.

<u>Procedure:</u> Pour 2-3 drops of the arsenate anions into a test tube, add 3 drops of magnesian blend.

3. Reaction with silver nitrate $AgNO_3$

Arsenate-ions form brown precipitate of Ag_3AsO_4 with silver ions:

$$AsO_4^{3-} + 3Ag^+ \rightarrow Ag_3AsO_4\downarrow \text{ brown}$$

Precipitate is dissolved in HNO_3 and NH_4OH:

$$Ag_3AsO_4\downarrow + 3H^+ \rightarrow 3Ag^+ + H_3AsO_4$$

$$Ag_3AsO_4\downarrow + 6NH_3 \rightarrow 3[Ag(NH_3)_2]^+ + AsO_4^{3-}$$

<u>Procedure:</u> Pour 2-3 drops of the arsenate anions into a test tube, add 3 drops of silver nitrate.

4. Reaction with potassum iodide KI

Arsenate-ions oxidize iodide-ions up to free iodine in concentrated HC1 medium, which tinctures the chloroform layer in red-violet:

$$AsO_4^{3-} + 2H^+ + 2I^- \rightarrow AsO_3^{3-} + H_2O + I_2 \text{ red-violet}$$

<u>Procedure:</u> Pour 2-3 drops of the arsenate anions into a test tube, add concentrated HCl and 3 drops of potassum iodide.

Arsenite (AsO_3^{3-}) ions reactions

1. Reaction with precipitating agent $BaCl_2$

Arsenite-ions form white precipitate of $Ba_3(AsO_4)_2$ with barium ions:

$$2AsO_3^{3-} + 3Ba^{2+} \rightarrow Ba_3(AsO_3)_2\downarrow \text{ white}$$

Precipitate is dissolved in inorganic acids:

$$Ba_3(AsO_3)_2\downarrow + 6H^+ \rightarrow 3Ba^{2+} + 2H_3AsO_3$$

<u>Procedure:</u> Pour 2-3 drops of the arsenite anions into a test tube, add 3 drops of $BaCl_2$.

2. Reaction with silver nitrate $AgNO_3$

Arsenite-ions form yellow precipitate of Ag_3AsO_3 with silver ions:

$$AsO_3^{3-} + 3Ag^+ \rightarrow Ag_3AsO_3\downarrow \text{ yellow}$$

Precipitate is dissolved in ammonia solution and concentrated HNO_3:

$$Ag_3AsO_3\downarrow + 6NH_3 \rightarrow 3[Ag(NH_3)_2]^+ + AsO_3^{3-}$$

$$Ag_3AsO_3\downarrow + 3H^+ \rightarrow H_3AsO_3 + 3Ag^+$$

<u>Procedure:</u> Pour 2-3 drops of the arsenite anions into a test tube, add 3 drops of silver nitrate.

3. Reaction with iodine solution I_2

Arsenite-ions discolour iodine solution in alkalescent medium, created by saturated solution of $NaHCO_3$:

$$-2\bar{e} + AsO_3^{3-} + 2OH^- \rightarrow AsO_4^{3-} + H_2O \text{ colorless}$$

$$+2\bar{e} + [I_3]^- \rightarrow 3I^-$$

$$AsO_3^{3-} + 2OH^- + [I_3]^- \rightarrow AsO_4^{3-} + H_2O + 3I^-$$

<u>Procedure:</u> Pour 2-3 drops of the arsenite anions into a test tube, add $NaHCO_3$ and 3 drops of solution I_2.

Tetraborate ($B_4O_7^{2-}$) and metaborate (BO_2^-) ions reactions

1. Reaction with precipitating agent $BaCl_2$

Tetraborate-ions form white precipitate of $Ba(BO_2)_2$ with barium salts:

$$B_4O_7^{2-} + Ba^{2+} + 3H_2O \rightarrow Ba(BO_2)_2\downarrow + 2H_3BO_3$$

Precipitation of $B_4O_7^{2}$ - ion is reached only in strong alkaline medium:

$$2H_3BO_3 + 2OH + Ba^{2+} \rightarrow Ba(BO_2)_2\downarrow + 4H_2O$$

Precipitate is dissolved in inorganic acids:

$$Ba(BO_2)_2\downarrow + 2H^{+} + 2H_2O \rightarrow Ba^{2+} + 2H_3BO_3$$

Procedure: Pour 4-5 drops of the tetraborate anions into a test tube; add 4-5 drops of $BaCl_2$.

2. Flame colouring

The borate-ions form boric-ethyl ether in presence of sulphuric acid and ethanol. The ether tinctures the flame in green:

$$Na_2B_4O_7 + H_2SO_4 + 5H_2O \rightarrow 4H_3BO_3 + Na_2SO_4$$

$$H_3BO_3 + 3C_2H_5OH \rightarrow (C_2H_5O)_3B + 3H_2O$$

Chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$) ions reactions

1. Reaction with precipitating agent $BaCl_2$

Chromate and dichromate anions can be precipitated from aqueous solution as yellow precipitate by adding $BaCl_2$:

$$CrO_4^{2-} + Ba^{2+} \rightarrow BaCrO_4\downarrow \quad \text{yellow}$$

$$Cr_2O_7^{2-} + 2Ba^{2+} + H_2O \rightarrow 2BaCrO_4\downarrow + 2H^{+} \quad \text{yellow}$$

Procedure: Pour 4-5 drops of the chromate anions into a test tube; add 4-5 drops of $BaCl_2$.

Topic 18
Chemistry of the Group IInd anions
(classification based on the formation of insoluble salts of barium and silver)

1. The main purpose of the topic:

Drugs that contain anions IInd analytical group are used in medical practice. Especially wide is the use of variety of chlorides, bromides and iodides. For example, sodium chloride - the main component of salt and colloidal salt solutions that are used as substitutes for plasma. Sodium and potassium bromides are used as sedatives. Iodide is used in the lack of iodine in the body and in some inflammatory diseases.

Introduction to qualitative reactions of anions IInd analytical group will allow future professionals identify drugs that contain these anions, as well as contribute to further study of the core subjects: pharmaceutical chemistry, pharmacognosy, pharmaceutics and others.

2. Basic questions:

2.1. IInd analytical group anions (classification based on the formation of insoluble salts of barium and silver), general characteristic, characteristic reactions of IInd group anions.
2.2. The group reagent, conditions for it application.
2.3. Characteristic reactions of Cl^- anions.
2.4. Characteristic reactions of I^- anions.
2.5. Characteristic reactions of S^{2-}anions.
2.6. Characteristic reactions of Br^- anions.

3. Brief exposition of theoretical material:

The IInd analytical group of anions consists of Cl^-, Br^-, I^- and S^{2-} which form sparingly soluble salts with silver nitrate (group reagent).

4. Control test and patterns of responses:

4.1. Explain the necessity of carrying out of systematic analysis course of the halogen-ions mixture.

<u>Answer:</u>

Detection of halogen ions, while their joint presence requires a systematic course of analysis because these ions react identically with the ions of silver (I).

I. Identification of Cl - ions

Silver nitrate solution (I) (acidified nitrate acid) was added to separate portions of the original solution. The precipitate is formed:

$$Ag^+ + Cl^- \rightarrow AgCl\downarrow \qquad SP = 1{,}78\cdot10^{-10}$$

$$Ag^+ + Br^- \rightarrow AgBr\downarrow \qquad SP = 5{,}3\cdot10^{-13}$$

$$Ag^+ + I^- \rightarrow AgI\downarrow \qquad SP = 8{,}3\cdot10^{-17}$$

Solution of ammonium carbonate 12% was added to precipitate, which dissolves only silver (I) chloride. As a result of hydrolysis of $(NH_4)_2CO_3$, a limited amount of ammonia was formed, which is sufficient only for dissolution silver (I) chloride, the product of solubility is greatest:

$$(NH_4)_2CO_3 \rightarrow 2NH_4^+ + CO_3^{2-}$$

$$NH_4^+ + HOH \rightarrow NH_3 \cdot H_2O + H^+$$

$$CO_3^{2-} + HOH \rightarrow HCO_3^- + OH^-$$

$$AgCl \downarrow + 2NH_3 \rightarrow \left[Ag(NH_3)_2\right]^+ + Cl^-$$

The precipitate is separated by centrifugation.

HNO_3 solution is added to the supernate. The formation of white cheesy precipitate indicates the presence of Cl- ions:

$$\left[Ag(NH_3)_2\right]^+ + Cl^- + H^+ \rightarrow AgCl \downarrow + 2NH_4^+$$

II. Detection of Br $^-$ and I$^-$ ions

Chloroform and water chloride is added to the original solution is acidified by 1M solution of sulfuric acid. Red-purple chloroform layer indicates the presence of iodide-ions. I$^-$- stronger reducing agent than Br-, because it is oxidized first:

$$\begin{array}{l|l}
-2e + 2I^- \rightarrow I_2 & E^0_{I_2/2I^-} = 0{,}545B \\
+2e + Cl_2 \rightarrow 2Cl^- & E^0_{Cl_2/2Cl^-} = 1{,}359B \\
\hline
2I^- + Cl_2 \rightarrow I_2 + 2Cl^- &
\end{array}$$

With further adding chloric water, red-purple colour disappears due to oxidation of I_2 to $IO_3^-$and there is golden colour chloroform layer free bromine:

$$\begin{array}{l|l}
-10e + I_2 + 6H_2O \rightarrow 2IO_3^- + 12H^+ & 1 \\
+2e + Cl_2 \rightarrow 2Cl^- & 5 \\
\hline
I_2 + 6H_2O + 5Cl_2 \rightarrow 2IO_3^- + 12H^+ + 10Cl^- &
\end{array}$$

$$\begin{array}{l|l}
-2e + 2Br^- \rightarrow Br_2 & E^0_{Br_2/2Br^-} = 1{,}087B \\
+2e + Cl_2 \rightarrow 2Cl^- & E^0_{Cl_2/2Cl^-} = 1{,}359B \\
\hline
2Br^- + Cl_2 \rightarrow Br_2 + 2Cl^- &
\end{array}$$

5. Tasks for homework (write in a textbook for protocols):

5.1. Explain the sequence of precipitation solution ions Cl$^-$, I$^-$and Br$^-$ by the action group reagent in the second group anions.

5.2. Write the scheme for separation and identification ions in the following sample solutions that contains:

- Cl$^-$, S^{2-};
- Br$^-$, Cl$^-$;
- S^{2-}, Cl$^-$, I$^-$.

The situation tasks are solved according to the systematic analysis of the IInd analytical group anions mixture.

6. Laboratory experiment

Laboratory experiment 18.1.

Characteristic reactions of the IInd analytical groups of anions

Chloride (Cl^-) ions reactions

1. Reaction with precipitating agent $AgNO_3$

Chloride anions can be precipitated from aqueous solution as white precipitate by addition $AgNO_3$:

$$Cl^- + Ag^+ \rightarrow AgCl\downarrow \quad \text{white}$$

AgCl can be dissolved in aqueous ammonium and ammonium carbonate:

$$AgCl\downarrow + 2NH_3 \rightarrow [Ag(NH_3)_2]^+ + Cl^-$$

Procedure: Pour 3-4 drops of NaCl or KC1 into a test tube, add some drops of silver nitrate.

Bromide (Br^-) ions reactions

1. Reaction with precipitating agent $AgNO_3$

Bromide anions can be precipitated from aqueous solution as yellow precipitate by addition $AgNO_3$:

$$Ag^+ + Br^- \rightarrow AgBr\downarrow \quad \text{yellow}$$

Procedure: Pour 3-4 drops of NaBr or KBr into a test tube, add some drops of silver nitrate.

2. Reaction with chlorine water

Pour five drops of solution of the anion into a test tube and add five drops of chlorine water. Brown coloration due to the liberation of Br_2 confirms Br^-. If the solution is shaken with a few drops of mineral oil, brown colour will be concentrated in the top layer, which is mineral oil.

$$2Br^- + Cl_2 \rightarrow Br_2 + 2Cl^-$$

Iodide (I^-) ions reactions

1.Reaction with precipitating agent $AgNO_3$

Iodide anions can be precipitated from aqueous solution as yellow precipitate by adding $AgNO_3$:

$$I^- + Ag^+ \rightarrow AgI\downarrow \quad \text{yellow}$$

Procedure: Pour 3-4 drops of Kl into a test tube, add some drops of silver nitrate.

2. Reaction with lead (II) cations $Pb(NO_3)_2$

Iodide anions can be precipitated from aqueous solution as yellow precipitate by adding $Pb(NO_3)_2$:

$$2I^- + Pb^{2+} \rightarrow PbI_2\downarrow \quad \text{yellow}$$

Procedure: Pour 3-4 drops of $Pb(NO_3)_2$ into a test tube, add some drops of Kl. Dissolve the precipitate in acetic acid. Heat the test tube in a boiling—water bath for some minutes.

3. Reaction with chlorine water

Pour five drops of solution of the iodide anions into a test tube and add five drops of chlorine water, add a few drops of mineral oil. Violet colour in the top (mineral oil) layer confirms I^-.

$$Cl_2 + 2I^- \rightarrow 2Cl^- + I_2$$

Sulfide (S^{2-}) ions reactions

1. Reaction with precipitating agent $AgNO_3$

Sulfide anions can be precipitated from aqueous solution as black precipitate by addition $AgNO_3$:

$$S^{2-} + 2Ag^+ \rightarrow Ag_2S\downarrow \quad \text{black}$$

Procedure: Pour 2-3 drops of Na_2S or K_2S into a test tube; add some drops of silver nitrate.

2. Reaction with mineral acids

Pour five drops of solution of the sulfide into a test tube add 10 drops of 6M HC1. Hold a piece of filter paper that has been moistened with 0,2M $Pb(CH_3COO)_2$ over the mouth of the test tube so that any gas that escapes comes into contact with the paper. A brownish or silver black stain (PbS) on the paper confirms the presence of S^{2-}:

$$S^{2-} + 2H^+ \rightarrow H_2S\uparrow \quad \text{(the odor of rotten eggs)}$$
$$H_2S + Pb^{2+} \rightarrow PbS\downarrow + 2H^+ \quad \text{black}$$

Topic 19

Chemistry of the Group III^d anions (classification based on the formation of insoluble salts of barium and silver)

1. The main purpose of the topic:

Many anions III^d analytical group part of the drugs (basic Pb (II) acetate, nitrate Bi main - astringent and antiseptic for gastrointestinal diseases, nitroglycerin, sustak et al.).

Comprehension of the characteristic reactions of anions of the III^d analytical group contributes to students' theoretical bases of chemical analysis and practical skills and his performance, lays the groundwork for further study of specialized subjects.

2. Basic questions:

2.1. III^d analytical group anions (the classification is based on the formation of insoluble salts of barium and silver), general characteristic, characteristic reactions of III^d group anions.
2.2. The group reagent, conditions of its application.
2.3. Characteristic reactions of NO_3^- anions.
2.4. Characteristic reactions of NO_2^- anions.
2.5. Characteristic reactions of CH_3COO^- anions.

3. Brief exposition of theoretical material:

The III^rd^ analytical group of anions contains NO_3^-, NO_2^- and CH_3COO^- ions. The majority of their salts are water soluble. This analytical group has no group reagent.

4. Control test and patterns of responses:

4.1. Detection of nitrite and nitrate anions in their joint presence. What anions prevent the opening of these ions and why? Give the reactions.

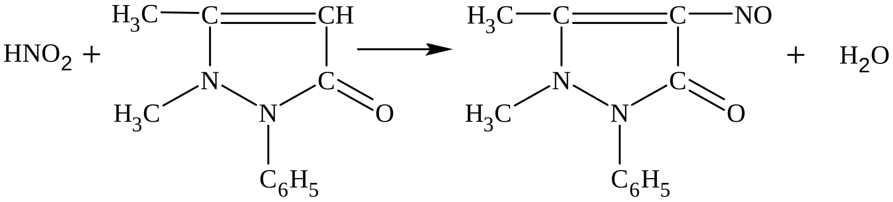
Answer:

Nitrite ions interfere with the detection of nitrate ions because reactions with reducing agents (FeSO4, diphenilamin etc.) of their analytical effects are similar.

I. Identification of NO_2^- ions

A separate portion of the original solution is acidified solution of dilute HCl, add crystalline antipirin. Green colour indicates the presence of NO_2^- ion.

$$NO_2^- + H^+ \rightarrow HNO_2$$



II. Removal of NO_2^- ions

To separate the portions of the original solution add crystalline NH_4Cl and heat them to complete removal of N_2:

$$NO_2^- + NH_4^+ \xrightarrow{\Delta} N_2\uparrow + 2H_2O$$

Plenitude removal of NO_2^-checks the reaction of potassium iodide in acidic medium:

$$\begin{array}{l|r} +e + NO_2^- + 2H^+ \rightarrow NO\uparrow + H_2O & 2 \\ -2e + 2I^- \rightarrow I_2 & 1 \\ \hline \end{array}$$

$$2NO_2^- + 4H^+ + 2I^- \rightarrow 2NO\uparrow + 2H_2O + I_2$$

III. Detection of NO_3^- ions

In the solution, obtained by p.II, there is iron (II) sulfate in the presence of concentrated sulfate acid. The appearance of brown ring indicates the presence of NO_3^- ions:

$$\begin{array}{l|r} Fe^{2+} - 1e \rightarrow Fe^{3+} & 3 \\ NO_3^- + 4H^+ - 3e \rightarrow NO\uparrow + 2H_2O & 1 \\ \hline \end{array}$$

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

$$SO_4^{2-} + Fe^{2+} + NO \rightarrow [Fe(NO)]SO_4$$

I^-, Br^- interfere with the reaction because they are oxidized with concentrated H_2SO_4 for I_2 and Br_2. So they removed the influence of with chloric water in the presence of HCl when heated to a complete removal.

5. Tasks for homework (write in a textbook for protocols):

5.1. 1M solution of sulphate acid 2-3 drops, 4-5 drops of solution of potassium iodide and a few drops of starch added to solution containing the anion of the 3rd group (the classification is based on the solubility of salts of barium and silver). The mixture is mixed. Observe the intense blue colour of the solution. What anion is present in the solution? Write the reaction.

