UKRAINE
NATIONAL UNIVERSITY OF LIFE AND ENVIRONMENTAL SCIENCES OF UKRAINE
Department of Analytical and Bioinorganic Chemistry & Water Quality

WORKBOOK
in CHEMISTRY (V) (analytical)

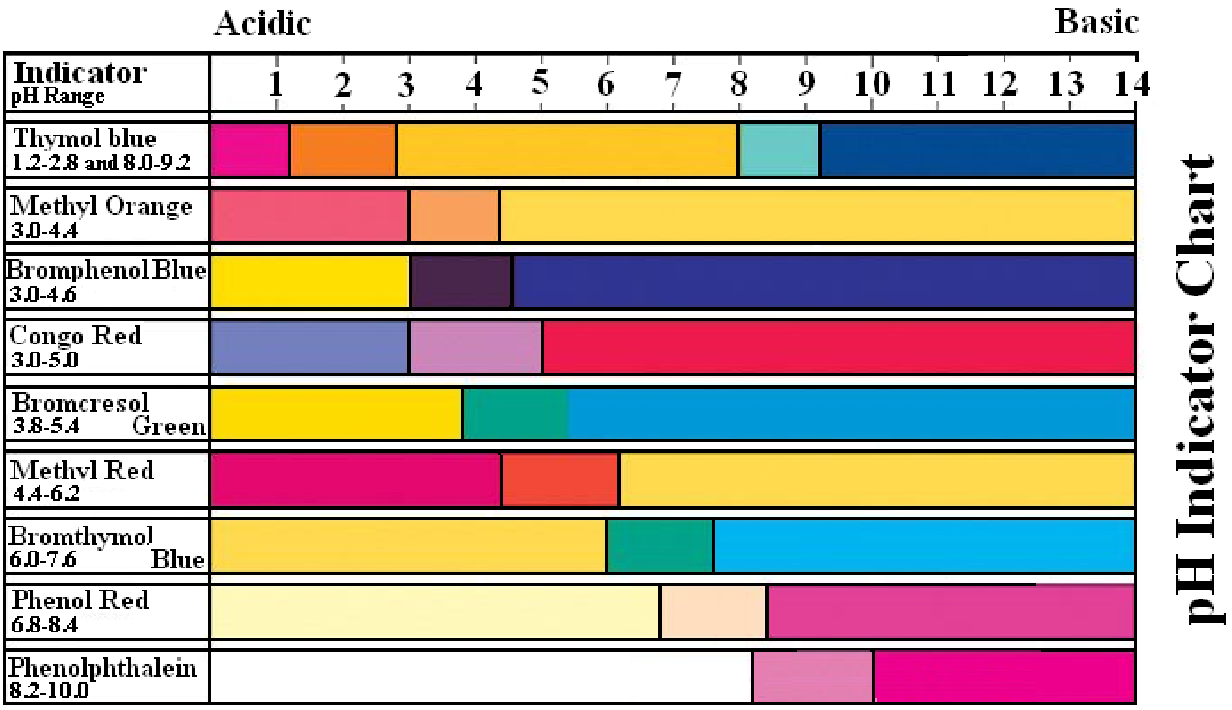
of student____

(Name, Surname)

____

(group, year of study)

Branch of knowledge – 10 Natural Sciences
Speciality – 101 Ecology



Kyiv-2019

УДК 546 (07)

Робочий зошит призначено для виконання лабораторного практикуму з аналітичної хімії. Включає методики виконання експериментальних задач, форми протоколів аналізу, питання для самоперевірки.

Рекомендовано методичною радою факультету захисту рослин, біотехнологій та екології Національного університету біоресурсів і природокористування України для спеціальності 101 – Екологія, для яких викладання ряду дисциплін проводиться англійською мовою (протокол № ___ від ________ 2019 р.).

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Voitenko, L.V. Workbook in analytical (V) chemistry (Speciality 101-Ecology) / Kyiv : DDP “Expo-druk”. – 2019. – 92 p.

Відповідальний за випуск: к.х.н., доц. Войтенко Л.В.

UDC 546 (07)

The workbook is intended to train in lab course of Analytical chemistry. It contains the description of experimental strategies, lab techniques, the templates of lab reports, test questions for own training.

Recommended for publication by the by the Methodical board of the Plant Protection, the Biotechnologies & Ecology faculty of National University of Life and Environmental Sciences, for Speciality 101 – Ecology.
Report # ___, Data ________2019.

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CONTENT

INTRODUCTION

GENERAL CHEMISTRY SAFETY AND LABORATORY RULES

Chemistry laboratories can be hazardous if the rules are not followed. During a chemistry course a student may handle materials which are carcinogenic, poisonous, flammable, and explosive. Some of these materials and equipment may also cause severe burns, cuts, or bruises if handled improperly or carelessly. Most accidents that occur in the chemistry laboratory are a result of carelessness, impatience, improper or unauthorized experimentation, and disregard for safety rules or proper operating procedures. In order to minimize the chances of an accident in the laboratory certain rules and regulations must be obeyed at all times when one is working or observing in a chemical laboratory. Therefore, it is not advisable for anyone to work in a laboratory without proper knowledge of the dangers involved. Due to the inherent dangers present in a chemical laboratory exercise, it should be understood that the following rules must be obeyed to minimize the chance of an accident. The student is expected to exercise proper judgement and extreme caution at all times when working in the laboratory.

1. Do not perform unauthorized experiments or work in a laboratory alone.
2. Approved eye protection must be worn at all times in the laboratory. If you do get a chemical in your eye rinse immediately with large quantities of water using the eye-wash stations.
3. Long hair and loose clothing must be confined while in a laboratory.
4. Appropriate clothing must be worn at all times while in the laboratory. Your legs must be completely covered below the knee by your choice of clothing. If your clothing does not meet the requirement you may choose to wear an approved laboratory coat or apron which does cover your legs to your knees.
5. Closed shoes with socks must be worn.
6. Know the location and proper use of fire extinguishers, fire blankets, eye wash devices, and first aid kits.
7. Before obtaining any chemicals carefully read the label on the reagent bottles.
8. Eating, smoking, and drinking are not allowed in a chem laboratory.
9. Thoroughly wash your hands after leaving the laboratory.
10. Use the fume hoods when toxic or irritating vapours are involved.
11. Mouth suction is never used to fill a pipette.
13. Never direct the open end of test tube toward yourself or anyone else.

14. Never pour water into concentrated acid (**especially H_2SO_4**).

15. Learn the proper procedure for igniting and operating a laboratory burner. Always extinguish the flame when the burner is not being used. Make sure that all flammable reagents are well removed before lighting the burner.

16. Liquid and solid waste containers must be properly used at all times.

17. Never place chemicals directly on the balance pan. Always use a proper weighing container when using a balance to weigh a chemical. Never pour chemicals directly over the balance.

18. Never return unused chemicals to their original container (unless directed to do so by the instructor).

19. Securely replace lids, caps, and stoppers after removing reagents from containers.

20. Always wipe spatulas clean before and after inserting into reagent bottles.

21. Report any accident and/or injury, however minor, to your instructor immediately.

22. Never place anything that is not directly required for the experiment on laboratory desks; other items may interfere with the experiment.

23. All personal belongings should be placed in the bookcases as you enter the laboratory.

24. Clean up any spill immediately.

25. Before leaving the laboratory, make sure your work area is clean and dry.

26. Your instructor is available for any assistance you may need. Never hesitate to ask questions especially if there is any question concerning proper operating procedure. Be sure that you understand every instruction before proceeding.