5.2. Write the scheme for separation and identification ions in the following sample solutions that contains:

- CH_3COO^-, NO_3^-;
- CH_3COO^-, NO_2^-;
- CH_3COO^-, NO_3^-, NO_2^-.

The situation tasks are solved according to the systematic analysis of the III^d analytical group anions mixture.

6. Laboratory experiment

Laboratory experiment 19.1.

Characteristic reactions of the III^d analytical groups of anions

Nitrate (NO_3^-) ions reactions

1. Reaction with iron (II) cations

Pour 10 drops of solution of the nitrate anions into a small test tube, add five drops of $FeSO_4$ solution, and mix the solution. Carefully, without agitation, pour concentrated H_2SO_4 down the inside of the test tube so as form two layers. Let it stay for 1 or 2 min. The formation of a brown ring between the two layers confirms NO_3^-:

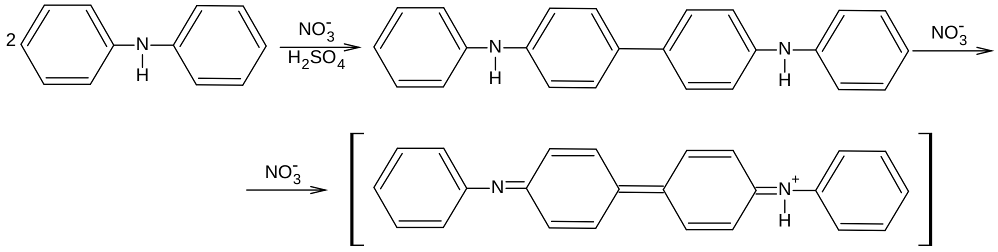
$$\begin{array}{l|r} Fe^{2+} - \bar{e} \rightarrow Fe^{3+} & 3 \\ NO_3^- + 4H^+ + 3\bar{e} \rightarrow NO\uparrow + 2H_2O & 1 \\ \hline \end{array}$$

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

$$SO_4^{2-} + Fe^{2+} + NO \rightarrow [Fe(NO)]SO_4 \text{ brown}$$

2. Reaction with diphenilamin

Pour 10 drops of $NaNO_3$ or KNO_3 into a small test tube, add some drops of diphenilamin. The formation of blue solution confirms NO_3^- (interfere NO_2^-).



Nitrite (NO_2^-) ions reactions

1. Reaction with potassium iodide KI

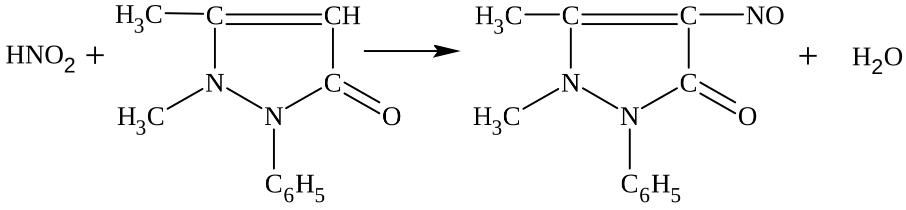
Pour 2-3 drops of potassium iodide into a small test tube, add 3-4 drops of sulfuric acid, 3-4 drops of chloroform and 2-3 drops of $NaNO_2$. The violet colour of the chlotoform confirms NO_2^-:

$$\begin{array}{l|r} NO_2^- + 2H^+ + e \rightarrow NO\uparrow + H_2O & 2 \\ 2I^- - 2e \rightarrow I_2 & 1 \\ \hline 2NO_2^- + 4H^+ + 2I^- \rightarrow 2NO\uparrow + 2H_2O + I_2 & \end{array}$$

2. Reaction with antipirin

Pour 4-5 drops of $NaNO_2$ into a small test tube, add 4-5 drops of antipirin and I drop of sulfuric or hydrochloric acid. The formation of green solution confirms NO_2^-.

$$NO_2^- + H^+ \rightarrow HNO_2$$



3. Reaction with potassium permanganate

Pour 2-3 drops of potassium permanganate into a small test tube, add 2-3 drops of sulfuric acid and 3-4 drops of $NaNO_2$:

$$\begin{array}{l|r} MnO_4^- + 8H^+ + 5e \rightarrow Mn^{2+} + 4H_2O & 2 \\ NO_2^- + H_2O - 2e \rightarrow NO_3^- + 2H^+ & 5 \\ \hline 2MnO_4^- + 6H^+ + 5NO_2^- \rightarrow 2Mn^{2+} + 3H_2O + 5NO & \end{array}$$

colorless

Acetate (CH_3COO^-) ions reactions

1. Reaction with mineral acids

Acetate ions under the action of mineral acids form CH_3COOH that detect the smell:

$$CH_3COO^- + H^+ \rightarrow CH_3COOH$$

Procedure: Pour 6-5 drops of solution of sodium acetate into test tube and add 3-2 drops of sulfuric acid solution and gently heat it. Feel the specific smell of acetic acid.

2. Reaction with iron (III) chloride (reaction Pharmacopeias)

Acetate ions with ions of iron (III) form precipitate of iron (III) red:

$$3Fe^{3+} + 9CH_3COO^- + 2H_2O \rightarrow [Fe_3(OH)_2(CH_3COO)_6]CH_3COO \downarrow + 2CH_3COOH$$

Procedure: Pour 7-6 drops of solution of sodium acetate into test tube and add 3-2 drops of solution of iron chloride (III). The solution is coloured in red-brown colour. Gently heat the tube contents to boiling. When boiling into red-brown precipitate basic acetate of iron (III).

Topic 20
Reactions of organic acids anions

1. The main purpose of the topic:

Medicines containing anions of organic acids are widely used in medical practice. Salicylic acid is known for its ability to ease aches and pains and reduce fevers. In modern medicine, salicylic acid and its compounds are used as constituents of some rubefacient products (methyl salicylate is used as a liniment to soothe joint and muscle pain, choline salicylate – topically to relieve the pain of aphthous ulcers. salicylic acid is ingredient in many skin-care products for the treatment of dermatitis.

Benzoic acid is a constituent of Whitfield's ointment which is used for the treatment of fungal skin diseases. Benzoic acid is also a major ingredient in antiseptic tinctures, which have a long history of use as topical antiseptics and inhalant decongestants. Sodium benzoate is used as a preservative in medicines and cosmetics.

Citric acid is widely used as a pH adjusting agent. Citric acid and citrate salts (which contain potassium and sodium) belong to a class of drugs known as urinary alkalinizers. The combination of citric acid and sodium citrate is used to prevent gout or kidney stones, or metabolic acidosis in people with kidney problems.

2. Basic questions:

2.1. Characteristic reactions of tartrate-anions.
2.2. Characteristic reactions of citrate-anions.
2.3. Characteristic reactions of benzoate-anions.
2.4. Characteristic reactions of salicyate-anions.

3. Control test and patterns of responses:

3.1. Benzoate-anions can be identified by action of iron (III) chloride solution in neutral medium. Explain the selection of medium for this reaction. Write the equations of the conforming reactions and explain the analytical effects.

<u>Answer:</u>

Benzoate ions with iron (III) ions form pink-yellow precipitate in neutral medium:

$$6C_6H_5COO^- + 2Fe^{3+} + 10H_2O \rightarrow (C_6H_5COO)_3Fe \cdot Fe(OH)_3 \cdot 7H_2O \downarrow + 3C_6H_5COOH$$

If the reaction is carried out in acidic medium, the formation of pink-yellow precipitate is not observed. But the formation of white precipitate of benzoic acid is possible.

If the reaction is carried out in an alkaline medium, the formation of brown precipitate of iron (III) hydroxide is not observed:

$$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3 \downarrow$$

4. Tasks for individual work (write in a textbook for protocols):

4.1. Is it possible to identify salicyate-anions by action of iron (III) chloride solution in presence of benzoate-anions? Write the equations of the conforming reactions and explain the analytical effects.

4.2. Suggest the analytical reactions for the identification of tartrate-anions. Write the equations of the conforming reactions and explain the analytical effects.

4.3. What organic acids anions can be identified by the action of iron (III) chloride solution? Explain the selection of medium for this reaction. Write the equations of the conforming reactions.

5. Laboratory experiment

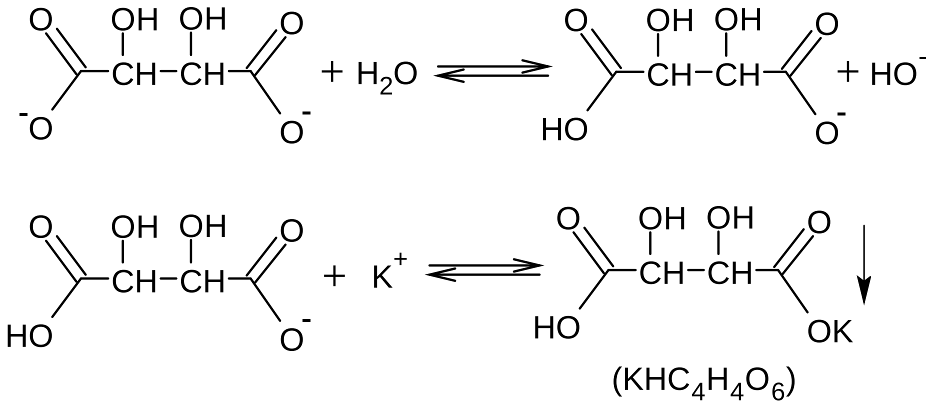
Laboratory experiment 20.1

Characteristic reactions of the organic acids anions

Reactions of tartrate-ions

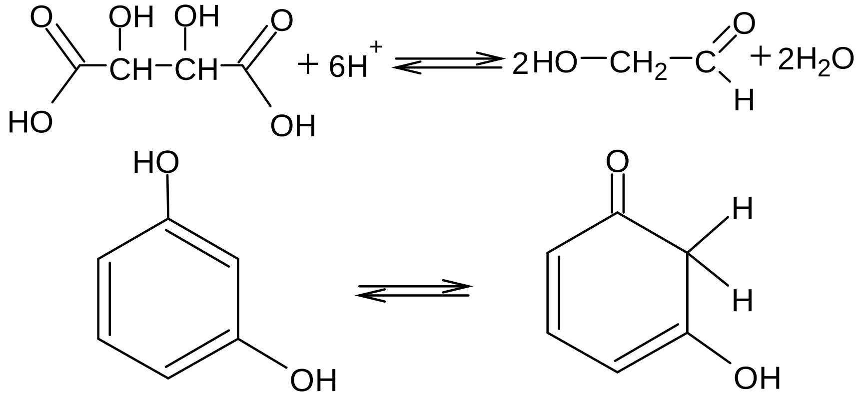
1. Action of potassium chloride solution

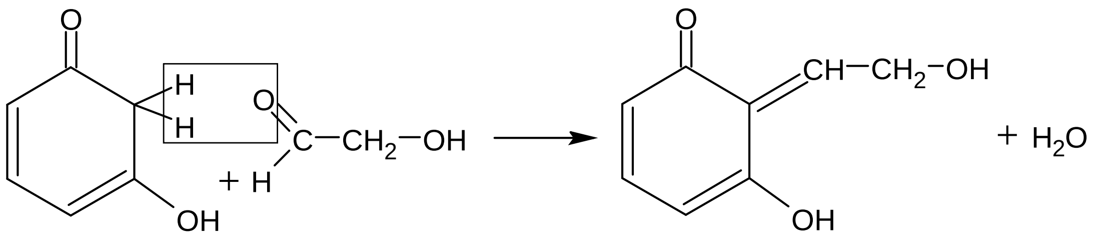
Tartrate-ions form white crystalline precipitate of potassium hydrotartrate $KHC4H_4O_6$ with potassium ions:



2. ***Action of resorcin***

Due to the action of concentrated sulfuric acid the tartrate-ions turn into glycol aldehyde $HOCH_2CHO$, which performs condensation reaction with resorcin in a ketoform. A cherry-red colored compound is formed by that reaction:

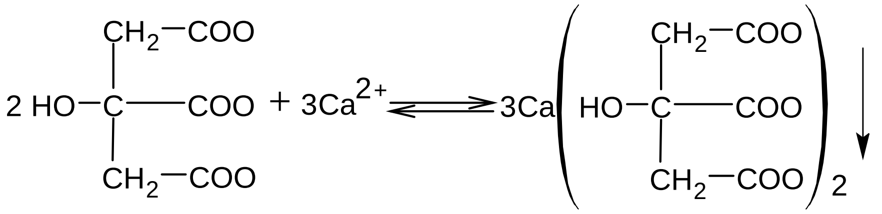




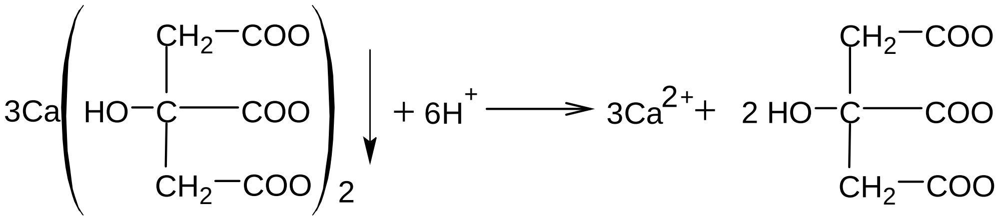
Reactions of citrate-ions

1. Action of calcium chloride

Citrate-ions form white precipitate of calcium citrate with calcium-ions in neutral medium at boiling:



The precipitate is dissolved in acids:



2. Action of acetic anhydride

Citrate-ions form a compound coloured in cherry-red colour with acetic anhydride.

Reaction of benzoate-ions

1. Action of iron (III) chloride solution

Benzoate-ions form a pink-yellow compound with iron (III) ions:

$$6C_6H_5COO^- + 2Fe^{3+} + 10H_2O \rightarrow (C_6H_5COO)_3Fe \cdot Fe(OH)_3 \cdot 7H_2O \downarrow + 3C_6H_5COOH$$

2. Action of concentrate sulphuric acid

The reaction is carried out in a dry way. Several drops of concentrate sulphuric acid are added to several cristals of benzoic acid salt. Benzoic acid is formed, it is sublimation and precipitate on inside of the teste tube in a form of white cristals.

$$2C_6H_5COONa + H_2SO_4 \rightarrow 2C_6H_5COOH + Na_2SO_4$$

3. Action of mineral acids

Benzoate-ions form white precipitate of free bemzoic acid with mineral acid (for example, HC1):

$$HOC_6H_4COO^- + H^+ \rightarrow HOC_6H_4COOH \downarrow$$

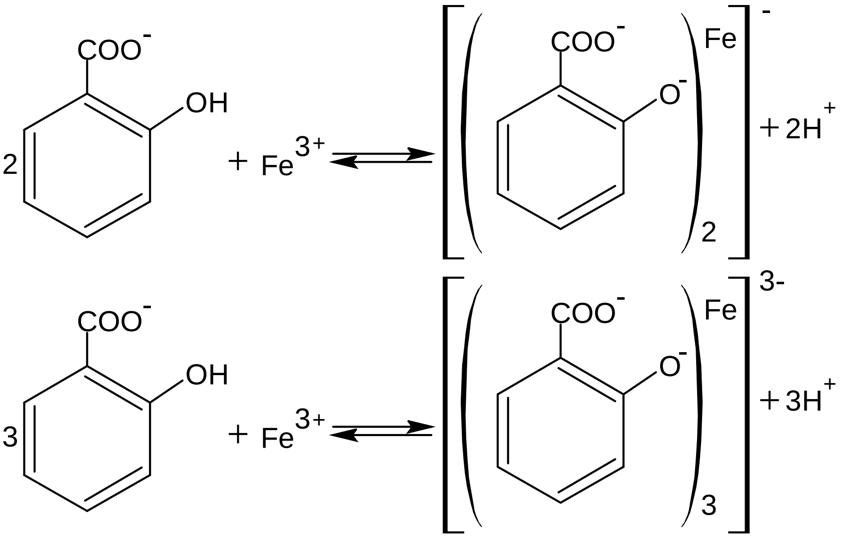
Reactions of salicylate-ions

1. Action of iron (III) chloride solution

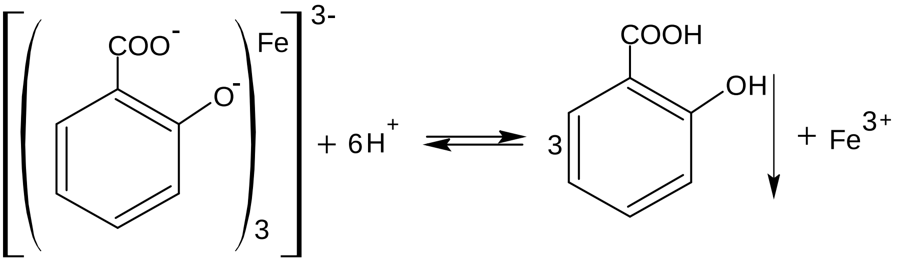
Salicylate-ions form blue-violet, red-violet or yellow compounds of different composition with iron (III) ions:

$$3HOC_6H_4COO^- + Fe^{3+} \Leftrightarrow [Fe(HOC_6H_4COO)_3]$$

$$[Fe(HOC_6H_4COO)_3] + 3H^+ \rightarrow Fe^{3+} + 3HOC_6H_4COOH \downarrow$$



Colouring remains during adding acetic acid, but disappears at action of HC1. White precipitate of salicylic acid is formed by this prosess:



Topic 21
Analysis of mixtures of anions

1. The main purpose of the topic:

In the analysis of pharmaceutical raw materials, drug substances, forensic objects, analytical control of different stages of technological processes of preparation of drugs have to open a limited number of anions. Thus anions are identified by fractional method using specific analytical reactions or by instrumental methods.

However, in some cases anions can be identified in a particular sequence (special cases of anions mixtures analysis).

2. Basic questions:

2.1. Characteristic reactions of the Ist analytical group anions.
2.2. Characteristic reactions of the IInd analytical group anions.
2.3. Characteristic reactions of the III^{d} analytical group anions.
2.4. Characteristic reactions of organic acids anions.
2.5. Special cases of anions mixtures analysis.
2.6. Fractional method of analysis mixture of anions.
2.7. Analysis systematic course of mixture of anions.

3. Brief exposition of theoretical material:

Analysis of mixtures of anions

The analysis of anions is fulfilled after the cations detection. It is stipulated by the following reasons:

- a question of presence or absence of some anions is solved simultaneously with cations detection. As an example, it is possible to cite the determination of As(III), As(V), Mn^{2+}, Cr^{3+} and corresponding AsO_4^{3-}, CrO_4^{2-}, $Cr_2O_7^{2-}$, MnO_4^{-};
- salts solubility of detected cations also allows to make a conclusion about some anions absence. For example, if the examined substance is dissolved in water and contains cations, which form slightly soluble salts with S^{2-}, SO_4^{2-}, CO_3^{2-}, PO_4^{3-}, the last ones are absent;
- anions analysis is prevented by all cations, except K^+, Na^+, NH_4^+, because the most of them form precipitates with series of anions or make oxidation-reduction reactions with them.

Therefore before the anions analysis the cations of heavy and alkaline-earth metals should be removed. For this purpose the analytical operation of soda extract obtaining is fulfilled. The examined mixture is boiled with saturated solution of Na_2CO_3, Cations of the IInd, III^{d}, Vth, VIth analytical groups form precipitate of corresponding oxides, carbonates, oxyhydroxides or basic salts (except IVth analytical group cations).

Table 12

Reactions of IInd–VIth analytical group cations while preparing soda extract

Analytical group of cations	Equation of reaction
II	$2Ag^{+} + CO_3^{2-} \Leftrightarrow Ag_2CO_3\downarrow \xrightarrow{\Delta} Ag_2O\downarrow + CO_2\uparrow$
	$2Pb^{2+} + 2CO_3^{2-} + H_2O \Leftrightarrow (PbOH)_2CO_3\downarrow + CO_2\uparrow$
	$Hg_2^{2+} + CO_3^{2-} \Leftrightarrow Hg_2CO_3\downarrow \rightarrow HgO\downarrow + Hg\downarrow + CO_2$
III	$Ba^{2+} + CO_3^{2-} \Leftrightarrow BaCO_3\downarrow$
	$Sr^{2+} + CO_3^{2-} \Leftrightarrow SrCO_3\downarrow$
	$Ca^{2+} + CO_3^{2-} \Leftrightarrow CaCO_3\downarrow$
IV	$2Al^{3+} + 3CO_3^{2-} + 3H_2O \Leftrightarrow 2Al(OH)_3\downarrow + 3CO_2\uparrow$
	$Al(OH)_3\downarrow + 3OH^{-} \rightarrow [Al(OH)_6]^{3-}$
	$2Cr^{3+} + 3CO_3^{2-} + 3H_2O \Leftrightarrow 2Cr(OH)_3\downarrow + 3CO_2\uparrow$
	$Cr(OH)_3\downarrow + 3OH^{-} \rightarrow [Cr(OH)_6]^{3-}$
	$Zn^{2+} + CO_3^{2-} + H_2O \Leftrightarrow Zn(OH)_2\downarrow + CO_2\uparrow$
	$Zn(OH)_2\downarrow + 2OH^{-} \rightarrow [Zn(OH)_4]^{2-}$
	$Sn^{2+} + CO_3^{2-} + H_2O \Leftrightarrow Sn(OH)_2\downarrow + CO_2\uparrow$
	$Sn(OH)_2\downarrow + 4OH^{-} \rightarrow [Sn(OH)_6]^{4-}$
	$[SnCl_6]^{2-} + 2CO_3^{2-} + 2H_2O \Leftrightarrow Sn(OH)_4\downarrow + 2CO_2\uparrow + 6Cl^{-}$
	$Sn(OH)_4\downarrow + 2OH^{-} \rightarrow [Sn(OH)_6]^{2-}$
V	$Fe^{2+} + CO_3^{2-} \Leftrightarrow FeCO_3\downarrow$ turns brown rapidly in air: $4FeCO_3\downarrow + 6H_2O + O_2 \rightarrow 4Fe(OH)_3\downarrow + 4CO_2\uparrow$
	$2Fe^{3+} + 3CO_3^{2-} + H_2O \Leftrightarrow 2Fe(OH)_3\downarrow + 3CO_2\uparrow$
	$Mn^{2+} + CO_3^{2-} \Leftrightarrow MnCO_3\downarrow$
	$2Mg^{2+} + 2CO_3^{2-} + H_2O \Leftrightarrow (MgOH)_2CO_3\downarrow + CO_2\uparrow$
	$2Bi^{3+} + 3CO_3^{2-} + H_2O \Leftrightarrow 2BiOHCO_3\downarrow + CO_2\uparrow$
	$2[SbCl_6]^{3-} + 3CO_3^{2-} + 3H_2O \Leftrightarrow 2Sb(OH)_3\downarrow + CO_2\uparrow + 12Cl^{=}$
	$[SbCl_6]^{-} + 3CO_3^{2-} + H_2O \Leftrightarrow HSbO_3\downarrow + 2CO_2\uparrow + 6Cl^{=} + HCO_3^{-}$
VI	$2Co^{2+} + 2CO_3^{2-} + H_2O \Leftrightarrow (CoOH)_2CO_3\downarrow + CO_2\uparrow$
	$Ni^{2+} + CO_3^{2-} \Leftrightarrow NiCO_3\downarrow$
	$2Cu^{2+} + 2CO_3^{2-} + H_2O \Leftrightarrow (CuOH)_2CO_3\downarrow + CO_2\uparrow$
	$2Hg^{2+} + 2CO_3^{2-} + H_2O \Leftrightarrow (HgOH)_2CO_3\downarrow + CO_2\uparrow$
	$(HgOH)_2CO_3\downarrow \Leftrightarrow 2HgO\downarrow + CO_2\uparrow + H_2O$

There are anions and cations of the IVth analytical group (hydrocomplexes and oxoanions) and cations of the Ist analytical group present in the solution after centrifuging.

In the obtained alkaline solution NO_3^- and NO_2^- anions are discovered, then the solution is neutralized by diluted nitric acid. Neutralization is carried out cautiously, as the environment anions of nonresistant acids are decomposed in acid. But in alkaline environment $C0_3^{2-}$ -ions, which form a precipitate of $BaCO_3$ during the Ist analytical group anions analysis by group reagent $BaCl_2$, and this group of anions will be rediscovered. At soda extract obtaining carbonate-ions are added, therefore they must be discovered in a separate portion of a solution before carrying out of this operation.

The majority of the anions detection is made by fractional method in separate portions of a solution. However in some cases anions detection should be carried out in particular consequence, because some of them prevent each other's detection (special cases in anions analysis).

Special cases in anions analysis

Analysis of a mixture of S^{2-}, $S_2O_3^{2-}$, SO_4^{2-}, SO_3^{2-}

For S^{2-}, $S_2O_3^{2-}$, SO_4^{2-}, SO_3^{2-} detection at their simultaneous presence the systematic analysis course must be carried out for the following reasons:

1. S^{2-} and SO_3^{2-} are the anions of nonresistant acids, which form following gasic products at acidification:

$$S^{2-} + 2H^+ \rightarrow H_2S\uparrow$$

$$SO_3^{2-} + 2H^+ \rightleftharpoons H_2SO_3 \rightarrow SO_2\uparrow + H_2O$$

Their products H_2S and SO_2 interact with sulfur formation:

$$SO_2\uparrow + 2H_2S\uparrow \rightarrow 3S\downarrow + 2H_2O$$

Depending on relation between amount of S^{2-} and SO_3^{2-}-ions in the solution as a result of these transformations sulfur and one of gases (SO_2 or H_2S) always is formed. If there is SO_2 excess, at solution acidification SO_2 and sulfur are formed, which are also formed at $S_2O_3^{2-}$-ions decomposition.

$$S_2O_3^{2-} + 2H^+ \rightarrow H_2S_2O_3$$

$$H_2S_2O_3 \rightarrow S\downarrow + SO_2\uparrow + H_2O$$

2. Thus S^{2-}, SO_3^{2-} and $S_2O_3^{2-}$-anions can not be detected at simultaneous presence; – mixture of $SO_3^{2-}$and $S_2O_3^{2-}$ at acidification forms the same products, as $S_2O_3^{2-}$ ions.

3. In presence of $S_2O_3^{2-}$ or S^{2-} and SO_3^{2-} it is difficult to detect SO_4^{2-}, because during the analysis at solution acidification and action of group reagent $BaCl_2$ the sulfur precipitate is formed, which can be recognized as $BaS0_4$.

Analysis systematic course of sulfur-containing anions

1. S^{2-} detection and separation

To NaOH solution (up to pH > 7) and natrium nitroprusside a separate portion of the examined solution is added. At S^{2-}anions presence the red-violet complex is formed:

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

From the separate portion of solution S^{2-} is separated by the action of $CdCO_3$ solution:

$$Cd^{2+} + S^{2-} \rightarrow CdS\downarrow$$

CdS↓ is separated by centrifuging. There are $S_2O_3^{2-}$, SO_3^{2-} and SO_4^{2-} in centrifugate.

2. $S_2O_3^{2-}$ and SO_3^{2-}, SO_4^{2-} - ions separation

Strontium salt solution is added to the centrifugate, obtained on phase *1* . At that process such precipitates are formed:

$$Sr^{2+} + SO_3^{2-} \rightarrow SrSO_3\downarrow$$
$$Sr^{2+} + SO_4^{2-} \rightarrow SrSO_4\downarrow$$

The precipitate containing $SrSO_3$ and $SrSO_4$ is separated by centrifuging and is washed out by water untill complete $S_2O_3^{2-}$- anions removing. There are $S_2O_3^{2-}$-ions in the centrifugate.

3. SO_4^{2-} and SO_3^{2-} - ions detection

2M solution of HC1 is added to the precipitate, obtained on phase 2:

$$SrSO_3\downarrow + 2H^+ \rightarrow Sr^{2+} + SO_2\uparrow + H_2O$$

Incomplete precipitate dissolution testifies to SO_4^{2-} presence because $SrSO_4\downarrow$ is not dissolved in acids. Precipitate is separated by centrifuging and is not analysed.

For SO_3^{2-}-ions detection, iodine solution is added to centrifugate, obtained on phase *3*. If SO_3^{2-}- ions are present, the iodine solution discolouration well be observed:

$$\begin{array}{l|l} SO_2 + 2H_2O - 2e \rightarrow SO_4^{2-} + 4H^+ & 1 \\ [I_3]^- + 2e \rightarrow 3I^- & 1 \\ \hline SO_2 + 2H_2O + [I_3]^- \rightarrow SO_4^{2-} + 4H^+ + 3I^- & \end{array}$$

4. $S_2O_3^{2-}$-ions detection

2M solution of HC1 is added to a separate portion of the centrifugate, obtained on phase *2*,.

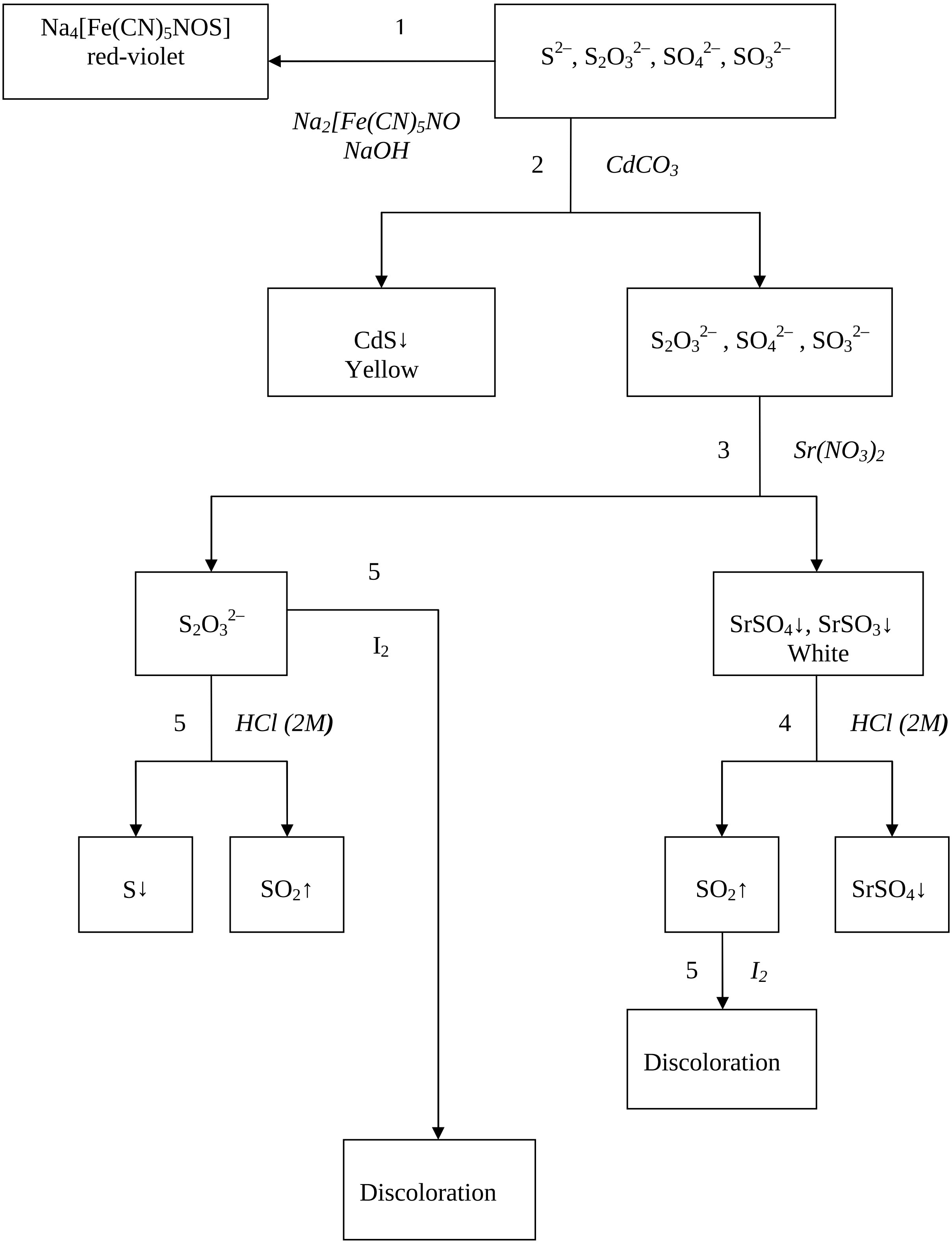
White slime (S) formation and iodine solution discoloration by educed gas ($SO_2\uparrow$) (equation of reaction see above) indicates $S_2O_3^{2-}$- ions presence:

$$\begin{array}{l|l} 2S_2O_3^{2-} - 2e \rightarrow S_4O_6^{2-} & 1 \\ [I_3]^- + 2e \rightarrow 3I^- & 1 \\ \hline 2S_2O_3^{2-} + [I_3]^- \rightarrow S_4O_6^{2-} + 3I^- & \end{array}$$

Analysis of sulphur-containing anions must be carried out according to the scheme.

Scheme 9

Analysis of sulphur-containing anions



Analysis systematic course of a mixture of Cl^-, Br^-, I^-

Halogen-ions detection at their simultaneous presence requires a systematic course of analysis, because they react with silver ions (group reagent) over nitric acid with formation of precipitates:

$Ag^+ + Cl^- \rightarrow AgCl\downarrow$ white $\quad K_{SP} = 1.78\cdot10^{-10}$

$Ag^+ + Br^- \rightarrow AgBr\downarrow$ pale yellow $\quad K_{SP} = 5.3\cdot10^{-13}$

$Ag^+ + I^- \rightarrow AgI\downarrow$ slight yellow $\quad K_{SP} = 8.3\cdot10^{-17}$

1. Cl^- - ions detection

12 % solution of ammonium carbonate is added to the precipitate, obtained by reaction of a separate portion of an examined solution with silver nitrate. At that process only silver chloride is dissolved. It relates to $(NH_4)_2CO_3$ hydrolysis, when ammonia forms of restricted amount, sufficient only for silver chloride dissolutition, which has the greatest value of solubility product:

$$(NH_4)_2CO_3 \rightarrow 2NH_4^+ + CO_3^{2-}$$

$$NH_4^+ + HOH \rightarrow NH_3\cdot H_2O + H^+$$

$$CO_3^{2-} + HOH \rightarrow HCO_3^- + OH^-$$

$$AgCl\downarrow + 2NH_3 \rightarrow \left[Ag(NH_3)_2\right]^+ + Cl^-$$

The precipitate is separated by centrifuging and is not analyzed.

To centrifugate HNO_3 solution is added. The formation of white curdled precipitate indicates of Cl^- -ions presence:

$$[Ag(NH_3)_2]^+ + Cl^- + 2H^+ \rightarrow AgCl\downarrow + 2NH_4^+$$

2. Br^- and I^--ions detection

Chloroform and chlorine water are added by drops to a separate portion of initial solution, which is acidified by 1M solution of sulfuric acid,. Red-violet colouring of chloroform layer testifies the iodide-ions presence.