1.2. LAB GLASSWEARE CLEANING RULES

In the analysis of samples the preparation of scrupulously clean glassware is mandatory. Lab glassware cleaning procedures must follow specific method requirements. If procedures are not listed then the method of cleaning should be adapted to both the substances that are to be removed, and the determinations (tests) to be performed. Recommendations for such cleaning procedures are listed below.

Analysis/Parameter	Cleaning Procedure (In order specified)
ORGANICS	

INORGANICS	
Trace Metals:	1-4, 9, 8 (optional), 4
Nutrients, Minerals:	1-4, 8, 4
Solids:	1-4, 11 (Volatile Solids 16)
Non-Metals, Physical Properties: (Cyanide)	1-4, 14
MICROBIOLOGY	1-4 (Sterilize per approved method)
BIOASSAY	
Freshwater:	18, 2, 3, 9 or 8, 4, 5, 4, 20
Marine & Estuarine:	19, 2, 3, 9 or 8, 4, 5, 4, 20
RADIONUCLIDES	17, 3, 8, 4

Cleaning Procedures:

1. Remove all labels using sponge or acetone.
2. Wash with hot tap water and a brush to scrub inside of glassware, stopcocks, and other small pieces, if possible, using a suitable laboratory-grade detergent. Organics - Liquinox, Alconox or equivalents. Inorganic anions - Liquinox or equivalent. Inorganic cations - Liquinox, Acationox, Micro or equivalents.
3. Rinse thoroughly with hot tap water.
4. Rinse thoroughly with distilled water (DW).
5. Rinse thoroughly with pesticide grade Acetone.
6. Rinse thoroughly with pesticide grade Methanol.
7. Rinse thoroughly with pesticide grade Hexane.
8. Rinse or soak with 1:1 HCl (Hydrochloric Acid).
9. Rinse or soak with >10% HNO_3 (Nitrate Acid).
10. Bake at 105 °C for 1 hour.
11. Bake at 180 °C (prior to use as per method).
12. Drain, then heat in muffle furnace for 30-60 minutes at 400 °C.
13. Clean, dry glassware should be sealed and stored in dust-free environment.
14. Soak in oxidizing agent (Chromic acid or equivalent); preferably hot (40-50 °C).
15. Last step (prior to use) should be a rinse with the solvent used in analysis.
16. Drain, then heat in muffle furnace for 1 hour at 550 °C.
17. Heat 1 hour in EDTA solution at 90-100 °C.
18. New glassware must be soaked overnight in 10% HNO_3 or HCl.
19. New glassware must be soaked overnight in seawater.
20. Rinse thoroughly with DW.

CHAPTER 1. QUALITATIVE ANALYSIS

1.1. ANALYTICAL REAGENTS AND REACTIONS

Using chemical method the analyzed substance is transformed into new compound having characteristic properties: colour, odour, and defined physical state. Chemical transformation which takes place is called qualitative analytical reaction and the substances initiated this transformation are called **analytical reagents.**

Group reagents react with the group of ions and provide the same effect; **specific reagents** react with only one ion; **selective reagents** react with a few ions.

Analytical reactions to be carried out are mostly influenced by the following:

- pH;
- Ion concentration;
- Temperature.

The sensitivity of the reaction is determined by the following:

- Detectable minimum;
- Minimum concentration;
- Maximum dilution.

Detectable minimum (m) is the less quantity of substance or ion, which can be detected by given reaction at certain conditions. It is expressed in $\gamma = 10^{-6}$ g.

Concentration limit (c) is the minimum concentration of determined ion in solution at which the analytical reaction gives positive effect. Concentration limit is expressed as the ratio of substance mass (1 g) to solution volume (in mL). For example, for qualitative determination of Cu^{2+} by reaction with water solution of ammonia $NH_3 \cdot H_2O$ minimum concentration is 1 : 250 000. It means that 1 g of Cu^{2+} may be detected in 250 liters of analyzing solution. Analytical tests must have **not less than 1 : 1000.**

Maximum dilution (MD) is an index inverse to minimum concentration: MD = 1/c. Maximum dilution indicates at which solution volume 1 g of the substance should be presented in order the reaction to be visible.

So the sensitivity of reaction is higher if maximum dilution is bigger; but detectable minimum and minimum concentration are is smaller.

Detectable minimum and concentration limit are interrelated:

$m = c \cdot V \cdot 10$;

$c = m/V \cdot 10^6$, where

V - volume of solution, mL.

1.2. QUALITATIVE REACTIONS OF THE CATIONS

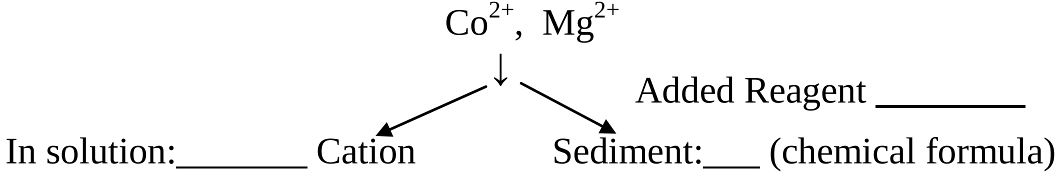
Ammonia-phosphate classification of cations is based (table 1) on the difference in solubility of phosphates in water, weak and strong acids, alkali and ammonia.

Environmental practice is connected with studying of the next common biologically active cations:

- Macronutrients: NH_4^+, Ca^{2+}, K^+, Na^+, Mg^{2+};
- Micronutrients: Mn^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Ag^+, Fe^{2+}, Fe^{3+};
- Cations of toxic and radioactive elements: Al^{3+}; Sr^{2+}, Cu^{2+}, Ag^+, Pb^{2+}.

The main idea is to use the separation of cations analyzing the mixture.

For example, **propose** the order of separation of cations in mixture.



Answer:

1. Cation Co^{2+} is included to the 3d group, Ca^{2+} – 2^d group, A-subgroup (see Table 1).

2. The 2^d and 3^d cations group reagent is the same in fact – $(NH_4)_2HPO_4$ (see Table 1). So, adding this reagent, both cations of mixture were precipitated:

$3Co(NO_3)_2 + 2(NH_4)_2HPO_4 + 2NH_3{\cdot}H_2O = Co_3(PO_4)_2\downarrow + 6NH_4NO_3 + 2H_2O$;

$Mg(NO_3)_2 + (NH_4)_2HPO_4 + NH_3{\cdot}H_2O = MgNH_4PO_4\downarrow + 2NH_4NO_3 + H_2O$.

3. For separating of sediments obtained we use their different solubility in excess of water ammonia $NH_3{\cdot}H_2O$: sediments of the 2^d cations group are insoluble, the 3^d one – soluble:

$Co_3(PO_4)_2\downarrow + 18NH_3{\cdot}H_2O$ (in excess) $= [Co(NH_3)_6]_3(PO_4)_2$(soluble) $+ 18H_2O$;

$MgNH_4PO_4\downarrow + NH_3{\cdot}H_2O$ (in excess) → not solute.