I^--ion is a more strong reducer, than Br^--ion (E°($I_2/2I^-$)=0.545V, E°($Br_2/2Br^-$)=1.087V), that is why it acidifies first free iodine tinctures chloroform layer in red-violet:

$2I^- - 2\bar{e} \rightarrow I_2$	1	E°($I_2/2I^-$)=0.545V
$Cl_2 + 2\bar{e} \rightarrow 2Cl^-$	1	E°($Cl_2/2\ Cl^-$)=1.359V
$Cl_2 + 2I^- \rightarrow 2Cl^- + I_2$		

By further adding of chloral water red-violet colouring vanishes owing to oxidizing up to colourless iodate-ions:

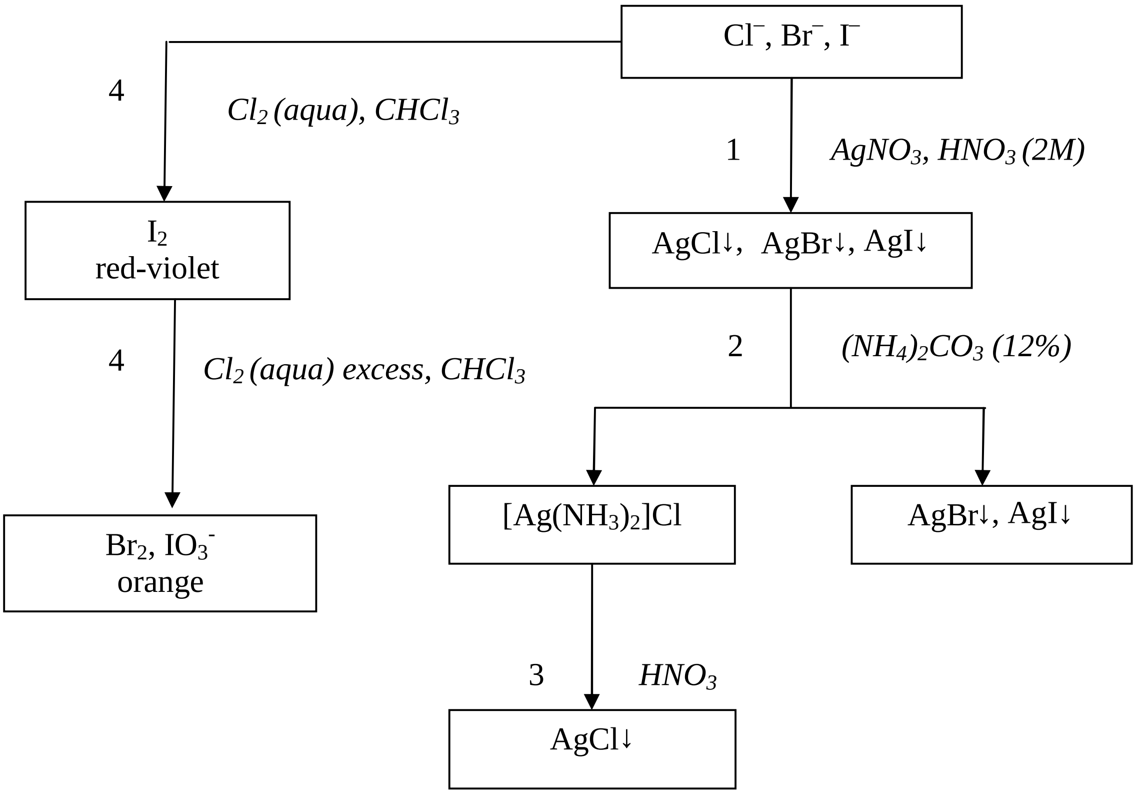
$I_2 + 6H_2O - 10\bar{e} \rightarrow 2IO_3^- + 12H^+$	1	
$Cl_2 + 2\bar{e} \rightarrow 2Cl^-$	5	E°($Cl_2/2Cl^-$)=1.359V
$I_2 + 6H_2O + 5Cl_2 \rightarrow 2IO_3^- + 12H^+ + 10Cl^-$		

Educed free bromine tinctures the chloroform layer in orange:

$2Br^- - 2\bar{e} \rightarrow Br_2$	1	E°($Br_2/2Br^-$)=1.087V
$Cl_2 + 2\bar{e} \rightarrow 2Cl^-$	1	E°($Cl_2/2Cl^-$)=1.359V
$Cl_2 + 2Br^- \rightarrow 2Cl^- + Br_2$		

Scheme 10

Analysis systematic course of mixture of halogen-ions Cl^-, Br^-, I^-



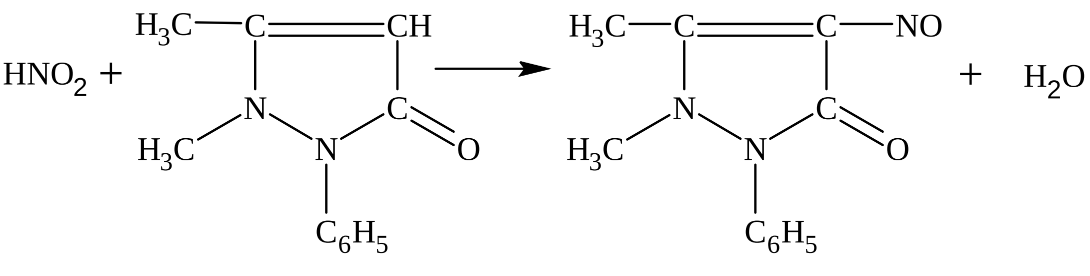
Analysis systematic course of mixture of NO_3^-, NO_2^-

Nitrite-ions prevent nitrate-ions detection, since in reactions with reducers ($FeSO_4$, diphenylamine etc.) their analytical effects are identical.

1. NO_2^- -ions detection

A separate portion of initial solution is acidified with diluted HCI solution, and crystalline antipyrine is added. Emerald-green colouring testifies the NO_2^- -ions presence:

$$NO_2^- + H^+ \rightarrow HNO_2$$



NO_2^- -ions do not prevent NO_2 ions detection with this reagent.

2. NO_2^- -ions removing

Crystalline NH_4CI is added to a separate portion of initial solution and it is heated up to complete N_2 removal:

$$NO_2^- + NH_4^+ \xrightarrow{\Delta} N_2\uparrow + 2H_2O$$

NO_2^- removing completeness is checked up by reaction with potassium iodide in acid environment:

$$\begin{array}{l|l} NO_2^- + 2H^+ + e \rightarrow NO\uparrow + H_2O & 2 \\ 2I^- - 2e \rightarrow I_2 & 1 \\ \hline 2NO_2^- + 4H^+ + 2I^- \rightarrow 2NO\uparrow + 2H_2O + I_2 & \end{array}$$

3. NO_3^- -ions detection

The chip of iron (II) sulphate and concentrated sulfuric acid are added to the solution, obtained on phase *2*. The formation of a brown ring testifies to NO_3^- -ions presence:

$$\begin{array}{l|l} Fe^{2+} - 1e \rightarrow Fe^{3+} & 3 \\ NO_3^- + 4H^+ + 3e \rightarrow NO\uparrow + 2H_2O & 1 \\ \hline 3Fe^{2+} + NO_3^- + 4H^+ \rightarrow 3Fe^{3+} + NO\uparrow + 2H_2O & \end{array}$$

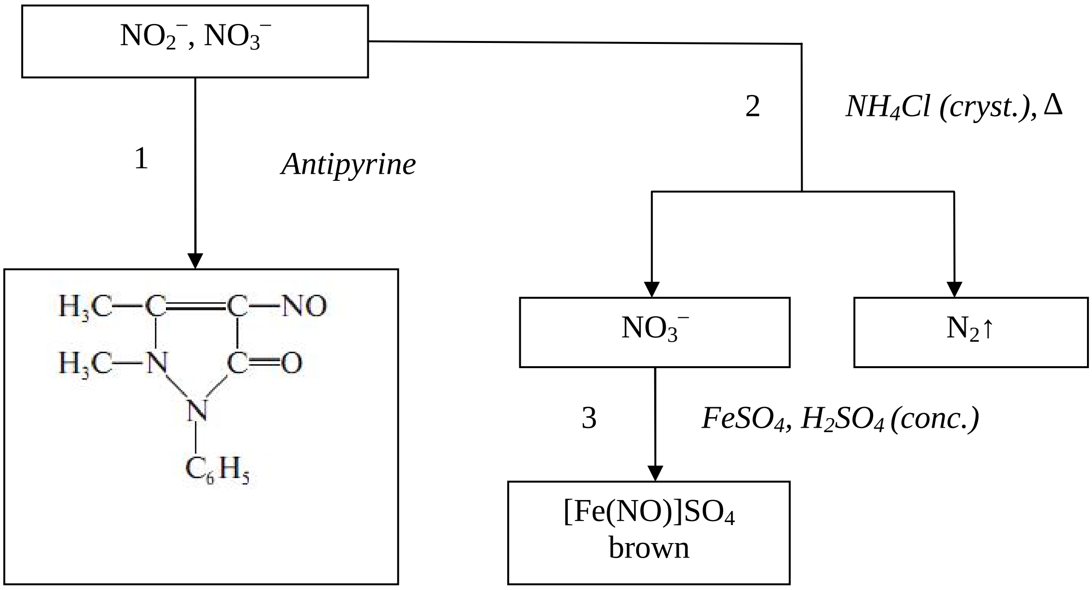
$$SO_4^{2-} + Fe^{2+} + NO \rightarrow [Fe(NO)]SO_4$$

Carrying out of the reaction is prevented by I^-, Br^- ions, since they are acidified by concentrated H_2SO_4 up to I_2 and Br_2. Therefore they are preliminarily affected by chloric water over HC1 at heating to complete I_2 and Br_2 removal.

The analysis of mixture of NO_3^-, NO_2^- ions is carried out according to the Scheme.

Scheme 11

Analysis systematic course of mixture of nitrate- and nitrite- anions
NO_3^-, NO_2^-



4. Tasks for individual work:

4.1. What anions of the Ist analytical group react with iodine? Write the equations of the conforming reactions and explain the analytical effects.

4.2. Is it possible to detect Br^--ions in the presence of I^--ions? Write the equations of the conforming reactions and explain the analytical effects.

4.3. Why is it necessary to remove NO_2^- -ions before identification of NO_3^--ions? What reaction is used for checking NO_2^- -ions removing completeness? Write the equations of the conforming reactions and explain the analytical effects.

4.4. Suggest the systematic analysis of solution which contains ions:

- $S_2O_3^{2-}$, SO_3^{2-}, CO_3^{2-};
- SO_4^{2-}, Cl^-, NO_3^-.

The situation tasks are solved according to the analysis course of mixture anions.

5. Laboratory experiment

Laboratory experiment 21.1.

Analysis of mixture of anions

1. Previous studies

1.1. Test for the first analytical group anions

2-3 drops of barium chloride $BaCl_2$ solution (group reagent) are added to a test-tube which contains 3-2 drops of neutral or alkaline (pH~7-9) analyzed solution. The formation of precipitate indicates the presence of the Ist analytical group anions.

If the precipitation is not dissolved in 2N hydrochloric acid HCl solution, the sulfate ions are present, and possibly thiosulphate-ions (sulfur residue).

If the precipitation is dissolved in acetic acid solution, it indicates a possible presence of carbonate, phosphate, tetraborate and arsenate only.

1.2. Test for the second analytical group anions

2-3 drops of silver nitrate $AgNO_3$ solution (group reagent), acidified diluted nitric acid, are added to a test-tube which contains 3-2 drops of analyzed solution. The formation of precipitate indicates the presence of the IInd analytical group anions.

1.3. Test for reducing anions

a) Action of iodine I_2 solution in the light alkaline medium

2-3 drops of sodium hydrogen carbonate $NaHCO_3$ saturated solution and 1-2 drops of iodine dilute solutions are added to a test-tube which contains 3-2 drops of theanalyzed solution. Discolouration of the solution indicates the presence of arsenite-ions AsO_3^{3-}.

b) Action of iodine solution in the presence of sulfuric acid

2-3 drops of 1M sulfuric acid solution and 1-2 drops of iodine dilute solutions are added to a test-tube which contains 3-2 drops of analyzed solution. Discolouration of the solution indicates the possible presence of thiosulfate-, sulfite- and sulfide-ions.

1.4. Test for oxidizing anion

a) Action of potassium iodide KI solution in the light acidic medium

2-3 drops of 1M sulfuric acid solution, 5 drops of chloroform and 2-3 drops of potassium iodide solution are added to a test-tube which contains 3-2 drops of analyzed solution. A red-violet chloroform layer indicates the presence oxidizing ions.

b) Action of potassium iodide KI solution in an environment of concentrated hydrochloric acid

3-2 drops of concentrated hydrochloric acid, 5 drops of chloroform and 2-3 drops of potassium iodide solution are added to a test-tube which contains 3-2 drops of analyzed solution. A red-violet chloroform layer indicates the presence arsenate-ions AsO_4^{3-}.

1.5. Test for anions of nonresistant acids

3-2 drops of 2N sulfuric acid solution are added to a test-tube which contains 3-2 drops of analyzed solution. The formation of the gaseous products (CO_2, SO_2, H_2S, NO_2) indicates the presence of the anions of nonresistant acids (carbonate-, thiosulfate-, sulfite-, nitrit-, sulfide-ions).

2. Anions detection

Anions are detected according to the conclusions based on previous studies by the fractional method using characteristic reactions in separate portions of a solution. If it is necessary special cases of anions mixture analysis are used.

Topic 22

Analysis of mixture with an unknown composition

1. The main purpose of the topic:

Identification of substances and their components is one of the major sections of the qualitative analysis in control of drugs. Chemical methods of analysis, which up to date have been studied well, are widely used for identification of drug substances and their components. Therefore, future professionals, pharmacists, need to learn the theory and practice of chemical analysis.

2. Basic questions:

2.1. Preparation of the sample for analysis.
2.2. Preliminary observations and tests obtaining the solution from the solid sample.
2.3. Qualitative reactions of cations and anions, the terms of their performance.
2.4. Analysis of mixture of cations.
2.5. The analysis of mixtures of anions.
2.6. Analytical operation "soda extract".

3. Brief exposition of theoretical material:

Analysis of mixture with an unknown composition

The analysis of mixture with an unknown composition is carried out according to the following stages: preliminary observations and tests, transformation of the mixture into the solution, analysis of cations and analysis of anions.

Preliminary observations and tests

First the mixture is thoroughly examined by the magnifying glass and, if necessary, by the microscope. The attention should be paid to the colour, shape and size of particles contained in the mixture's composition. For example, if there are crystals of dark green colour in the mixture, it is likely to contain chromium salt. Thus, it allows to determine not only the heterogeneity of a sample but to have an idea about a possible number of components in the mixture.

The composition of the essay examined must conform to an average composition of the whole mass of the mixture analyzed. A small portion of the mixture, which corresponds to the whole mass of the mixture analyzed in its chemical composition and properties, is called an **average sample**. For obtaining it the mixture is thoroughly mixed and triturated in the mortar, sifted through the sieve, mixed again and an averagely is collected. A small portion of an average sample is taken for the analysis.

Depending on a physical state of the mixture analyzed different preliminary tests are carried out: a test for flame coloration, heating in a difficultly fusible test-tube, a test for oxidants, bead formation, a test with concentrated H_2SO_4 etc.

Transformation of the mixture into solution

Separated small portions of the average sample are dissolved in water at 20-25°C and while heating, pH medium is determined in this solution, and then these portions are dissolved successively, in 3M HC1, 12M HC1 and 2M HNO_3.

After transferring the mixture analyzed into the solution, it is divided into three parts: for cation analysis, for anion analysis and a reserve solution.

Analysis of cations

The analysis of the mixture for the Ist-VIth analytical groups cations is carried out according to the scheme of the systematic course of the analysis of the mixture for the Ist-VIth analytical groups cations.

Analysis of anions

Before determining anions it is necessary to remove the IInd-VIth analytical groups cations from the solution analyzed. For this purpose, soda extract is prepared. The reactions of the Ist-VIth analytical groups cations occurring when soda extract is prepared are given.

The further determination of anions is carried out according to the analysis of the mixture for anions.

4. Control test and patterns of responses:

4.1. Suggest the course of analysis for the unknown composition: KCl. Write the corresponding equations of chemical reactions.

Answer:

1. Preliminary observations:

a) State of matter – precipitate (crystalline). The mixture is homogeneous, it means: we have one component only in the mixture.

b) The colour – white.

c) The smell – odorless.

d) The ratio of the water - studied substance soluble in water at the room temperature:

$$KCl \rightarrow K^+ + Cl^-$$

pH media of the solution is neutral, it means: salt is formed by strong acid and strong base or salts by weak base and weak acid (studied substance does not hydrolyze or hydrolyze with the formation of acid and basic hydroxides identical in strength).

2. Analysis of cations

2.1. Test for the first analytical group cations

2-3 drops of sodium carbonate Na_2CO_3 solution are added to a test-tube which contains 3-5 drops of analyzed solution. The formation of precipitate is not observed, it indicates the presence of the I^{st} analytical group cations only.

Finding of ammonium cations in the separate sample

Ammonium cations are found by adding of surplus of 2M solution of sodium or potassium hydroxide under heating. NH_3 gas formation is not observed, red litmus paper doesn’t turn blue, it indicates the absence of NH_4^+ ions.

Finding of potassium cations

2-3 drops of sodium hexanitrocobaltate (III) are added to a test-tube which contains 3-5 drops of analyzed solution. The formation of yellow precipitate is observed, it indicates the presence of K^+ cations:

$$2K^+ + Na_3[Co(NO_2)_6] \rightarrow NaK_2[Co(NO_2)_6]\downarrow + 2Na^+$$

3. Analysis of anions

3.1. Test for the first analytical group anions

2-3 drops of barium chloride solution are added to a test-tube which contains 3-5 drops of analyzed solution. The formation of the precipitate is not observed, it indicates the absence of the I^{st} analytical group anions.

3.2. Test for the second analytical group anions

2-3 drops of barium chloride solution are added to a test-tube which contains 3-5 drops of analyzed solution. It is resulted in generation of white precipitate that is dissolved completely in ammonium solution:

$$Ag^+ + Cl^- \rightarrow AgCl\downarrow$$

$$AgCl\downarrow + 2NH_3 \cdot H_2O \rightarrow [Ag(NH_3)_2]^+ + Cl^- + 2H_2O$$

2-3 drops of concentrated HNO_3 solution is added into the test-tube. The formation of white curdled precipitate is observed:

$$[Ag(NH_3)_2]^+ + Cl^- + 2H^+ \rightarrow AgCl\downarrow + 2NH_4^+$$

Described analytical effects indicate of Cl^- -ions presence.

Therefore the dry substance is potassium chloride KCl is investigated.

5. Tasks for individual work (write in a textbook for protocols):

5.1. Why should the analysis of an unknown substance begin with preliminary observations and tests?

5.2. Why is it necessary to perform the operation "soda extract" prior to the analysis of anions? In which case is this step not necessary to perform?

5.3. Suggest the course of analysis of the mixtures:

- Ammonium chloride;

- Iron (III) nitrate.

6. Laboratory experiment

Laboratory experiment 22.1
(control experimental problem)

Each student receives a dry mixture with unknown composition by the teacher and independently experimentally determines what components are included in the mixture. During the analysis of mixtures of unknown composition,the students should apply the knowledge of the theoretical foundations of qualitative analysis, and also the practical skills acquired during practical lessons in analytical chemistry.

The course of the analysis, observations, equations of chemical reactions, the conclusions should be described in the copybooks for registration of laboratory works.

Analysis of mixture of dry salt

1. Preliminary observations

Before carrying out the chemical analysis the object of the analysis is b carefully examined by the magnifying glass. Homogeneity of the mixture, its colour, shape and particle's size are determined. An average sample is prepared.

2. Transferring the mixture into the solution

Separate small portions of the powdered mixture are tried to get dissolved in:

- water at 20-25°C;
- hot water;
- diluted 2M HC1;
- the concentrated HC1;
- 2M nitric acid.

pH media is determined in the first solution. If the mixture isn't dissolved in the first solvent, the next one should be successfully taken. If the mixture examined is not completely dissolved in acids, it may be chlorides of the IInd group cations, sulfates of the III^{d} groups cations, $PbSO_4$, some oxides (SiO_2, $nMnO_2 \cdot mH_2O$ etc.). In this case special methods, such as the fusion of the residue with Na_2CO_3, are used.

After transferring the mixture into the solution, it is divided into three parts: for analysis of cations, for analysis of anions, a reserve solution.

3. Analysis of cations

The analysis of cations is carried out according to the systematic course of analysis of the mixture of the Ind-VIth of analytical group cations (topics 7; 15).

4. Analysis of anions

Two cases are distinguished:

- the mixture examined contains only the Ist group cations;
- the IInd-VIth group cations are also present in the mixture. In the first case the mixture is directly analyzed according to the analysis scheme of the mixture of anions, in the second case it is necessary to separate the IInd-VIth of group cations at

first. For this purpose special solution is prepared, it is soda extract. But at first a fractional determination of carbonate-ions is performed.

4.1. Preparation of a soda extract

Mix 0,1 g of the substance examined with 0,4 g Na_2CO_3 in a crucible, add 2.5-3 cm^3 of the distilled water. Boil the mixture for 5 minutes, add water while evaporating then transfer the contents of the crucible in a conical test-tube and separate precipitate (simultaneously the II^{nd}, III^{d}, V^{th}, VI^{th} group cations in the form of oxides, hydroxides, carbonates, basic salts) by centrifuge. The centrifugate's volume should be approximately 3 cm^3. The solution has anions included in the composition of the analyzed mixture, as well as hydroxoanions, oxoanions of the IV group cations and the I^{st} analytical group cations.

5.2. Analysis of anions

The analysis of anions is carried out according to the course of analysis of the mixture of anions (topic 21).

Thematic module 3

Objective: to check knowledge of students as they received in lectures and practical lessons in the following sections:

1. Characteristic reactions of the I^{st} analytical groups of anions (topic 17).
2. Characteristic reactions of the II^{nd} analytical groups of anions (topic 18).
3. Characteristic reactions of the III^{d} analytical groups of anions (topic 19).
4. Reactions of organic acids anions (topic 20).
5. Analysis of mixtures of anions (topic 21).
6. Analysis of a mixture with unknown composition (topic 22).

Control card of thematic module 3 includes the tasks:

- 8 tests. You must choose the correct answer and give a brief explanation, write the corresponding equations of chemical reactions;
- Situational task for analysis of unknown compounds composition. Suggest a scheme for the systematic analysis of the substance (identify cations and anions). Write the equation of chemical reactions, provide conditions for their implementation, interfering ions, analytical effects.

Final control of module 1
Qualitative analysis

Appendix 1

Tests

Topic 1. Characteristic reactions of the Ist analytical group cations. Analysis systematic course of the Ist analytical group cations

1**.** Choose the solution with group I cations:
A. Na^+, K^+, NH_4^+
B. NH_4^+, Cu^{2+}, Hg_2^{2+}
C. Na^+, Fe^{2+}, Fe^{3+}
D. K^+, Ag^+, Al^{3+}
E. K^+, NH_4^+, Zn^{2+}

2. There is K^+ in aqueous solution (pH>7). What will happen, if we add hexanitrocobaltate sodium to this solution:
A. White precipitate
B. Yellow precipitate
C. Colorless solution
D. Yellow solution
E. Brown precipitate

Topic 2. Sensitivity of Chemistry Reactions

1. What is the name of the reaction and reagents that can be used to identify this ion in the presence of others:
A. General
B. Selective
C. Group
D. Specific
E. Characneristic

2. Sensitivity analysis of reactions determines the ability of detecting substances in solution. Sensitivity reactions characterize all the following values except:
A. The minimum amount of reagent
B. Minimal concentration
C. Maximum of dilution
D. Detection minimal
E. Minimum volume of solution

Topic 3. Characteristic reactions of the IInd analytical group cations. Analysis systematic course of the IIst analytical group cations

1. Hydrochloric acid solution was added to solution containing cations of the second analytical group. It resulted in generation of white precipitate that was partly soluble in ammonium solution and was black. What cations are contained in the solution?
A. Mercury (II) and mercury (I) ions
B. Silver and barium ions
C. Silver and lead ions
D. Silver and mercury (II) ions

E. Silver and mercury (I) ions

2. Adding of a chlorohydrogen acid diluted solution to solution under examination resulted in white caseous sediment formation. It is the evidence of the following ions presence:
A. Iron (II)
B. Iodine
C. Ammonium
D. Barium
E. Silver

Topic 4. Ionization theory

1. Weak electrolytes - substances that have:
A. A small value of the constant of instability
B. A low value of the constant of ionization
C. A low value of the solubility product constant
D. A low value of oxidation number
E. A low value of the hydrolysis constant

2. The acidity of the medium is characterized by pH value. Choose a pH value 0.1 M solution NClO4:
A 2
B. 0
C. 4
D. 1
E. 3

Topic 5. Characteristic reactions of the III^d analytical group cations. Analysis systematic course of the III^d analytical group cations

1. There are Ca^{2+}, Sr^{2+} and Ba^{2+} of group III cations (acid – base classification). Choose the group reagent for these cations:
A. Nitric acid
B. Sulfuric acid + alcohol
C. Hydrochloric acid
D. Acetic acid
E. Oxalic acid

2. Calcium sulfate saturated solution was added to solution containing cations of the third analytical group and heated. It resulted in generation of white precipitate. What cation is contained in the solution?
A. Lead
B. Calcium
C. Magnesium
D. Strontium
E. Mercury (II)

Topic 6. Solubility Equilibria

1. All chemical processes are characterized by certain constants associated with the nature of the reactants. Characteristic of the thermodynamic state of precipitate - saturated solution are:
A. Ionic strength solution
B. Ion product
C. Constant resistance
D. The product of solubility
E. Dissociation constant

2. In saturated solution of strontium phosphate equilibrium concentration of ions Sr^{2+} i PO_4^{3-} are connected with the real product of solubility of the salt value:
A. $[Sr^{2+}]^3 [PO_4^{3-}]^2 = SP$
B. $[Sr^{2+}]$ 3 $[PO_4^{3-}] = SP$
C. $[Sr^{2+}]^2 [PO_4^{3-}]^2 = SP$
D. $[Sr^{2+}]^3 [PO_4^{3-}] = SP$
E. $[Sr^{2+}] [PO_4^{3-}]^2 = SP$

Topic 7. Analysis systematic course of mixture of the I^st^ – III^d^ analytical group cations

1. In the analysis of mixtures of cations ($Sa^{2+,}$ $Ba^{2+,}$ Pb^{2+}) c precipitate of sulfate acid was conducted. As can be separated from $PbSO_4$ mixture of barium sulfate and calcium?
A. Washing of precipitate 30% solution of ammonium acetate
B. Recrystallization precipitate
C. Washing of precipitate concentrated H_2SO_4
D. Washing precipitate acetate acid solution
E. Washing of precipitate ammonia solution

2. What are the cations Ist-III^{d} analytical group (acid-base classification) studied in solution, if the alkali solution formed precipitate, soluble in excess alkali?
A. Pb (II)
B. Mercury (I)
C. Barium
D. Silver (I)
E. Mercury (II)

Topic 9. Characteristic reactions of the IVth analytical group cations. Analysis systematic course of the IVth analytical group cations

1. There are Al^{3+}, Sn^{2+}, Sn (IV), As (V), As (III), Zn^{2+} and Cr^{3+} of group IV cations (acid – base classification). Choose the group reagent for these cations:
A. Sulfuric acid + alcohol
B. Nitric acid
C. Sodium hydroxide + H_2O_2
D. Acetic acid

E. Ammonium hydroxide

2. What cations of group IV cations (acid – base classification) form red precipitate with Aluminon reagent in presence of ammonium hydroxide?
A. Tin (II)
B. Chromium (III)
C. Tin (IV)
D. Zinc
E. Aluminum

Topic 10. Acid – base equilibrium

1. What salt does the expression $K_H = \frac{K_W}{K_a}$ for hydrolysis constant correspond with?

A. NaCN
B. $(NH_4)_2SO_4$
C. $(NH_4)_3PO_4$
D. CH_3COONH_4
E. Na_2SO_4

2. Buffer solutions are used in the analysis for:
A. pH control
B. Solution coloration
C. Complex compounds formation
D. Precipitate analytical group cations completeness
E. Change pH of solution

Topic 11. Characteristic reactions of the V^th analytical group cations. Analysis systematic course of the V^th analytical group cations

1. Under certain conditions of qualitative analysis $K_4[Fe(CN)_6]$ is a specific reagent to Fe^{3+} cations. What is the colour of the precipitate?
A. Red
B. Black
C. White
D. Brown
E. Blue

2. Magnesium can be precipitated from aqueous solution by adding the reagent Na_2HPO_4 in presence of ammonium chloride – ammonium hydroxide buffer system. What is the colour of the precipitate?
A. Red
B. Black
C. White
D. Brown
E. Blue

Topic 12. Oxidation – reduction equilibrium

1. When choosing the redox reaction for the needs analysis is necessary to provide complete and direction of passage of this oxidativ-reduction reactions. Set these parameters can be:
A.Value of pH
B.Largest standard electrode potentials of reactions of participants
C.The largest jump in the potential oxidativ-reduction reactions
D.The difference of standard electrode potentials of the reactions of participants
E.Largest concentrations of reaction participants

2. The relationship between the standard electrode potential and equilibrium redox couples is established by the law:
A. Rayleigh
B. Faraday
C. Bouguer-Lambert-Ber
D. Nernst
E. Avogadro

Topic 13. Characteristic reactions of the VIth analytical group cations. Analysis systematic course of the VIth analytical group cations

1. What cations of group VI form a blue organic layer with ammonium thiocyanate:
A. Hg^{2+}
B. Cu^{2+}
C. Ni^{2+}
D. Co^{2+}
E. Cd^{2+}

2. Nickel (II) cations can be precipitated from aqueous solution by adding the reagent dimethylglyoxime in presence of ammonium chloride – ammonium hydroxide buffer system. What is the color of the precipitate?
A. Redish-brown
B. Black
C. White
D. Strawberry red
E. Dark blue

Topic 14. Complex ion equilibrium

1. The drug contains a $[Co(NH_3)_6]Cl_2$. Indicate the central ion, which forms a complex:
A. Chloride, charge -1
B. Cobalt, a charge +3
C. Ammonia, the charge 0
D. Cobalt charge of +2
E. Chlorine, charge 0

2. The cations of which analytical groups (acid-base) form of classification group reagent soluble compounds?
A. II
B. V
C. VI
D. IV
E. III

Topic 15. Analysis systematic course of a mixture of the IV^th^ – VI^th^ analytical group cations

1. Potassium hexacyanoferrate (II) solution was added to solution containing IV – VI group cations. It resulted in generation of the white precipitate that was insoluble in dilute hydrochloric acid. What cations are contained in the solution?
A. Manganese
B. Cadmium
C. Aluminum
D. Mercury (II)
E. Zinc

2. There are iron (III) and copper (II) cations in aqueous solution. What reagent can we use to separate these cations:
A. Ammonium hydroxide concentrated solution
B. Sodium hydroxide and hydrogen peroxide aqueous solution
C. Hydrochloric acid aqueous solution
D. Sodium hydroxide aqueous solution
E. Sulfuric acid aqueous solution

Topic 17. Characteristic reactions of the Ist analytical groups of anions

1. What anions of group I anions form yellow precipitate with precipitating agent?
A. Sulfate-ions
B. Cromate-ions
C. Phosphate -ions
D. Sulfite-ions
E. Oxalate -ions

2. There is PO_4^{3-} anions in aqueous solution. What will happen, if we add the ammonium molybdate?
A. Precipitate dissolving
B. Gas evolution
C. Formation of yellow precipitate
D. Solution color appearance
E. Formation of white precipitate

Topic 18. Characteristic reactions of the IInd analytical groups of anions

1. What anions can react with silver nitrate in the presence of nitric acid to form white precipitate that soluble in 12% ammonium carbonate solution?
A. Thiocyanate – ions
B. Bromine – ions
C. Sulfide – ions
D. Iodine – ions
E. Chloride – ions

2. What anion forms a yellow-brown colour of organic layer after adding chlorine water?
A. Iodine – ions
B. Chloride – ions
C. Bromine – ions
D. Thiocyanate – ions
E. Sulfide – ions

Topic 19. Characteristic reactions of the III^{d} analytical groups of anions

1. What anion forms a blue colour of solution after adding diphenilamin?
A. Acetate -ions
B. Carbonate-ions
C. Sulfide -ions
D. Nitrate-ions
E. Iodine -ions

2. What anion of group III anions forms red-brown precipitate with iron (III) chloride?
A. Nitrate -ions
B. Carbonate-ions
C. Sulfide -ions
D. Acetate -ions
E. Iodine -ions

Topic 21. Analysis of mixtures of anions

1. Analysis of mixtures of anions I - III analytical groups begins with:
A. Preliminary observations and tests
B. Tests for anions of Ist group
C. Tests for anions IInd group
D. Tests for anions of III^{d} group
E. Tests for anions volatile acids

Appendix 2

The activity coefficients at different ionic strength

Ionic strength	Activity coefficients of ions, f_x				
	One chargers	**Two chargers**	**Three chargers**	**Four chargers**	**Five chargers**
0,0002	0,98	0,94	0,87	0,77	
0,0005	0,97	0,90	0,80	0,67	
0,001	0,96	0,86	0,73	0,56	
0,002	0,95	0,81	0,64	0,45	
0,0025	0,95	0,81	0,63	0,44	
0,005	0,93	0,74	0,52	0,33	
0,01	0,90	0,67	0,42	0,23	
0,025	0,86	0,56	0,29	0,13	
0,05	0,84	0,50	0,21	0,06	0,013
0,1	0,81	0,44	0,16	0,04	0,0058
0,2	0,80	0,41	0,14	0,03	0,0038
0,3	0,81	0,42	0,14	0,03	0,0046
0,4	0,82	0,45	0,17	0,04	0,0072
0,5	0,84	0,50	0,21	0,06	0,013
0,6	0,87	0,56	0,27	0,10	0,027
0,7	0,88	0,63	0,36	0,16	0,058
0,8	0,92	0,72	0,48	0,27	0,13
0,9	0,96	0,83	0,66	0,48	0,31
1,0	0,99	0,96	0,91	0,85	0,78

Appendix 3

SOLUBILITY PRODUCT CONSTANTS (K_{sp})
(water, $25^{o}C$)