So, the chart of operation is:

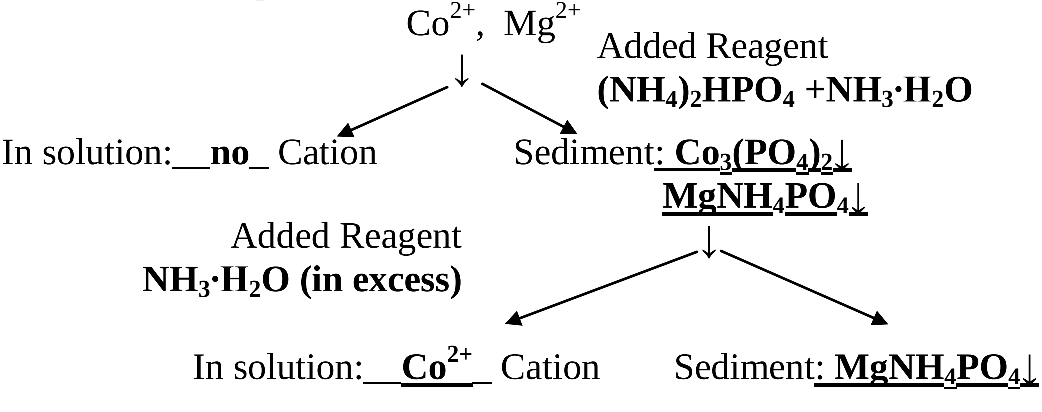
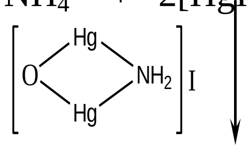
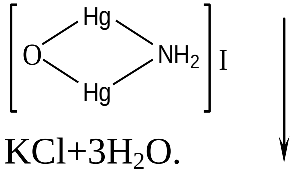


Table 1 – Principles of ammino-phosphate classification of cations

Group		Cations	Group reagent	Properties of sediments				
				Solubility in:				
				H_2O	$NH_3 \cdot H_2O$	CH_3COOH	HCl, HNO_3	NaOH
1		NH_4^+, Na^+, K^+	no	–	–	–	–	–
2	A	Mg^{2+}, Mn^{2+}, Ca^{2+}, Sr^{2+}, Fe^{2+}	$(NH_4)_2HPO_4$ + $NH_3 \cdot H_2O$	Insoluble in water	Insoluble	Soluble	Soluble	Insoluble
	B	Fe^{3+}, Al^{3+}				Insoluble		Only $AlPO_4$ soluble, forming $Na[Al(OH)_4]$
3		Cu^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}	$(NH_4)_2HPO_4$ or Na_2HPO_4	Insoluble in water	$[Me^{n+}(NH_3)_{(2-3)n}]^{n+}$ soluble	Soluble	Soluble	Only $Zn_3(PO_4)_2$ soluble, forming $Na_2[Zn(OH)_4]$
4		Ag^+, Pb^{2+}	HCl	Insoluble ($PbCl_2$ soluble partially in boiling H_2O)	$[Ag(NH_3)_2]Cl$ soluble	Insoluble	Insoluble	AgCl – insoluble; $PbCl_2$ soluble, forming $Na_2[Pb(OH)_4]$

1.3. THE FIRST GROUP OF CATIONS

1.3.1. Characteristic reactions of Ammonia cations NH_4^+

Content	Description	Observation	Explanation
1. Alkali (*NaOH, KOH*) *at heating.* Reaction is *highly sensitive*, *specific*; *concentration limit* *c*=1:5000000.	Add 4-5 drops of NaOH or KOH solution to 3-4 drops of ammonia salt and heat in a water bath. Gas may be identified by its odour (cautiously smell the vapor after moving the test-tube from the water bath), or by its turning moistened litmus paper blue.		$NH_4^+ + OH^- = NH_3 + H_2O$ $NH_4Cl + NaOH \xrightarrow{t} NH_3\uparrow + NaCl + H_2O$.
2. Nessler's reagent *$K_2[HgI_4]$+KOH (alkaline solution of potassium tetraiodomercurate(II))*. Reaction is *extremely sensitive, concentration limit c* = 1:10000000. Interferences cations formed insoluble hydroxides (Fe^{2+}, Fe^{3+}, Cu^{2+} et al.)	Add 2-3 drops of Nessler's reagent to 1 drop of any soluble ammonia salt.		$NH_4^+ + 2[HgI_4]^{2-} + 4KOH =$  $+ 7 I^- + 3H_2O$; $NH_4Cl + 2K_2[HgI_4] + 4KOH =$  $+ 7KI + KCl + 3H_2O$.

1.3.2. Characteristic reactions of Potassium cations K^+

Content	Description	Observation	Explanation
1. Potassium hexanitritocobaltate(III) ***$Na_3[Co(NO_2)_6]$.*** The NH_4^+ ions prevent the determination, because ammonia gives similar sediment. *Non specific, concentration limit c = 1:50000.*	Add 3-4 drops of reagent to 2-3 drops of potassium salt solution. Analyzed solution should have pH>7 because reagent easily decomposed: $Na_3[Co(NO_2)_6]+3NaOH=Co(OH)_3\downarrow+6NaNO_2$. At pH<7 unstable acid forms which not reacts with K^+ ions: $Na_3[Co(NO_2)_6]\downarrow+3HCl=H_3[Co(NO_2)_6]$ (solution) + 3NaCl; $2H_3[Co(NO_2)_6]+4HCl=5NO + 2CoCl_2 +7NO_2 + 5H_2O$.		$2K^+ + Na^+ +[Co(NO_2)_6]^{3-} = K_2Na[Co(NO_2)_6]\downarrow$; $2\ KCl + Na_3[Co(NO_2)_6] = K_2Na[Co(NO_2)_6]\downarrow + 2NaCl$.
2. Sodium hydrotartrate ***$NaHC_4H_4O_6$.*** The NH_4^+ ions prevent the determination, because ammonia gives similar sediment. *Non specific, low concentration limit c = 1:1000.*	Add to 4-5 drops of K^+ salt solution the same volume of reagent. Conditions: - pH = 5÷7; - Ammonia ions absence, because the similar sediment forms: $NH_4Cl + NaHC_4H_4O_6 = NH_4HC_4H_4O_6\downarrow + NaCl$; - Cooling; - Crystallization center formation (rub the tube inner surface by glass stick).		$K^+ + HC_4H_4O_6^- = KHC_4H_4O_6\downarrow$; $KCl + NaHC_4H_4O_6 = KHC_4H_4O_6\downarrow + NaCl$.

1.3.3. Characteristic reactions of Sodium cations Na^+

Content	Description	Observation	Explanation
1. Potassium hexahydroxostibiate ***$K[Sb(OH)_6]$*** *Non specific* - the NH_4^+ ions prevent the determination, because the ammonia salts are hydrolyzed in acidic medium. $K[Sb(OH)_6]$ decomposes forming sediment of methastibate acid $[Sb(OH)_6]^- + H^+ = HSbO_3\downarrow + 3H_2O$; pH 5-7. *Concentration limit c=1:3300.*	Add 5-6 drops of NaCl solution to 10-15 drops $K[Sb(OH)_6]$; rub the tube well by glass stick; cooling tube content in cold water.		$Na^+ + [Sb(OH)_6]^- = Na[Sb(OH)_6]\downarrow$ $NaCl + K[Sb(OH)_6] = Na[Sb(OH)_6]\downarrow + KCl$.
2. Zinc-Uranyl-Acetate ***$Zn(UO_2)_3(CH_3COO)_8$*** forms crystalline sediment. Reaction is *sensitive* (concentration limit *c=1:4000*), *highly specific* (acetic acid medium).	Initialization of crystallization by rubbing of tube sides by glass stick. Add 8-10 drops of *Zinc-Uranyl-Acetate* **(reagent - in lab fume hood)** to 3-4 drops of sodium salt solution and rub of tube sides by glass stick.		$Na^+ + Zn^{2+} + 3\ UO_2^{2+} + 8CH_3COO^- + CH_3COOH + 9H_2O = = NaZn(UO_2)_3(CH_3COO)_9 \cdot 9H_2O\downarrow$; $NaCl + Zn(UO_2)_3(CH_3COO)_8 + CH_3COOH + 9H_2O = NaZn(UO_2)_3(CH_3COO)_9 \cdot 9H_2O\downarrow + HCl$.