Substance	K_{sp}	Substance	K_{sp}	Substance	K_{sp}
$AgBr$	$5,0\cdot10^{-13}$	$AgBrO_3$	$5,8\cdot10^{-5}$	Ag_2CO_3	$8,7\cdot10^{-12}$
$Ag_2C_2O_4$	$1,1\cdot10^{-11}$	$AgCl$	$1,8\cdot10^{-10}$	Ag_2CrO_4	$1,2\cdot10^{-12}$
$Ag_2Cr_2O_7$	$2,0\cdot10^{-7}$	AgI	$2,3\cdot10^{-16}$	Ag_2S	$7,2\cdot10^{-50}$
$Al(OH)_3$	$5,7\cdot10^{-32}$	$BaCO_3$	$4,9\cdot10^{-9}$	$BaCrO_4$	$1,1\cdot10^{-10}$
$BaSO_3$	$8,0\cdot10^{-7}$	$BaSO_4$	$1,8\cdot10^{-10}$	$BaWO_4$	$5,0\cdot10^{-9}$
$Be(OH)_2$	$8,0\cdot10^{-22}$	$Bi(OH)_3$	$3,0\cdot10^{-36}$	Bi_2S_3	$8,9\cdot10^{-105}$
$CaCO_3$	$4,4\cdot10^{-9}$	CaF_2	$4,0\cdot10^{-11}$	$Ca(IO_3)_2$	$1,9\cdot10^{-6}$
$CaSO_4$	$3,7\cdot10^{-5}$	$CaWO_4$	$1,6\cdot10^{-9}$	$Cd(OH)_2$	$2,2\cdot10^{-14}$
CdS	$6,5\cdot10^{-28}$	$Co(OH)_2$	$1,6\cdot10^{-15}$	CoS	$1,8\cdot10^{-20}$
$Cr(OH)_3$	$1,1\cdot10^{-30}$	$CuCN$	$3,2\cdot10^{-20}$	$CuCl$	$2,2\cdot10^{-7}$
CuI	$1,1\cdot10^{-12}$	$Cu(OH)_2$	$5,6\cdot10^{-20}$	CuS	$1,4\cdot10^{-36}$
$Fe(OH)_2$	$7,9\cdot10^{-16}$	$FeO(OH)$	$2,2\cdot10^{-42}$	FeS	$3,4\cdot10^{-17}$
Hg_2Br_2	$7,9\cdot10^{-23}$	Hg_2Cl_2	$1,5\cdot10^{-18}$	Hg_2I_2	$5,4\cdot10^{-29}$
HgS	$1,4\cdot10^{-45}$	KIO_4	$8,3\cdot10^{-4}$	Li_2CO_3	$1,9\cdot10^{-3}$
LiF	$1,5\cdot10^{-3}$	Li_3PO_4	$3,2\cdot10^{-9}$	MgF_2	$6,4\cdot10^{-9}$
$Mg(OH)_2$	$6,0\cdot10^{-10}$	$Mn(OH)_2$	$2,3\cdot10^{-13}$	MnS	$2,5\cdot10^{-10}$
$Ni(OH)_2$	$1,6\cdot10^{-14}$	NiS	$9,3\cdot10^{-22}$	$PbBr_2$	$5,0\cdot10^{-5}$
$Pb(BrO_3)_2$	$1,6\cdot10^{-4}$	PbC_2O_4	$7,3\cdot10^{-11}$	$PbCl_2$	$1,7\cdot10^{-5}$
$PbCrO_4$	$2,8\cdot10^{-13}$	PbF_2	$2,7\cdot10^{-8}$	PbI_2	$8,7\cdot10^{-9}$
$Pb(OH)_2$	$5,5\cdot10^{-16}$	PbS	$8,7\cdot10^{-29}$	$PbSO_4$	$1,7\cdot10^{-8}$
$RaSO_4$	$4,3\cdot10^{-11}$	SnS	$3,0\cdot10^{-28}$	$SrCrO_4$	$2,7\cdot10^{-5}$
$SrSO_4$	$2,1\cdot10^{-7}$	Tl_2CO_3	$4,0\cdot10^{-3}$	$TlCl$	$1,9\cdot10^{-4}$
Tl_2CrO_4	$1,0\cdot10^{-12}$	Tl_2S	$3,0\cdot10^{-9}$	Tl_2SO_4	$1,5\cdot10^{-4}$
$Zn(OH)_2$	$3,0\cdot10^{-16}$	ZnS	$7,9\cdot10^{-24}$		

Appendix 4

Ionization constants of the most important acids and bases

ACIDS

Common Name	Formula	Acidity Constant, K_a
Arsenic acid	H_3AsO_4	$K_1 = 5,6 \cdot 10^{-3}$ $K_2 = 1,7 \cdot 10^{-7}$ $K_3 = 2,95 \cdot 10^{-12}$
Arsenious acid	H_3AsO_3	$K = 5,9 \cdot 10^{-10}$
Boric acid	H_3BO_3	$K_1 = 7,1 \cdot 10^{-10}$ $K_2 = 1,8 \cdot 10^{-13}$ $K_3 = 1,6 \cdot 10^{-14}$
Boric acid	$H_2B_4O_7$	$K_1 = 1,8 \cdot 10^{-4}$ $K_2 = 2,0 \cdot 10^{-8}$
Bromic acid	$HBrO_3$	$K = 2,0 \cdot 10^{-1}$
Hydrobromous acid	$HBrO$	$K = 2,2 \cdot 10^{-9}$
Carbonic acid	H_2CO_3 $(CO_2 \cdot aq + H_2O)$	$K_1 = 4,5 \cdot 10^{-7}$ $K_2 = 4,8 \cdot 10^{-11}$
Hydrocyanic acid	HCN	$K = 5,0 \cdot 10^{-10}$
Ascorbic acid	$H_2C_6H_6O_6$	$K_1 = 9,1 \cdot 10^{-5}$ $K_2 = 4,6 \cdot 10^{-12}$
Cyanic acid	$HOCN$	$K = 2,7 \cdot 10^{-4}$
Tartaric acid	$H_2C_4H_4O_6$	$K_1 = 9,1 \cdot 10^{-4}$ $K_2 = 4,3 \cdot 10^{-5}$
Citric acid	$H_4C_6H_5O_7$	$K_1 = 7,4 \cdot 10^{-4}$ $K_2 = 2,2 \cdot 10^{-5}$ $K_3 = 4,0 \cdot 10^{-7}$ $K_4 = 1,0 \cdot 10^{-16}$
lactic acid	$HC_3H_5O_3$	$K = 1,5 \cdot 10^{-4}$
Formic acid	$HCOOH$	$K = 1,8 \cdot 10^{-4}$
Acetic acid	CH_3COOH	$K = 1,74 \cdot 10^{-5}$
Salicylic acid	$C_6H_4(OH)\ COOH$	$K_1 = 1,1 \cdot 10^{-3}$ $K_2 = 2,6 \cdot 10^{-14}$
Sulfanilic acid	$H_2NC_6H_4SO_3H$	$K = 6,3 \cdot 10^{-4}$
Trichloroacetic acid	CCl_3COOH	$K = 2,0 \cdot 10^{-1}$
Phenol	C_6H_5OH	$K = 1,0 \cdot 10^{-10}$
Chloroacetic acids	$CH_2ClCOOH$	$K = 1,4 \cdot 10^{-3}$
Oxalic acid	$H_2C_2O_4$	$K_1 = 5,6 \cdot 10^{-2}$ $K_2 = 5,4 \cdot 10^{-5}$
Ethylenediaminetetraacetic acid	H_4Y (EDTA)	$K_1 = 1,0 \cdot 10^{-2}$ $K_2 = 2,1 \cdot 10^{-3}$ $K_3 = 6,9 \cdot 10^{-7}$ $K_4 = 5,5 \cdot 10^{-11}$
Malic (apple) acid	$H_2C_4H_4O_5$	$K_1 = 3,5 \cdot 10^{-4}$ $K_2 = 8,9 \cdot 10^{-6}$

Succinic acid	$H_2C_4H_4O_4$	$K_1 = 1{,}6\cdot10^{-5}$ $K_2 = 2{,}3\cdot10^{-6}$
Hypochlorous acid	$HClO$	$K = 2{,}95\cdot10^{-8}$
Chlorous acid	$HClO_2$	$K = 1{,}1\cdot10^{-2}$
Chromic acid	H_2CrO_4	$K_1 = 1{,}6\cdot10^{-1}$ $K_2 = 3{,}2\cdot10^{-7}$
Dichromic acid	$H_2Cr_2O_7$	$K_2 = 2{,}3\cdot10^{-2}$
Hydrogen fluoride acid	HF	$K = 6{,}2\cdot10^{-4}$
Hydrogen peroxide	H_2O_2	$K_2 = 2{,}0\cdot10^{-12}$
Iodic acid	HIO_3	$K = 1{,}7\cdot10^{-1}$
Hypoiodous acid	HIO	$K = 2{,}3\cdot10^{-11}$
Manganic acid	H_2MnO_4	$K_1 = 1{,}0\cdot10^{-1}$ $K_2 = 7{,}1\cdot10^{-11}$
Molybdic acid	H_2MoO_4	$K_1 = 2{,}9\cdot10^{-3}$ $K_2 = 1{,}4\cdot10^{-4}$
Hydrazoic acid	HN_3	$K = 2{,}0\cdot10^{-5}$
Nitrous acid	HNO_2	$K = 5{,}1\cdot10^{-4}$
Phosphoric acid	H_3PO_4	$K_1 = 7{,}1\cdot10^{-3}$ $K_2 = 6{,}2\cdot10^{-8}$ $K_3 = 5{,}0\cdot10^{-13}$
Pyrophosphoric acid	$H_4P_2O_7$	$K_1 = 1{,}2\cdot10^{-1}$ $K_2 = 7{,}9\cdot10^{-3}$ $K_3 = 2{,}0\cdot10^{-7}$ $K_4 = 4{,}8\cdot10^{-10}$
Benzoic acid	C_6H_5COOH	$K = 6{,}6\cdot10^{-5}$
Thiocyanic acid	$HSCN$	$K = 1{,}4\cdot10^{-1}$
Hydrogen sulfide acid	H_2S	$K_1 = 1{,}0\cdot10^{-7}$ $K_2 = 2{,}5\cdot10^{-13}$
Sulfurous acid	H_2SO_3	$K_1 = 1{,}4\cdot10^{-2}$ $K_2 = 6{,}2\cdot10^{-8}$
Sulfuric acid	H_2SO_4	$K_2 = 1{,}15\cdot10^{-2}$
Thiosulfuric acid	$H_2S_2O_3$	$K_1 = 2{,}5\cdot10^{-1}$ $K_2 = 1{,}9\cdot10^{-2}$
Antimonic acid	$H[Sb(OH)_6]$	$K = 4{,}0\cdot10^{-5}$

BASIS

Common Name	Formula	K_b
Ammonium hydroxide	$NH_3\cdot H_2O$	$K = 1{,}76\cdot10^{-5}$
Silver hydroxide	$AgOH$	$K = 5{,}0\cdot10^{-3}$
Barium hydroxide	$Ba(OH)_2$	$K_2 = 2{,}3\cdot10^{-1}$
Aniline	$C_6H_5NH_2 + H_2O$	$K = 4{,}3\cdot10^{-10}$
Hydrazine hydrate	$N_2H_4 + H_2O$	$K = 9{,}3\cdot10^{-7}$
Diphenylamin	$(C_6H_5)_2NH + H_2O$	$K = 6{,}2\cdot10^{-14}$
Calcium Hydroxide	$Ca(OH)_2$	$K_2 = 4{,}0\cdot10^{-2}$
Lead hydroxide	$Pb(OH)_2$	$K_1 = 9{,}55\cdot10^{-4}$ $K_2 = 3{,}0\cdot10^{-8}$

Standard electrode potentials of some systems in aqueous solutions

Chemical equation of the process	E^0,B
Silver	
$Ag_2S + 2e = 2Ag + S^2$	−0.710
$Ag(CN)_2 + e = Ag + 2CN$	−0.290
$Ag_2S + H^+ + 2e = 2Ag + HS^-$	−0.272
$AgI + e = Ag + I^-$	−0.152
$Ag(S_2O_3)_2^{3-} + e = Ag + 2S_2O_3^{2-}$	0.010
$AgBr + e = Ag + Br^-$	0.071
$AgSCN + e = Ag + SCN$	0.090
$AgCl + e = Ag + Cl^-$	0.222
$Ag_2O + H_2O + 2e = Ag + 2OH^-$	0.342
$Ag(NH_3)_2^+ + e = Ag + 2NH_3$	0.373
$Ag(SO_3)_2^{3-} + e = Ag + 2SO_3^{2-}$	0.430
$Ag_2SO_4 + 2e = 2Ag + SO_4^2$	0.653
$Ag^- + e = Ag$	0.7994
$Ag^{2+} + e = Ag^+$	2.00
Aluminum	
$AlO_2^- + 2H_2O + 3e = Al + 4OH^-$	−2.350
$Al(OH)_3 + 3e = Al + 3OH^-$	−2.290
$AlF_6^3 + 3e = Al + 6F^-$	−2.070
$Al^{3+} + 3e = Al$	−1.66
Arsenic	
$As + 3H_2O + 3e = AsH_3 + 3OH^-$	−1.430
$AsO_4^{3-} + 2H_2O + 2e = AsO_2^- + 4OH^-$	−0.710
$AsO_2^- + 2H_2O + 3e = As + 4OH^-$	−0.680
$As + 3H^+ + 3e = AsH_3$	−0.600
$HAsO_2 + 3H^+ + 3e = As + 2H_2O$	0.284
$H_3AsO_4 + 2H^+ + 2e = HAsO_2 + 2H_2O$	0.560
Aurum	
$Au(CN)_2^- + e = Au + 2CN$	−0.610
$AuBr_4 + 2e = AuBr_2^- + 2Br^-$	0.800
$AuBr_4^- + 3e = Au + 4Br$	0.850
$AuCl_4 + 2e = AuCl_2^- + 2Cl$	0.920
$AuBr^- + e = Au + 2Br^-$	0.960
$AuCl_4 + 3e = Au + 4Cl^-$	1.000
$Au^{3+} + 2e = Au^+$	1.410
$Au^{3+} + 3e = Au$	1.500
$Au^+ + e = Au$	1.680
Bismuth	
$Bi + 3H^+ + 3e = BiH_3$	< −0.800
$Bi(OH)_3 + 3e = Bi + 3OH^-$	−0.460
$BiOCl + 2H^+ + 3e = Bi + H_2O + Cl^-$	0.160
$BiCl_4^- + 3e = Bi + 4Cl^-$	0.160
$BiO^+ + 2H^+ + 3e = Bi + H_2O$	0.320
$NaBiO_3 + 4H^+ + 2e = BiO^+ + Na^+ + 2H_2O$	> 1.800

Bromine

$2BrO^- + 2H_2O + 2e = Br_2 + 4OH^-$	0.450
$2BrO_3^- + 6H_2O + 10e = Br_2 + 12OH^-$	0.500
$BrO_3^- + 2H_2O + 4e = BrO^- + 4OH^-$	0.540
$BrO_3^- + 3H_2O + 6e = Br^- + 6OH^-$	0.610
$BrO^- + H_2O + 2e = Br^- + 2OH^-$	0.760
$Br_3^- + 2e = 3Br^-$	1.050
$Br_2 + 2e = 2Br^-$	1.087
$HBrO + H^+ + 2e = Br^- + H_2O$	1.340
$BrO_3^- + 6H^+ + 6e = Br^- + 3H_2O$	1.450
$2BrO_3^- + 12H^+ + 10e = Br_2 + 6H_2O$	1.520
$2HBrO + 2H^+ + 2e = Br_2 + 2H_2O$	1.600

Carbon

$2CO_2 + 2H^+ + 2e = H_2C_2O_4$	−0.490
$C_6H_6O_6 + 2H^+ + 2e = C_6H_8O_6$ (дегідроаскорбінова кислота) (аскорбінова кислота)	−0.326
$CO_2 + 2H^+ + 2e = HCOOH$	−0.200
$CO_2 + 2H^+ + 2e = CO + H_2O$	−0.120
$CH_3COOH + 2H^+ + 2e = CH_3CHO + H_2O$	−0.120
$HCOOH + 2H^+ + 2e = HCHO + H_2O$	−0.010
$CO_3^{2-} + 6H^+ + 4e = C + 3H_2O$	0.475
$C_6H_4O_2 + 2H^+ + 2e = C_6H_4(OH)_2$ (хінон) (гідрохінон)	0.6994

Calcium

$Ca(OH)_2 + 2e = Ca + 2OH^-$	−3.030
$Ca^{2+} + 2e = Ca$	−2.866

Cadmium

$CdS + 2e = Cd + S^{2-}$	−1.170
$Cd(CN)_4^{2-} + 2e = Cd + 4CN^-$	−1.090
$Cd(NH_3)_4^{2+} + 2e = Cd + 4NH_3$	−0.610
$Cd^{2+} + 2e = Cd$	−0.403

Chlorine

$HClO_2 - 3H^+ + 4e = Cl + 2H_2O$	1 560
$ClO_2 + 4H^+ + 5e = Cl + 2H_2O$	1.500
$2HOCl + 2H^+ + 2e = Cl_2 + 2H_2O$	1.630
$2HClO_2 + 6H^+ + 6e = Cl_2 + 4H_2O$	1 630
$HClO_3 + 2H^+ + 2e = HClO + H_2O$	1.640
$2ClO^- + 2H_2O + 2e = Cl_2 + 4OH^-$	0.400
$ClO_4^- + 4H_2O + 8e = Cl^- + 8OH^-$	0.560
$ClO_3^- + 3H_2O + 6e = Cl^- + 6OH$	0.630
$ClO^- + H_2O + 2e = Cl^- + 2OH^-$	0.880
$ClO_4^- + 2H^+ + 2e = ClO_3^- + H_2O$	1.190
$Cl_2 + 2e = 2Cl^-$	1.359
$ClO_4^- + 8H^+ + 8e = Cl^- + 4H_2O$	1.380
$ClO_3^- + 6H^+ + 6e = Cl^- + 3H_2O$	1.450
$HClO + H^+ + 2e = Cl^- + H_2O$	1.500

Cobalt

$CoS\ \text{бета} + 2e = Co + S^2$	−1.020
$CoS\ \text{альфа} + 2e = Co + S^{2-}$	−0.890
$Co(CN)_6^{3-} + e = Co(CN)_6^{4-}$	−0.830
$Co(OH)_2 + 2e = Co + 2OH^-$	−0.710
$Co(NH_3)_6^{2+} + 2e = Co + 6NH_3$	−0.420
$Co^{2+} + 2e = Co$	−0.290
$Co(NH_3)_6^{3+} + e = Co(NH_3)_6^{2+}$	0.100
$Co(OH)_3 + e = Co(OH)_2 + OH^-$	0.170
$Co^{3+} + 3e = Co$	0.460
$Co^{3+} + e = Co^{2+}$	1.950

Chromium

$Cr(OH)_2 + 2e = Cr + 2OH^-$	−1.400
$Cr(OH)_3 + 3e = Cr + 3OH^-$	−1.300
$CrO_2^- + 2H_2O + 3e = Cr + 4OH^-$	−1.200
$Cr^{2+} + 2e = Cr$	−0.910
$Cr^{3+} + 3e = Cr$	0.740
$Cr^{3+} + e = Cr^{2+}$	−0.410
$CrO_4^{2-} + 4H_2O + 3e = Cr(OH)_3 + 5OH^-$	−0.130
$CrO_4^2 + 4H^+ + 3e = CrO_2^- + 2H_2O$	0.945
$CrO_2 + 4H^+ + e = Cr^{2+} + 2H_2O$	1.188
$Cr_2O_7^{2-} + 14H^+ + 6e = 2Cr^{3+} + 7H_2O$	1.333
$CrO_4^2 + 8H^+ + 3e = Cr^{3+} + 4H_2O$	1.477