1.4. THE SECOND GROUP OF CATIONS

1.4.1. Action of group reagent $(NH_4)_2HPO_4$

Content	Description	Observation	Explanation
The reaction is carried out in presence of mixture $NH_3\cdot H_2O$ + NH_4Cl (buffer solution pH=9-10). At such conditions the cations Ca^{2+}, Sr^{2+}, Fe^{2+}, Fe^{3+}, Al^{3+} are deposited as orthophosphates: $Ca_3(PO_4)_2\downarrow$ $Sr_3(PO_4)_2\downarrow$ $Fe_3(PO_4)_2\downarrow$ $FePO_4\downarrow$ $AlPO_4\downarrow$, and cation Mg^{2+}, Mn^{2+} are deposited as double salts of Magnesium-ammonium phosphate and Manganese-ammonium phosphate: $MgNH_4PO_4\downarrow$, $MnNH_4PO_4\downarrow$	Take 7 tubes. Add 3-5 drops $NH_3\cdot H_2O$, 3-5 drops NH_4Cl and 4-5 drops $(NH_4)_2HPO_4$. Add 2-3 drops $MgCl_2$ in the 1st tube, $CaCl_2$ – in the 2d one, $Sr(NO_3)_2$ – in the 3d, $MnSO_4$ – in the 4th, $FeSO_4$ (**bottle with this solution is placed in lab fume hood)** – in the 5th, $FeCl_3$ – in the 6th, $Al_2(SO_4)_3$ – in the 7th. Note on the colour of sediments.	1st tube ___________ colour of sediment 2d tube ___________ colour of sediment 3d tube ___________ colour of sediment 4th tube ___________ colour of sediment 5th tube ___________ colour of sediment 6th tube ___________ colour of sediment 7th tube ___________ colour of sediment	**1.** $MgCl_2 + (NH_4)_2HPO_4 + NH_3\cdot H_2O = MgNH_4PO_4\downarrow + 2NH_4Cl + H_2O$; $Mg^{2+} + HPO_4^{2-} + NH_3\cdot H_2O = MgNH_4PO_4\downarrow + H_2O$. **2.** $3CaCl_2 + 2(NH_4)_2HPO_4 + 2NH_3\cdot H_2O = Ca_3(PO_4)_2\downarrow + 6NH_4Cl + 2H_2O$; $3Ca^{2+} + 2HPO_4^{2-} + 2NH_3\cdot H_2O = Ca_3(PO_4)_2\downarrow + 2NH_4^+ + 2H_2O$; **3.** $3Sr(NO_3)_2 + 2(NH_4)_2HPO_4 + 2NH_3\cdot H_2O = Sr_3(PO_4)_2\downarrow + 6NH_4NO_3 + 2H_2O$; $3Sr^{2+} + 2HPO_4^{2-} + 2NH_3\cdot H_2O = Sr_3(PO_4)_2\downarrow + 2NH_4^+ + 2H_2O$; **4.** $MnSO_4 + (NH_4)_2HPO_4 + NH_3\cdot H_2O = MnNH_4PO_4\downarrow + (NH_4)_2SO_4 + H_2O$; $Mn^{2+} + HPO_4^{2-} + NH_3\cdot H_2O = MnNH_4PO_4\downarrow + H_2O$. **5.** $3FeSO_4 + 2(NH_4)_2HPO_4 + 2NH_3\cdot H_2O = Fe_3(PO_4)_2\downarrow + 3(NH_4)_2SO_4 + 2H_2O$; $3Fe^{2+} + 2HPO_4^{2-} + 2NH_3\cdot H_2O = Fe_3(PO_4)_2\downarrow + 2NH_4^+ + 2H_2O$; **6.** $FeCl_3 + (NH_4)_2HPO_4 + NH_3\cdot H_2O = FePO_4\downarrow + 3NH_4Cl + H_2O$ $Fe^{3+} + HPO_4^{2-} + NH_3\cdot H_2O = FePO_4\downarrow + NH_4^+ + H_2O$; **7.** $Al_2(SO_4)_3 + 2(NH_4)_2HPO_4 + 2NH_3\cdot H_2O = 2AlPO_4\downarrow + 3(NH_4)_2SO_4 + 3H_2O$; $Al^{3+} + HPO_4^{2-} + NH_3\cdot H_2O = AlPO_4\downarrow + NH_4^+ + H_2O$.

Solubility of sediments obtained at the action of group reagent			
Content	**Description**	**Observation**	**Explanation**
All above mentioned precipitates aren’t dissolved in excess of $NH_3·H_2O$. Phosphates of both sub-groups are soluble in mineral acids. As related to solubility of phosphates in acetic acid, cations of the second group subdivide into **two** groups: II-A sub-group – includes cations Mg^{2+}, Ca^{2+}, Sr^{2+}, Mn^{2+}, Fe^{2+}, phosphates are soluble in acetic acid. II-B sub-group – includes cations Fe^{3+}, Al^{3+} – phosphates of these cations are insoluble in acetic acid. Due to amphoteric property $AlPO_4$ is soluble in alkalis.	Add CH_3COOH by drops to content of tubes # 1-7. Describe the effects. Add 15-20 drops NaOH in tube # 7. Describe the effect.		1. $Me_3(PO_4)_2\downarrow + 4CH_3COOH = 2Me(CH_3COO)_2 + Me(H_2PO_4)_2$ *(where Me – Ca^{2+}, Sr^{2+}, Fe^{2+});* $Me_3(PO_4)_2 + 4CH_3COOH = 2Me^{2+} + 4CH_3COO^- + Me^{2+} + 2H_2PO_4^-$; 2. $MeNH_4PO_4\downarrow + 2CH_3COOH = Me(CH_3COO)_2 + NH_4H_2PO_4$ *(where Me – Mg^{2+}, Mn^{2+});* $MeNH_4PO_4\downarrow + 2CH_3COOH = Me(CH_3COO)_2 + NH_4H_2PO_4$; $Me_3(PO_4)_2 + 2CH_3COOH = 3Me^{2+} + 2CH_3COO^- + NH_4^+ + H_2PO_4^-$. $AlPO_4\downarrow + 4NaOH = Na[Al(OH)_4] + Na_3PO_4$; $AlPO_4\downarrow + 4OH^- = [Al(OH)_4]^- + PO_4^{3-}$.

1.4.2. Characteristic reactions of Magnesium cations Mg^{2+}

Content	Description	Observation	Explanation
Group reagent (*$(NH_4)_2HPO_4$*) at pH 9-10 (buffer mixture $NH_3 \cdot H_2O$ + NH_4Cl) deposits Magnesium ions as crystalline precipitate $MgNH_4PO_4$. That is the qualitative reaction of Mg^{2+} ions is the reaction that is similar to the action of group reagent.	Add 3-5 drops $NH_3 \cdot H_2O$, 3-5 drops NH_4Cl and 2-3 drops $MgCl_2$.		$MgCl_2 + (NH_4)_2HPO_4 + NH_3 \cdot H_2O = MgNH_4PO_4\downarrow + 2NH_4Cl + H_2O$; $Mg^{2+} + HPO_4^{2-} + NH_3 \cdot H_2O = MgNH_4PO_4\downarrow + H_2O$.

1.4.3. Characteristic reactions of Calcium cations Ca^{2+}

Content	Description	Observation	Explanation
1. Sulfate acid *H_2SO_4* or soluble sulfates in presence of acetone give $CaSO_4$ white precipitate. It is soluble in concentrated ammonium sulfate $(NH_4)_2SO_4$ solution in the result of complex salt $(NH_4)_2[Ca(SO_4)_2]$ forming. *Reaction is selective; the same effect is observed of Ca^{2+} cations.*	Add 2-3 drops of Sodium sulfate Na_2SO_4 to 4-5 drops of Calcium salt solution. Add 10-15 drops of saturated $(NH_4)_2SO_4$ (**bottle is placed in lab fume hood)** in a tube, boil in a water bath 1 min, and add to a tube with sedimentation $CaSO_4$.		$CaCl_2 + Na_2SO_4 = CaSO_4\downarrow + 2NaCl$. $Ca^{2+} + SO_4^{2-} = CaSO_4\downarrow$ $CaSO_4\downarrow + (NH_4)_2SO_4 = (NH_4)_2[Ca(SO_4)_2]$ $CaSO_4\downarrow + 2NH_4^+ + SO_4^{2-} = 2NH_4^+ + [Ca(SO_4)_2]^{2-}$.

2. Ammonium oxalate *$(NH_4)_2C_2O_4$* gives white crystalline precipitate with Calcium ions. It is soluble in mineral acids but is insoluble in acetic acid. *Reaction is selective the same effect is observed of Sr^{2+} cations.*	Add 2-3 drops of Ammonium oxalate to 3-4 drops of $CaCl_2$ solution. Dissolve obtained sediment, adding by drops HCl.		$CaCl_2 + (NH_4)_2C_2O_4 = CaC_2O_4\downarrow + 2NH_4Cl$; $Ca^{2+} + C_2O_4^{2-} = CaC_2O_4\downarrow$. $CaC_2O_4\downarrow + 2HCl = CaCl_2 + H_2C_2O_4$; $CaC_2O_4\downarrow + 2H^+ = Ca^{2+} + H_2C_2O_4$.

1.4.4. Characteristic reactions of Strontium cations Sr^{2+}

Content	Description	Observation	Explanation
1. Sulfate acid *H_2SO_4* and soluble sulfates give $SrSO_4$ precipitate. It is insoluble in $(NH_4)_2SO_4$ concentrated solution. *Reaction is selective; the same effect is observed of Ca^{2+} cations.*	Add 2-3 drops of Sodium sulfate Na_2SO_4 to 4-5 drops of $Sr(NO_3)_2$ solution.		$Sr(NO_3)_2 + H_2SO_4 = SrSO_4\downarrow + 2HNO_3$; $Sr^{2+} + SO_4^{2-} = SrSO_4\downarrow$.
2. Ammonium oxalate *$(NH_4)_2C_2O_4$* gives crystalline precipitate with Sr^{2+} ions. It is soluble in mineral acids but insoluble in cold acetic acid. *Reaction is selective; the same effect is observed of Ca^{2+} cations.*	Add 2-3 drops of Ammonium oxalate to 3-4 drops of $Sr(NO_3)_2$ solution. Add by drops HCl till dissolving of sediment.		$Sr(NO_3)_2 + (NH_4)_2C_2O_4 = SrC_2O_4\downarrow + 2NH_4NO_3$; $Sr^{2+} + C_2O_4^{2-} = SrC_2O_4\downarrow$; $SrC_2O_4\downarrow + 2HCl = SrCl_2 + H_2C_2O_4$; $SrC_2O_4\downarrow + 2H^+ = H_2C_2O_4 + Sr^{2+}$.
3. Gypsum Water *(saturated water solution of $CaSO_4$)* gives	Add 1-2 mL of Gypsum water **(reagent - in lab**		$Sr(NO_3)_2 + CaSO_4 = SrSO_4\downarrow + 2Ca(NO_3)_2$;

sediment $SrSO_4$ in form of white turbidity. Gypsum $CaSO_4$ is a slightly soluble substance ($SP=6{,}1\cdot10^{-5}$), but more soluble, that $SrSO_4$ ($SP-2{,}8\cdot10^{-7}$). Therefore concentration of SO_4^{2-} in $CaSO_4$ saturated solution is sufficient for exceeding of $SrSO_4$ solubility product (SP). *Reaction is selective, because Ag^+, Pb^{2+} gives insoluble sulfates too.*	**fume hood)** to 5-10 drops of Strontium salt solution. Heat mixture in a water bath 3-5 min.		$Sr^{2+} + SO_4^{2-} = SrSO_4\downarrow$.

1.4.5. Characteristic reactions of Manganese cations Mn^{2+}

Content	Description	Observation	Explanation
1. Sodium Bismuthate *$NaBiO_3$* oxidizes Mn^{2+} to MnO_4^- in diluted nitrate acid medium. *Reaction is very sensitive and high specific.*	Add 15-20 drops of diluted Nitrate acid, 1-2 drops of $MnSO_4$ and a few grains of solid Sodium Bismuthate (volume as one match-head) (**reagent - in lab fume hood**).		$2Mn(NO_3)_2+5NaBiO_3+16HNO_3= 2HMnO_4+5Bi(NO_3)_3+5NaNO_3+ 7H_2O$; $2Mn^{2+} + 5BiO_3^- + 14H^+ = 2MnO_4^- + 5Bi^{3+} + 7H_2O$; $Mn^{2+}-5e\rightarrow Mn^{7+} \quad \vert \; 2$ $Bi^{5+}+2e\rightarrow Bi^{3+} \quad \vert \; 5$
2. Hydrogen peroxide *H_2O_2* oxidizes Mn^{2+} up to Mn^{4+} in ammonia or alkaline medium and sedimentates Manganese in the form mixed oxide-hydroxide. The	Add 2-3 drops of Ammonium hydroxide and 3-4 drops of 3% or 10% H_2O_2 **(reagent - in lab fume hood)** to 2-3		$Mn(NO_3)_2 + H_2O_2 + 2\ NH_3\cdot H_2O = H_2MnO_3\downarrow + 2NH_4NO_3 + H_2O$; $Mn^{2+} + H_2O_2 + 2\ NH_3\cdot H_2O = H_2MnO_3\downarrow + 2NH_4^+ + H_2O$.

black precipitate is formed. *Reaction is selective; the same effect is observed of cations formed insoluble hydroxides with alkali ($Fe(OH)_3$, $Cu(OH)_2$ etc.).*	drops of $MnSO_4$ solution. Heat mixture in a water bath 1-2 min.		$Mn^{2+} - 2e \rightarrow Mn^{4+} \;\vert\; 1$ $2O^{1-} + 2e \rightarrow 2O^{2-} \;\vert\; 1$

1.4.6. Characteristic reactions of Ferrous cations Fe^{2+}

Content	Description	Observation	Explanation
1. Alkalis *(NaOH, KOH)* deposits Fe^{2+} ions. This reagent is used for separation of Ferrous ions. *Reaction is selective; the same effect is observed of cations formed insoluble hydroxides in alkaline medium ($Ni(OH)_2$, $Mn(OH)_2$ etc.).*	Add 3-5 drops of NaOH, 1-2 drops of $FeSO_4$ (**reagent - in lab fume hood**). Observe the colour changing as the result of oxidation of Fe^{2+} to Fe^{3+} by air oxygen.		$FeSO_4 + 2NaOH = Fe(OH)_2\downarrow + Na_2SO_4$; $Fe^{2+} + 2OH^- = Fe(OH)_2\downarrow$. Oxidation of sediment in the air: $4Fe(OH)_2 + O_2 + 2H_2O = 4Fe(OH)_3\downarrow$. $Fe^{2+} - 1e \rightarrow Fe^{3+} \;\vert\; 4$ $O_2 + 4e \rightarrow 2O^{2-} \;\vert\; 1$
2. Potassium ferrocyanide *$K_3[Fe(CN)_6]$* *(red blood salt)* gives precipitate $Fe_3[Fe(CN)_6]_2$ (*Turnbull’s blue)* in slightly acidic medium). It is not soluble in acids, but decomposes in alkalis forming $Fe(OH)_2$ precipitate. *Reaction is high sensitive and specific.*	Add 1 drop of HCl and 2-3 drops of Potassium ferrocyanide to 2-3 drops of $FeSO_4$ (**reagent - in lab fume hood**).		$3FeSO_4 + 2K_3[Fe(CN)_6] = Fe_3[Fe(CN)_6]_2\downarrow + 3K_2SO_4$; $3Fe^{2+} + 2[Fe(CN)_6]^{3-} = Fe_3[Fe(CN)_6]_2\downarrow$.