Copper

$Cu_2S + 2e = 2Cu + S^2$	−0.880
$CuS + 2e = Cu + S^2$	−0.700
$Cu(CN)_2 + e = Cu + 2CN^-$	−0.430
$Cu_2O + H_2O + 2e = 2Cu + 2OH^-$	−0.360
$Cu(OH)_2 + 2e = Cu + 2OH^-$	−0.220
$CuI + e = Cu + I^-$	−0.185
$Cu(NH_3)_2^+ + e = Cu + 2NH_3$	−0.120
$Cu(NH_3)_4^{2+} + 2e = Cu + 4NH_3$	−0.070
$Cu^{2+} + e = Cu^+$	0.159
$Cu^{2+} + 2e = Cu$	0.345
$Cu^{2+} + Cl^- + e = CuCl$	0.540
$Cu^{2+} + Br^- + e = CuBr$	0.640
$Cu^{2+} + I^- + e = CuI$	0.860
$Cu^{2+} + 2CN^- + e = Cu(CN)_2^-$	1.120

Fluorine

$OF_2 + 2H^+ + 4e = 2F^- + H_2O$	2.100
$F_2 + 2e = 2F^-$	2.870

Iron

$FeS + 2e = Fe + S^{2-}$	−0.950
$Fe(OH)_2 + 2e = Fe + 2OH^-$	−0.877
$FeCO_3 + 2e = Fe + CO_3^{2-}$	−0.756
$Fe(OH)_3 + e = Fe(OH)_2 + OH^-$	−0.560
$Fe^{2+} + 2e = Fe$	−0.473
$Fe_3O_4 + 8H^+ + 8e = 3Fe + 4H_2O$	−0.085
$Fe^{3+} + 3e = Fe$	−0.058
$Fe(CN)_6^{3-} + e = Fe(CN)_6^{4-}$	0.364
$Fe^{3+} + e = Fe^{2+}$	0.771
$Fe_3O_4 + 8H^+ + 2e = 3Fe^{2+} + 4H_2O$	1.210
$FeO_4^{2-} + 8H^+ + 3e = Fe^{3+} + 4H_2O$	1.900

Hydrogen

$H_2 + 2e = 2H^-$	−2.250
$2H_2O + 2e = H_2 + 2OH$	−0.828
$2H^+ (10^{-7}$ M$) + 2e = H_2$	−0.414
$2H^+ + 2e = H_2$	0.000
$HO_2^- + H_2O + 2e = 3OH$	0.880
$H_2O_2 + 2H^+ + 2e = 2H_2O$	1.770

Mercury

HgS (червоний) $+ 2e = Hg + S^{2-}$	−0.700
HgS (чорний) $+ 2e = Hg + S^{2-}$	−0.670
$Hg(CN)_4^{2-} + 2e = Hg + 4CN$	-0.370
HgO (червоний) $+ H_2O + 2e = Hg + 2OH^-$	0.098
$Hg_2Br_2 + 2e = 2Hg + 2Br^-$	0.1392
$Hg_2Cl_2 + 2e = 2Hg + 2Cl^-$	0.2682
$Hg_2C_2O_4 + 2e = 2Hg + C_2O_4^{2-}$	0.415
$Hg_2SO_4 + 2e = 2Hg + SO_4^{2-}$	0.615
$Hg_2^{2+} + 2e = 2Hg$	0.792
$Hg^{2+} + 2e = Hg$	0.850
$2Hg^{2+} + 2e = Hg_2^{2+}$	0.907

Iodine

$2IO_3^- + 6H_2O + 10e = I_2 + 12OH^-$	0.210
$IO_3^- + 3H_2O + 6e = I^- + 6OH^-$	0.260
$2IO^- + 2H_2O + 2e = I_2 + 4OH^-$	0.450
$IO^- + H_2O + 2e = I^- + 2OH^-$	0.490
$I_2 + 2e = 2I^-$	0.536
$I_3^- + 2e = 3I^-$	0.545
$HIO + H^+ + 2e = I^- + H_2O$	0.990
$IO_3^- + 6H^+ + 6e = I^- + 3H_2O$	1.080
$2IO_3^- + 12H^+ + 10e = I_2 + 6H_2O$	1.190
$H_5IO_6 + 7H^+ + 8e = I^- + 6H_2O$	1.240
$2HIO + 2H^+ + 2e = I_2 + 2H_2O$	1.450

Manganese

$Mn(OH)_2 + 2e = Mn + 2OH^-$	−1.550
$Mn^{2+} + 2e = Mn$	−1.170
$Mn(OH)_3 + e = Mn(OH)_2 + OH^-$	0.100
$MnO_4^- + e = MnO_4^{2-}$	0.558
$MnO_4^- + 2H_2O + 3e = MnO_2 + 4OH^-$	0.600
$MnO_2 + 4H^+ + 2e = Mn^{2+} + 2H_2O$	1.230
$MnO_4^- + 8H^+ + 5e = Mn^{2+} + 4H_2O$	1.510
$Mn^{3+} + e = Mn^{2+}$	1.510
$MnO_4^- + 4H^+ + 3e = MnO_2 + 2H_2O$	1.690
$Mn_3O_4 + 8H^+ + 2e = 3Mn^{2+} + 4H_2O$	1.750
$Mn(OH)_3 + 3H^+ + e = Mn^{2+} + 3H_2O$	1.840
$MnO_4^{2-} + 4H^+ + 2e = MnO_2 + 2H_2O$	2.257

Magnesium

$Mg(OH)_2 + 2e = Mg + 2OH^-$	−2.690
$Mg^{2+} + 2e = Mg$	−2.370
$Mg(OH)_2 + 2H^+ + 2e = Mg + 2H_2O$	−1.862

Nitrogen

$3N_2 + 2e = 2N_3^-$	−3.400
$3N_2 + 2H^+ + 2e = 2HN_3$	−3.100
$N_2 + 4H_2O + 2e = 2NH_2OH + 2OH^-$	−3.040
$N_2 + 2H_2O + 4H^+ + 2e = 2(NH_2OH \cdot H^+)$	−1.870
$N_2 + 4H_2O + 4e = N_2H_4 + 4OH^-$	−1.160
$NO_2^- + H_2O + e = NO + 2OH$	−0.460
$NO_3 + 2H_2O + 3e = NO + 4OH^-$	−0.140
$NO_3^- + 7H_2O + 8e = NH_3 \cdot H_2O + 9OH^-$	−0.120
$NO_3^- + H_2O + 2e = NO_2^- + 2OH$	0.010
$2NO_2^- + 4H_2O + 6e = N_2 + 8OH^-$	0.410
$NH_2OH + 2H_2O + 2e = NH_3 \cdot H_2O + 2OH^-$	0.420
$NO_3^- + 8H^+ + 6e = NH_2OH \cdot H^+ + 2H_2O$	0.730
$NO_3^- + 2H^+ + e = NO_2 + H_2O$	0.800
$2NO_3^- + 17H^+ + 14e = N_2H_4 \cdot H^+ + 6H_2O$	0.840
$NO_3^- + 10H^+ + 8e = NH_4^+ + 3H_2O$	0.870
$NO_2^- + 4H^+ + 3e = NO + 2H_2O$	0.960
$HNO_2 + H^+ + e = NO + H_2O$	0.980
$N_2O_4 + 2H^+ + 2e = 2HNO_2$	1.070
$N_2H_4 \cdot H^+ + 3H^+ + 2e = 2NH_4^+$	1.270
$2HNO_2 + 4H^+ + 4e = N_2O + 3H_2O$	1.290
$N_2O_4 + 8H^+ + 8e = N_2 + 4H_2O$	1.350
$2HNO_2 + 6H^+ + 6e = N_2 + 4H_2O$	1.440
$2NO + 4H^+ + 4e = N_2 + 2H_2O$	1.680
$N_2O + 2H^+ + 2e = N_2 + H_2O$	1.770

Nickel

NiS гама $+ 2e = Ni + S^{2-}$	−1.070
NiS альфа $+ 2e = Ni + S^{2-}$	−0.860
$Ni(OH)_2 + 2e = Ni + 2OH^-$	−0.720
$Ni(NH_3)_6^{2+} + 2e = Ni + 6NH_3$	−0.490
$Ni^{2+} + 2e = Ni$	−0.228
$Ni(OH)_3 + e = Ni(OH)_2 + OH^-$	0.490
$NiO_2 + 4H^+ + 2e = Ni^{2+} + 2H_2O$	1.680
$NiO_4^{2-} + 8H^+ + 4e = Ni^{2+} + 4H_2O$	1.800

Oxygen

$O_2 + H_2O + 2e = HO_2^- + OH$	−0.076
$O_3 + H_2O + 2e = O_2 + 2OH^-$	0.020
$O_2 + 2H_2O + 4e = 4OH^-$	0.401
$O_2 + 2H^+ + 2e = H_2O_2$	0.682
$HO_2^- + H_2O + 2e = 3OH^-$	0.880
$O_2 + 4H^+ + 4e = 2H_2O$	1.229
$H_2O_2 + 2H^+ + 2e = 2H_2O$	1.770
$O_3 + 2H^+ + 2e = O_2 + H_2O$	2.070

Phosphorus

$H_2PO_2^- + e = P + 2OH^-$	−2.050
$HPO_3^{2-} + 2H_2O + 2e = H_2PO_2^- + 3OH^-$	−1.570
$PO_4^{3-} + 2H_2O + 2e = HPO_3^{2-} + 3OH^-$	−1.120
$P + 3H_2O + 3e = PH_3 + 3OH^-$	−0.890
$H_3PO_2 + H^+ + e = P + 2H_2O$	−0.51
$H_3PO_4 + 5H^+ + 5e = P + 4H_2O$	−0.410
$H_3PO_4 + 4H^+ + 4e = HPH_2O_2 + 2H_2O$	−0.390
$H_3PO_4 + 2H^+ + 2e = H_2PHO_3 + H_2O$	−0.276
$P + 3H^+ + 3e = PH_3$	0.060
$H_4P_2O_6 + 2H^+ + 2e = 2H_3PO_3$	0.380

Lead

$PbS + 2e = Pb + S^{2-}$	−0.910
$PbO + H_2O + 2e = Pb + 2OH^-$	−0.580
$HPbO_2^- + H_2O + 2e = Pb + 3OH^-$	−0.540
$PbI_2 + 2e = Pb + 2I^-$	−0.364
$PbSO_4 + 2e = Pb + SO_4^{2-}$	−0.355
$PbF_2 + 2e = Pb + 2F^-$	−0.350
$PbBr_2 + 2e = Pb + 2Br^-$	−0.274
$PbCl_2 + 2e = Pb + 2Cl^-$	−0.266
$Pb^{2+} + 2e = Pb$	−0.126
$PbO_2 + H_2O + 2e = PbO + 2OH^-$	0.280
$Pb^{4+} + 4e = Pb$	0.770
$PbO_2 + 4H^+ + 2e = Pb^{2+} + 2H_2O$	1.455
$PbO_2 + SO_4^{2-} + 4H^+ + 2e = PbSO_4 + 2H_2O$	1.690
$Pb^{4+} + 2e = Pb^{2+}$	1.694

Sulfur

$SO_4^{2-} + H_2O + 2e = SO_3^{2-} + 2OH^-$	−0.930
$2SO_4^{2-} + 5H_2O + 8e = S_2O_3^{2-} + 10OH^-$	−0.760
$SO_3^{2-} + 3H_2O + 4e = S + 6OH^-$	−0.660
$2SO_3^{2-} + 3H_2O + 4e = S_2O_3^{2} + 6OH^-$	−0.580
$S + 2e = S^{2-}$	−0.480
$S_4O_6^{2-} + 2e = 2S_2O_3^{2-}$	0.090
$S + 2H^+ + 2e = H_2S$	0.171
$SO_4^{2} + 10H^+ + 8e = H_2S + 4H_2O$	0.310
$SO_4^{2-} + 8H^+ + 6e = S + 4H_2O$	0.360
$H_2SO_3 + 4H^+ + 4e = S + 3H_2O$	0.450
$S_2O_3^{2-} + 6H^+ + 4e = 2S + 3H_2O$	0.500
$(SCN)_2 + 2e = 2SCN^-$	0.770
$S_2O_8^{2-} + 2e = 2SO_4^{2}$	2.010

Antimony

$SbO_2^- + 2H_2O + 3e = Sb + 4OH^-$	−0.675
$Sb + 3H^+ + 3e = SbH_3$	−0.510
$SbO_3^- + H_2O + 2e = SbO_2^- + 2OH^-$	−0.430
$Sb_2O_3 + 6H^+ + 6e = 2Sb + 3H_2O$	0.152
$Sb^{3+} + 3e = Sb$	0.200
$SbO^+ + 2H^+ + 3e = Sb + H_2O$	0.212
$SbO_2^- + 4H^+ + 3e = Sb + 2H_2O$	0.446
$Sb_2O_5 + 6H^+ + 4e = 2SbO^+ + 3H_2O$	0.580
$Sb_2O_5 + 4H^+ + 4e = Sb_2O_3 + 2H_2O$	0.690

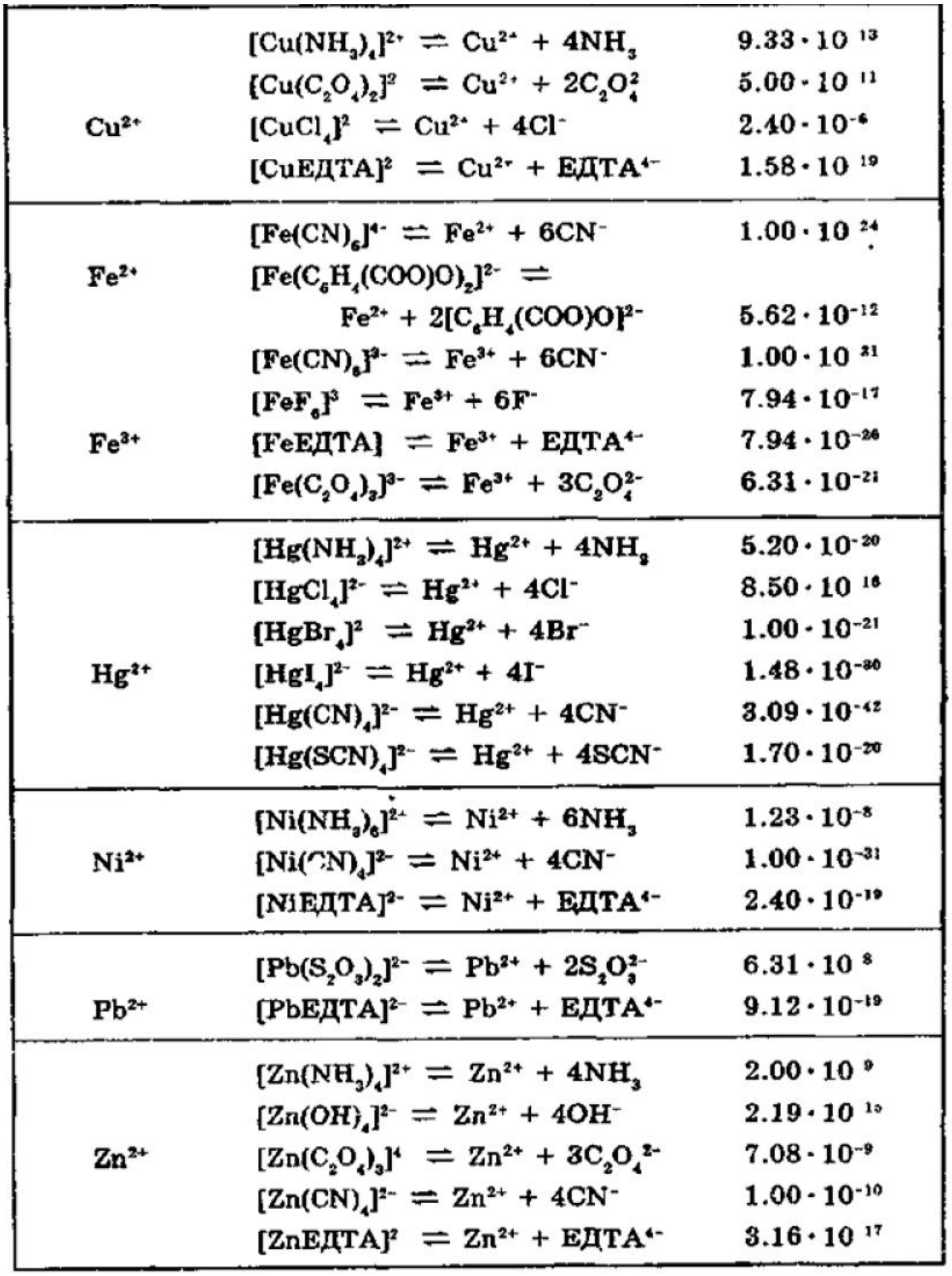
Zinc

$Zn(CN)_4^{2-} + 2e = Zn + 4CN^-$	−1.260
$Zn(NH_3)_4^{2+} + 2e = Zn + 4NH_3$	−1.040
$Zn^{2+} + 2e = Zn$	−0.764

Tin

$Sn(OH)_6^{2-} + 2e = HSnO_2^- + 3OH^- + H_2O$	−0.930
$SnF_6^{2-} + 4e = Sn + 6F^-$	−0.250
$SnCl_4^{2-} + 2e = Sn + 4Cl^-$	−0.190
$Sn^{2+} + 2e = Sn$	−0.140
$SnO_2 + 4H^+ + 4e = Sn + 2H_2O$	−0.106
$Sn^{4+} + 4e = Sn$	0.010
$Sn^{4+} + 2e = Sn^{2+}$	0.150