1.4.7. Characteristic reactions of Ferric cations Fe^{3+}

Content	Description	Observation	Explanation
1. Alkalis *(NaOH, KOH)* deposits Fe^{3+} ions. This reagent is used for separation of Ferric ions. *Reaction is selective; the same effect is observed of cations formed insoluble hydroxides in alkaline medium ($Co(OH)_2$, $Mg(OH)_2$ etc.).*	Add 3-5 drops of NaOH to 1-2 drops of $FeCl_3$.		$FeCl_3 + 3NaOH = Fe(OH)_3\downarrow + 3NaCl$; $Fe^{3+} + 3OH^- = Fe(OH)_3\downarrow$.
2. Potassium ferricyanide *K_4 [$Fe(CN)_6$]* *(yellow blood salt)* gives precipitate (*Prussian blue)* with Fe^{3+} ions in acid medium. It isn't soluble in acids but is decomposed in alkalis. *Reaction is highly specific and very sensitive (minimum concentration c= 1:1000000).*	Add 1 drop of HCl and 2-3 drops of potassium ferricyanide to 2-3 drops of $FeCl_3$ solution.		$4FeCl_3 + 3K_4[Fe(CN)_6] = Fe_4[Fe(CN)_6]_3\downarrow + 12\ KCl$; $4Fe^{3+} + 3[Fe(CN)_6]^{4-} = Fe_4[Fe(CN)_6]_3\downarrow$.
3. Ammonium or Potassium Thiocyanide *(NH_4SCN or KSCN)* gives the solution of blood colour. *Reaction is very sensitive and specific.*	Add 1 drop of HCl solution and 2-3 drops NH_4SCN to 2-3 drops of $FeCl_3$.		$FeCl_3 + 6NH_4SCN = (NH_4)_3[Fe(SCN)_6] + 3NH_4Cl$; $Fe^{3+} + 6SCN^- = [Fe(SCN)_6]^{3-}$.

1.4.8. Characteristic reactions of Aluminium cations Al^{3+}

Content	Description	Observation	Explanation
1. Alkalis *(NaOH, KOH)* form gelatinous precipitate $Al(OH)_3$. Added excess of alkali, sediment dissolved due to amphoteric character of aluminium compounds. *Reaction is selective; the same effect is observed of cations formed amphoteric hydroxides, soluble in alkali ($Zn(OH)_2$, $Pb(OH)_2$).*	Add solution of $Al_2(SO_4)_3$ (by drops) to 1-2 drops of alkali as long as white translucent precipitate is formed. Add by drops alkaline solution until sediment dissolves completely.		$Al_2(SO_4)_3 + 6NaOH = 2Al(OH)_3\downarrow + 3Na_2SO_4$; $Al^{3+} + 3OH^- = Al(OH)_3\downarrow$ In excess of alkali: $Al(OH)_3\downarrow + NaOH = Na[Al(OH)_4]$; $Al(OH)_3\downarrow + OH^- = [Al(OH)_4]^-$.
2. Ammonium chloride *NH_4Cl*. Aluminates hydrolyze in water solutions. Equilibrium is shifted to the left or to the right depends on concentrations of ions H^+ and OH^- in solution, i.e. pH of solution. If solid NH_4Cl add to alkaline solution of Aluminate, NH_4Cl reacts with NaOH firstly. But formation of $NH_3 \cdot H_2O$ leads to pH reducing to 7-8 and equilibrium shifts to $Al(OH)_3$. The best results are observed at heating. *Reaction is selective, interferences cations given insoluble hydroxides.*	Add $Al_2(SO_4)_3$ solution by drops to 1-2 drops of alkali until $Al(OH)_3$ precipitate. Add by drops alkaline solution until sediment dissolved completely. Add 2-3 mL of DW and NH_4Cl (solid) to the saturation (a few crystals fall down and don't solute completely). Heat the mixture in a water bath.		The 1st step – sedimentation of $Al(OH)_3$: $Al_2(SO_4)_3 + 6NaOH = 2Al(OH)_3\downarrow + 3Na_2SO_4$; $Al^{3+} + 3OH^- = Al(OH)_3\downarrow$ Dissolving in excess of alkali: $Al(OH)_3\downarrow + NaOH = Na[Al(OH)_4]$; $Al(OH)_3\downarrow + OH^- = [Al(OH)_4]^-$; Sedimenting of $Al(OH)_3$ in saturated NH_4Cl solution: $Na[Al(OH)_4] + NH_4Cl = Al(OH)_3\downarrow + NH_3 \cdot H_2O + NaCl$; $[Al(OH)_4]^- + NH_4^+ = Al(OH)_3\downarrow + NH_3 \cdot H_2O$.

1.5. THE THIRD GROUP OF CATIONS

1.5.1. Action of group reagent $(NH_4)_2HPO_4$

Content	Description	Observation	Explanation
The cations Cu^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+} are precipitated by $(NH_4)_2HPO_4$ as orthophosphates $Cu_3(PO_4)_2$, $Zn_3(PO_4)_2$, $Co_3(PO_4)_2$, and $Ni_3(PO_4)_2$. $Co_3(PO_4)_2$ and $Ni_3(PO_4)_2$ are unstable in open **air** in the presence of oxygen, changing colour in the result of cations oxidation.	Take 4 tubes. Add 1-2 drops $NH_3{\cdot}H_2O$, 1-2 drops NH_4Cl, and 4-5 drops $(NH_4)_2HPO_4$. Add 2-3 drops $CuSO_4$ in the 1st tube, $ZnSO_4$ – in the 2d one, $CoCl_2$ – in the 3d, and $NiSO_4$ – in the 4th. Note on the colour of sediments and its stability.	1st tube ___________ colour of sediment 2d tube ___________ colour of sediment 3d tube ___________ colour of sediment _________________ Stability of colour 4th tube ___________ colour of sediment _________________ Stability of colour	**1.** $3MeSO_4 + 2\ (NH_4)_2HPO_4 + 2NH_3{\cdot}H_2O = Me_3(PO_4)_2\downarrow + 3\ (NH_4)_2SO_4 + 2\ H_2O$; $3Me^{2+} + 2HPO_4^{2-} + 2NH_3{\cdot}H_2O = Me_3(PO_4)_2\downarrow + 2NH_4^+ + 2H_2O$ ***(where Me – Cu^{2+}; Zn^{2+}, Ni^{2+})***; **2.** $3\ CoCl_2 + 2\ (NH_4)_2HPO_4 + 2NH_3{\cdot}H_2O = Co_3(PO_4)_2\downarrow + 6\ NH_4Cl + 2\ H_2O$; $3Co^{2+} + 2HPO_4^{2-} + 2NH_3{\cdot}H_2O = Co_3(PO_4)_2\downarrow + 2NH_4^+ + 2H_2O$; Oxidation of precipitate in the air: $4Co_3(PO_4)_2\downarrow + 3O_2 + 6H_2O = 4(CoOH)_3(PO_4)_2$. $\begin{array}{l\|l} 3Co^{2+} - 3e \rightarrow Co^{3+} & 4 \\ O_2^0 + 4e \rightarrow 2O^{2-} & 3 \end{array}$