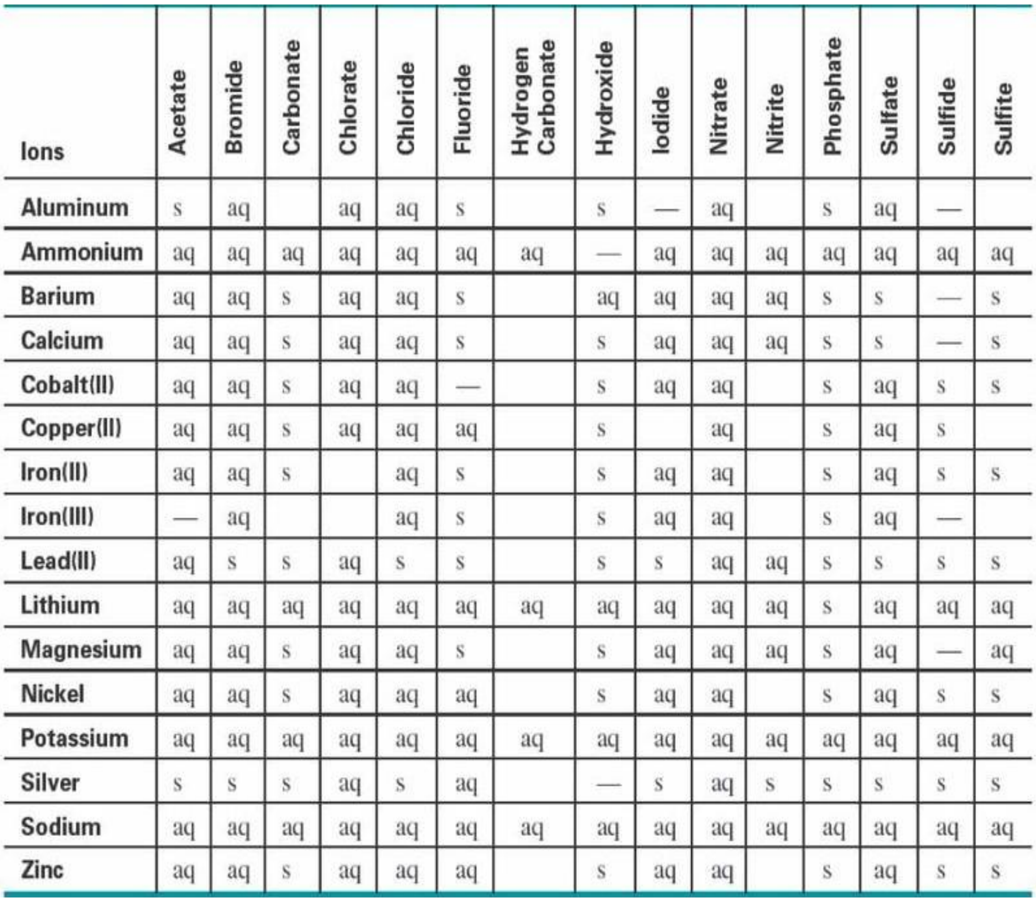
The value of constant instability of complex ions by 20-25°



Cu^{2+}	$[Cu(NH_3)_4]^{2+} \rightleftharpoons Cu^{2+} + 4NH_3$	$9.33 \cdot 10^{13}$
	$[Cu(C_2O_4)_2]^{2} \rightleftharpoons Cu^{2+} + 2C_2O_4^{2}$	$5.00 \cdot 10^{11}$
	$[CuCl_4]^{2} \rightleftharpoons Cu^{2+} + 4Cl^-$	$2.40 \cdot 10^{-6}$
	$[CuЕДТА]^{2} \rightleftharpoons Cu^{2+} + ЕДТА^{4-}$	$1.58 \cdot 10^{19}$
Fe^{2+}	$[Fe(CN)_6]^{4-} \rightleftharpoons Fe^{2+} + 6CN^-$	$1.00 \cdot 10^{24}$
	$[Fe(C_6H_4(COO)O)_2]^{2-} \rightleftharpoons Fe^{2+} + 2[C_6H_4(COO)O]^{2-}$	$5.62 \cdot 10^{-12}$
Fe^{3+}	$[Fe(CN)_6]^{3-} \rightleftharpoons Fe^{3+} + 6CN^-$	$1.00 \cdot 10^{31}$
	$[FeF_6]^{3} \rightleftharpoons Fe^{3+} + 6F^-$	$7.94 \cdot 10^{-17}$
	$[FeЕДТА] \rightleftharpoons Fe^{3+} + ЕДТА^{4-}$	$7.94 \cdot 10^{-26}$
	$[Fe(C_2O_4)_3]^{3-} \rightleftharpoons Fe^{3+} + 3C_2O_4^{2-}$	$6.31 \cdot 10^{-21}$
Hg^{2+}	$[Hg(NH_3)_4]^{2+} \rightleftharpoons Hg^{2+} + 4NH_3$	$5.20 \cdot 10^{-20}$
	$[HgCl_4]^{2-} \rightleftharpoons Hg^{2+} + 4Cl^-$	$8.50 \cdot 10^{16}$
	$[HgBr_4]^{2} \rightleftharpoons Hg^{2+} + 4Br^-$	$1.00 \cdot 10^{-21}$
	$[HgI_4]^{2-} \rightleftharpoons Hg^{2+} + 4I^-$	$1.48 \cdot 10^{-30}$
	$[Hg(CN)_4]^{2-} \rightleftharpoons Hg^{2+} + 4CN^-$	$3.09 \cdot 10^{-42}$
	$[Hg(SCN)_4]^{2-} \rightleftharpoons Hg^{2+} + 4SCN^-$	$1.70 \cdot 10^{-20}$
Ni^{2+}	$[Ni(NH_3)_6]^{2+} \rightleftharpoons Ni^{2+} + 6NH_3$	$1.23 \cdot 10^{-8}$
	$[Ni(CN)_4]^{2-} \rightleftharpoons Ni^{2+} + 4CN^-$	$1.00 \cdot 10^{-31}$
	$[NiЕДТА]^{2-} \rightleftharpoons Ni^{2+} + ЕДТА^{4-}$	$2.40 \cdot 10^{-19}$
Pb^{2+}	$[Pb(S_2O_3)_2]^{2-} \rightleftharpoons Pb^{2+} + 2S_2O_3^{2-}$	$6.31 \cdot 10^{8}$
	$[PbЕДТА]^{2-} \rightleftharpoons Pb^{2+} + ЕДТА^{4-}$	$9.12 \cdot 10^{-19}$
Zn^{2+}	$[Zn(NH_3)_4]^{2+} \rightleftharpoons Zn^{2+} + 4NH_3$	$2.00 \cdot 10^{9}$
	$[Zn(OH)_4]^{2-} \rightleftharpoons Zn^{2+} + 4OH^-$	$2.19 \cdot 10^{10}$
	$[Zn(C_2O_4)_3]^{4} \rightleftharpoons Zn^{2+} + 3C_2O_4^{2-}$	$7.08 \cdot 10^{-9}$
	$[Zn(CN)_4]^{2-} \rightleftharpoons Zn^{2+} + 4CN^-$	$1.00 \cdot 10^{-10}$
	$[ZnЕДТА]^{2} \rightleftharpoons Zn^{2+} + ЕДТА^{4-}$	$3.16 \cdot 10^{17}$

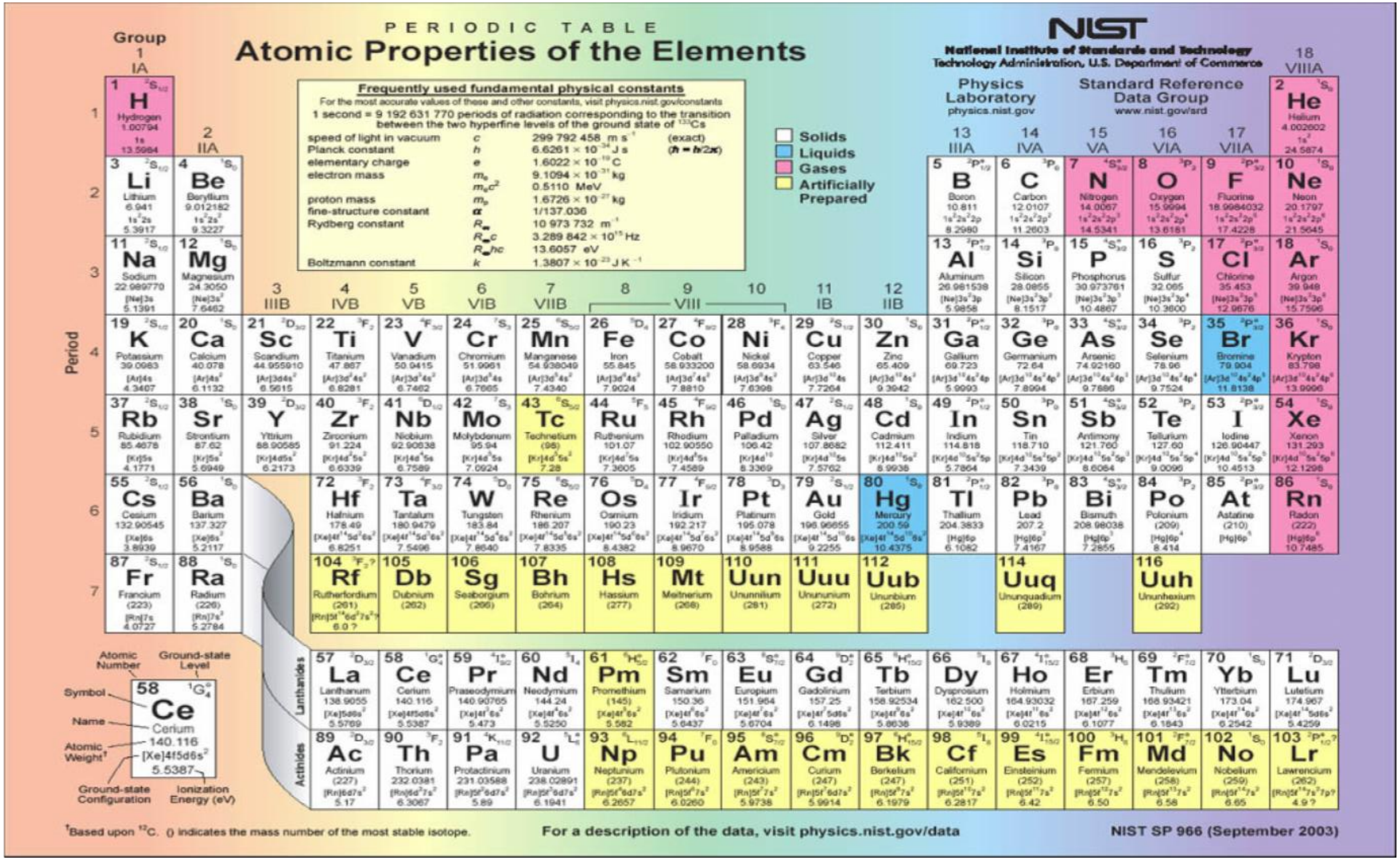
Ag^+	$[Ag(NH_3)_2]^+ \rightleftharpoons Ag^+ + 2NH_3$	$5.75 \cdot 10^{8}$
	$[AgCl_2]^- \rightleftharpoons Ag^+ + 2Cl$	$9.12 \cdot 10^{6}$
	$[AgI_2]^- \rightleftharpoons Ag^+ + 2I$	$5.50 \cdot 10^{-12}$
	$[Ag(S_2O_3)_2]^3 \rightleftharpoons Ag^+ + 2S_2O_3^{2}$	$3.47 \cdot 10^{14}$
	$[Ag(S_2O_3)]^- \rightleftharpoons Ag^+ + S_2O_3^{2-}$	$1.00 \cdot 10^{-13}$
	$[Ag(CN)_2]^- \rightleftharpoons Ag^+ + 2CN^-$	$1.41 \cdot 10^{-20}$
	$[Ag(SCN)_2]^- \rightleftharpoons Ag^+ + 2SCN^-$	$5.88 \cdot 10^{-9}$
	$[Ag(NO_2)_2] \rightleftharpoons Ag^+ + 2NO_2^-$	$1.8 \cdot 10^{-3}$
Al^{3+}	$[Al(OH)_4]^- \rightleftharpoons Al^{3+} + 4OH^-$	$1.0 \cdot 10^{-33}$
	$[Al(F_6)]^3 \rightleftharpoons Al^{3+} + 6F$	$2.14 \cdot 10^{-21}$
	$[Al(SO_4)_2]^- \rightleftharpoons Al^{3+} + 2SO_4^{2-}$	$1.26 \cdot 10^{-6}$
	$[Al(C_2O_4)_3]^{3-} \rightleftharpoons Al^{3+} + 3C_2O_4^{2-}$	$5.00 \cdot 10^{-17}$
	$[Al\text{ЕДТА}]^- \rightleftharpoons Al^{3+} + \text{ЕДТА}^{4-}$	$7.41 \cdot 10^{-1}$
Cd^{2+}	$[Cd(NH_3)_4]^{2+} \rightleftharpoons Cd^{2+} + 4NH_3$	$2.75 \cdot 10^{-7}$
	$[Cd(CN)_4]^{2-} \rightleftharpoons Cd^{2+} + 4CN^-$	$1.76 \cdot 10^{-18}$
	$[CdI_4]^2 \rightleftharpoons Cd^{2+} + 4I^-$	$7.94 \cdot 10^{-7}$
	$[Cd(S_2O_3)_2]^2 \rightleftharpoons Cd^{2+} + 2S_2O_3^{2-}$	$3.31 \cdot 10^{-7}$
Co^{2+} Co^{3+}	$[Co(NH_3)_6]^{2-} \rightleftharpoons Co^{2+} + 6NH_3$	$7.80 \cdot 10^{-6}$
	$[Co(NH_3)_6]^{3+} \rightleftharpoons Co^{3+} + 6NH_3$	$6.16 \cdot 10^{-35}$
	$[Co(CN)_6]^4 \rightleftharpoons Co^{2+} + 6CN^-$	$8.13 \cdot 10^{-20}$
	$[Co(CN)_6]^{3-} \rightleftharpoons Co^{3+} + 6CN^-$	$1.00 \cdot 10^{64}$
	$[Co\text{ЕДТА}]^{2-} \rightleftharpoons Co^{2+} + \text{ЕДТА}^{4-}$	$1.00 \cdot 10^{-17}$
	$[Co\text{ЕДТА}]^- \rightleftharpoons Co^{3+} + \text{ЕДТА}^{4-}$	$1.00 \cdot 10^{-36}$
Cu^+	$[Cu(NH_3)_2]^+ \rightleftharpoons Cu^+ + 2NH_3$	$1.36 \cdot 10^{-11}$
	$[Cu(CN)_4]^3 \rightleftharpoons Cu^+ + 4CN^-$	$5.00 \cdot 10^{-31}$

Solubilities of Ionic Compounds



Ions	Acetate	Bromide	Carbonate	Chlorate	Chloride	Fluoride	Hydrogen Carbonate	Hydroxide	Iodide	Nitrate	Nitrite	Phosphate	Sulfate	Sulfide	Sulfite
Aluminum	s	aq		aq	aq	s		s	—	aq		s	aq	—	
Ammonium	aq	aq	aq	aq	aq	aq	aq	—	aq	aq	aq	aq	aq	aq	aq
Barium	aq	aq	s	aq	aq	s		aq	aq	aq	aq	s	s	—	s
Calcium	aq	aq	s	aq	aq	s		s	aq	aq	aq	s	s	—	s
Cobalt(II)	aq	aq	s	aq	aq	—		s	aq	aq		s	aq	s	s
Copper(II)	aq	aq	s	aq	aq	aq		s		aq		s	aq	s	
Iron(II)	aq	aq	s		aq	s		s	aq	aq		s	aq	s	s
Iron(III)	—	aq			aq	s		s	aq	aq		s	aq	—	
Lead(II)	aq	s	s	aq	s	s		s	s	aq	aq	s	s	s	s
Lithium	aq	aq	aq	aq	aq	aq	aq	aq	aq	aq	aq	s	aq	aq	aq
Magnesium	aq	aq	s	aq	aq	s		s	aq	aq	aq	s	aq	—	aq
Nickel	aq	aq	s	aq	aq	aq		s	aq	aq		s	aq	s	s
Potassium	aq	aq	aq	aq	aq	aq	aq	aq	aq	aq	aq	aq	aq	aq	aq
Silver	s	s	s	aq	s	aq		—	s	aq	s	s	s	s	s
Sodium	aq	aq	aq	aq	aq	aq	aq	aq	aq	aq	aq	aq	aq	aq	aq
Zinc	aq	aq	s	aq	aq	aq		s	aq	aq		s	aq	s	s

aq = aqueous (dissolves in water)
s = solid (does not dissolves in water)



PERIODIC TABLE

Atomic Properties of the Elements

Frequently used fundamental physical constants

For the most accurate values of these and other constants, visit physics.nist.gov/constants

1 second = 9 192 631 770 periods of radiation corresponding to the transition between the two hyperfine levels of the ground state of ^{133}Cs

speed of light in vacuum	c	299 792 458 m s^{-1}	(exact)
Planck constant	h	6.6261×10^{-34} J s	($\hbar = h/2\pi$)
elementary charge	e	1.6022×10^{-19} C	
electron mass	m_e	9.1094×10^{-31} kg	
	m_ec^2	0.5110 MeV	
proton mass	m_p	1.6726×10^{-27} kg	
fine-structure constant	α	1/137.036	
Rydberg constant	R_∞	10 973 732 m^{-1}	
	$R_\infty c$	$3.289\,842 \times 10^{15}$ Hz	
	$R_\infty hc$	13.6057 eV	
Boltzmann constant	k	1.3807×10^{-23} J K^{-1}	

- ☐ Solids
- 🟦 Liquids
- 🟥 Gases
- 🟨 Artificially Prepared

NIST

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Technology Administration, U.S. Department of Commerce

Physics Laboratory
physics.nist.gov

Standard Reference Data Group
www.nist.gov/srd

†Based upon ^{12}C. () indicates the mass number of the most stable isotope.

For a description of the data, visit physics.nist.gov/data

NIST SP 966 (September 2003)

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CONTENTS

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