Solubility of sediments obtained at the action of group reagent

Content	Description	Observation	Explanation
All above mentioned precipitates are dissolved in excess of $NH_3{\cdot}H_2O$. They are soluble in mineral acids (HCl, H_2SO_4) and acetic acid CH_3COOH.	Add 10-15 drops of water ammonia to content of tubes # 1-4. Describe the visual effects.		1. $Me_3(PO_4)_2\downarrow + 12NH_3{\cdot}H_2O = [Me(NH_3)_4]_3(PO_4)_2 + 12\ H_2O$ *(where Me – Cu^{2+}, Zn^{2+});* $Me_3(PO_4)_2\downarrow + 12NH_3{\cdot}H_2O = 3[Me(NH_3)_4]^{2+} + 2PO_4^{3-} + 12\ H_2O$;

Zinc orthophosphate due to amphoteric character is soluble in excess of alkali solution.			2. $Me_3(PO_4)_2\downarrow + 18\ NH_3\cdot H_2O = [Me(NH_3)_6]_3(PO_4)_2 + 18\ H_2O$ *(where Me – Co^{2+}, Ni^{2+});* $Me_3(PO_4)_2\downarrow + 18\ NH_3\cdot H_2O = 3[Me(NH_3)_6]^{2+} + 2PO_4^{3-} + 18\ H_2O$; $Zn_3(PO_4)_2\downarrow + 12NaOH = 3\ Na_2[Zn(OH)_4] + 2Na_3PO_4$; $Zn_3(PO_4)_2\downarrow + 12OH^- = 3[Zn(OH)_4]^{2-} + 2PO_4^{3-}$.

1.5.2. Characteristic reactions of Copper cations Cu^{2+}

Content	Description	Observation	Explanation
1. Water ammonia $NH_3\cdot H_2O$ in stoichiometrical quantity gives precipitate of a basic copper salt; adding in excess – dissolved the sediment. Due to the colour of solution this test is *specific reaction of Cu^{2+} and highly sensitive (c=1:500000.*	Add 1-2 drops of water ammonia in test tube and add by drops $CuSO_4$ solution until precipitate formation. Note on the on its colour. After that add by drops an excess of water ammonia till the complete dissolving of precipitate. What's colour of solution?		The reaction is carried out in two stages: **the 1st:** $2CuSO_4 + 2NH_3\cdot H_2O = (CuOH)_2SO_4\downarrow + (NH_4)_2SO_4$; $2Cu^{2+} + SO_4^{2-} + 2NH_3\cdot H_2O = (CuOH)_2SO_4\downarrow + 2NH_4^+$; **the 2d:** $(CuOH)_2SO_4\downarrow + (NH_4)_2SO_4 + 6NH_3\cdot H_2O = 2[Cu(NH_3)_4]SO_4 + 8H_2O$; $(CuOH)_2SO_4\downarrow + 2NH_4^+ + 6NH_3\cdot H_2O = 2[Cu(NH_3)_4]^{2+} + 8H_2O$.
2. Alkalis (*NaOH, KOH)* give precipitate with copper(II) ions.	Add 2-3 drops of NaOH to solution of $CuSO_4$		$CuSO_4 + 2NaOH = Cu(OH)_2\downarrow + Na_2SO_4$;

This reaction is *selective*; uses for separation of Cu^{2+} ions from cations mixture.	until sedimentation. Copper hydroxide has weak amphoteric properties, dissolved in mineral and acetic acids.		$Cu^{2+} + 2OH^{-} = Cu(OH)_2\downarrow$.
3. Potassium ferricyanide *$K_4[Fe(CN)_6]$* *(yellow blood salt)* forms precipitate with Cu^{2+} ions (pH<7). Reaction *is selective; but highly sensitive (c=1:2500000).* Precipitate $Cu_2[Fe(CN)_6]$ isn't dissolve in diluted acids, but solves in excess of water ammonia.	Add 1 drop of HCl and 2-3 drops of $K_4[Fe(CN)_6]$ to 3-4 drops of $CuCl_2$ solution.		$2CuCl_2 + K_4[Fe(CN)_6] = Cu_2[Fe(CN)_6]\downarrow + 4KCl$; $2Cu^{2+} + [Fe(CN)_6]^{4-} = Cu_2[Fe(CN)_6]\downarrow$.
4. Potassium Iodide *KI* reacts with copper salt formed white precipitate CuI. But reactive mixture has brown-red colour due to free I_2 isolation. Reaction *is selective; but highly sensitive (c=1:300000).*	Add 2-3 drops of KI solution to 3-4 drops of $CuSO_4$ solution.		$2CuSO_4 + 4KI = 2CuI + I_2 + 2K_2SO_4$; $2Cu^{2+} + 4I^{-} \rightarrow 2CuI\downarrow + I_2$. $2I^{-} - 2e \rightarrow I_2 \;\vert\; 1$ $Cu^{2+} + 1e \rightarrow Cu^{+} \;\vert\; 2$

1.5.3. Characteristic reactions of Zinc cations Zn^{2+}

Content	Description	Observation	Explanation
1. Water ammonia *$NH_3 \cdot H_2O$* in stoichiometrical quantity precipitates zinc hydroxide; adding in excess – dissolves the sediment. This test is *selective reaction of Zn^{2+}*.	Add 1-2 drops of water ammonia in test tube and add by drops $ZnSO_4$ solution until the sedimentation. After then add by drops an excess of ammonia till the complete dissolving. Note on the colour of solution.		The reaction is carried out in two stages: **the 1st:** $ZnSO_4 + 2NH_3 \cdot H_2O = Zn(OH)_2\downarrow + (NH_4)_2SO_4$; $Zn^{2+} + 2NH_3 \cdot H_2O = Zn(OH)_2\downarrow + 2NH_4^{2+}$; **the 2d:** $Zn(OH)_2\downarrow + 4\ NH_3 \cdot H_2O_{\text{(in excess)}} = [Zn(NH_3)_4](OH)_2 + 4H_2O$; $Zn(OH)_2\downarrow + 4\ NH_3 \cdot H_2O = [Zn(NH_3)_4]^{2+} + 4H_2O$.
2. Alkalis *(NaOH, KOH)* give white $Zn(OH)_2$ gelatinous precipitate with Zn^{2+} ions. This sediment has amphoteric properties and soluble in mineral acids and excess of alkalis. This test is *selective, used for the separation of Zn^{2+} from cations mixture*.	Add slowly 10-12 drops of $ZnSO_4$ solution to 2-3 drops of NaOH or KOH solution up to forming of white precipitate $Zn(OH)_2$. After then add excess of alkali to complete dissolving of sediment obtained before.		The reaction is carried out in two stages: **the 1st:** $ZnSO_4 + 2NaOH = Zn(OH)_2\downarrow + Na_2SO_4$; $Zn^{2+} + 2OH^- = Zn(OH)_2\downarrow$; **the 2d:** adding excess of alkali: $Zn(OH)_2\downarrow + 2NaOH = Na_2[Zn(OH)_4]$; $Zn(OH)_2\downarrow + 2OH^- = [Zn(OH)_4]^{2-}$.

3. Potassium ferrocyanide ***$K_3[Fe(CN)_6]$*** *(red blood salt)* forms precipitate of mustard colour with Zn ions ($pH<7$). It solves in alkalis. This test is *selective, Fe^{3+} interferences.*	Add 1 drops HCl and 2-3 drops of $K_4[Fe(CN)_6]$ to 2-3 drops of $ZnSO_4$ solution.		$3ZnSO_4 + 2K_3[Fe(CN)_6] = Zn_3[Fe(CN)_6]_2\downarrow + 3K_2SO_4$; $3Zn^{2+} + 2[Fe(CN)_6]^{3-} = Zn_3[Fe(CN)_6]_2\downarrow$.

1.5.4. Characteristic reactions of Cobalt cations Co^{2+}

Content	**Description**	**Observation**	**Explanation**
1. Water ammonia ***$NH_3·H_2O$*** in stoichiometrical quantity precipitates basic cobalt salt; adding in excess – dissolves the sediment. Test is *selective.*	Add 1-2 drops of water ammonia in test tube and add by drops $CoCl_2$ solution till the sedimenting of precipitate. After then add by drops an excess of ammonia till the complete dissolving. Note on the colour of solution, which is changing quickly in the result of oxidation $Co^{2+} \rightarrow Co^{3+}$.		The reaction is carried out in two stages: **the 1st:** $CoCl_2 + NH_3·H_2O = CoOHCl\downarrow + NH_4Cl$; $Co^{2+} + Cl^- + NH_3·H_2O = CoOHCl\downarrow + NH_4^+$. **the 2d:** $CuOHCl\downarrow + 7\ NH_3·H_2O = [Co(NH_3)_6](OH)_2 + NH_4Cl + 6H_2O$; $CoOHCl\downarrow + 7\ NH_3·H_2O = [Co(NH_3)_6]^{2+} + 2OH^- + NH_4^+ + Cl^-$.
2. Alkalis ***(NaOH, KOH)*** give gelatinous precipitate of basic salt with Co^{2+} ions. Excess of alkali converts CoOHCl at heating in $Co(OH)_2$ of pink	Add 1 drop of NaOH to 3-4 drops of $CoCl_2$ solution. Note on the colour of sediment. Add excess of alkali. Observe change of		$CoCl_2 + NaOH = CoOHCl\downarrow + NaCl$; $Co^{2+} + OH^- + Cl^- = CoOHCl\downarrow$. $CoOHCl\downarrow + NaOH = Co(OH)_2\downarrow + NaCl$;

colour. Test is *selective.*	sediment colour. Oxidation by air oxygen, $Co(OH)_2$ converts to $Co(OH)_3$. Note on the colour of solution.		$CoOHCl\downarrow + OH^- = Co(OH)_2\downarrow + Cl^-$. Oxidation: $4Co(OH)_2 + O_2 + 2H_2O = 4Co(OH)_3\downarrow$: $Co^{2+} - 1e \rightarrow Co^{3+} \quad \mid 4$ $O_2^0 + 4e \rightarrow 2O^{2-} \quad \mid 1$
3. Ammonium or Potassium Thiocyanide ***(NH$_4$SCN or KSCN)*** *(Vogel reaction)* solution in organic solvents (acetone) gives the dark blue solution. Reaction *is very sensitive, but selective.* Interference of Fe^{3+} ions can be eliminated by adding some solid potassium fluoride crystals NaF. The colourless hexafluoroferrate(III) $[FeF_6]^{3-}$ complex does not interfere, because it is more stable that $[Fe(SCN)_6]^{3-}$. Concentration limit 1 : 100000.	Add 4-5 drops of NH_4SCN saturated solution in acetone (**reagent - in lab fume hood**) to 3-4 drops of $CoCl_2$. Shake up content of tube and wait a few seconds. Note on the colour of upper layer.		$CoCl_2 + 6NH_4SCN = (NH_4)_4[Co(SCN)_6] + 2NH_4Cl$; $Co^{2+} + 6SCN^- = [Co(SCN)_6]^{4-}$.
4. Potassium Nitrite KNO$_2$ in presence of acetic acid oxidizes Co^{2+} to Co^{3+} forming with excess of KNO_2 sediment $K_3[Co(NO_2)_6]$. Reaction *is very sensitive, but not specific.*	To 5-7 drops of $CoCl_2$ solution add solid crystals KNO_2 to saturation. Add concentrated acetic acid **(reagent - in lab fume hood)** by drops up to formation of precipitate.		$CoCl_2 + 7KNO_2 + 2CH_3COOH = K_3[Co(NO_2)_6]\downarrow + 2KCl + 2CH_3COOK + NO + H_2O$. $Co^{2+} - 1e \rightarrow Co^{3+} \quad \mid 1$ $N^{3+} + 1e \rightarrow N^{2+} \quad \mid 1$ $Co^{2+} + 7NO_2^- + 3K^+ + 2CH_3COOH = K_3[Co(NO_2)_6]\downarrow + 2CH_3COO^- + H_2O + NO$.

1.5.5. Characteristic reactions of Nickel cations Ni^{2+}

Content	Description	Observation	Explanation
1. Water ammonia $NH_3 \cdot H_2O$ in stoichiometrical quantity precipitates basic nickel salt; adding in excess – dissolved the sediment. Test is *selective,* Cu^{2+} and Co^{2+} ions interfere. Reaction *is selective.*	Add by drops $2NH_3 \cdot H_2O$ solution to 3-4 drops of $NiSO_4$ up to basic salt precipitate and then the excess of ammonia up to the dissolving of precipitate.		The reaction is carried out in two stages: **the 1st:** $2NiSO_4 + 2NH_3 \cdot H_2O = (NiOH)_2SO_4\downarrow + (NH_4)_2SO_4$; $2Ni^{2+} + 2SO_4^{2-} + 2NH_3 \cdot H_2O = (NiOH)_2SO_4\downarrow + 2NH_4^+$; **the 2d:** $(NiOH)_2SO_4\downarrow + (NH_4)_2SO_4 + 2NH_3 \cdot H_2O = 2[Ni(NH_3)_6]SO_4 + 12H_2O$; $(NiOH)_2SO_4\downarrow + 2NH_4^+ + 10NH_3 \cdot H_2O = 2[Ni(NH_3)_6]^{2+} + SO_4^{2+} + 12H_2O$.
2. Alkalis ***(NaOH, KOH)*** give gelatinous precipitate $Ni(OH)_2$. Nickel(II) hydroxide dissolves in mineral acids, excess of water ammonia, solutions of ammonia salts, but isn't soluble in excess of alkali. Reaction *is selective.*	Add by drops $NiSO_4$ to 1-2 drops of NaOH.		$NiSO_4 + 2NaOH = Ni(OH)_2\downarrow + Na_2SO_4$; $Ni^{2+} + 2OH^- = Ni(OH)_2\downarrow$.
3. Dimethylglioxime (Chugaev's reagent) $C_4H_8N_2O_2$ in ammonia medium (pH=9) forms precipitate of intra-complex salt with Ni^{2+}	Add 5-7 drops of water ammonia solution $NH_3 \cdot H_2O$ and 3-5 alcohol solution of Chugaev's		$NiSO_4 + 2C_4H_8N_2O_2 + 2NH_3 \cdot H_2O = [Ni(C_4H_7N_2O_2)_2]\downarrow + (NH_4)_2SO_4 + 2H_2O$; $Ni^{2+} + 2C_4H_8N_2O_2 + 2NH_3 \cdot H_2O = [Ni(C_4H_7N_2O_2)_2]\downarrow + 2NH_4^+ + 2H_2O$.

ions. It solves in acids, alkalis, but doesn't dissolve in diluted ammonia solution. Reaction *is very sensitive, concentration limit c=1:300000. Ions of Fe^{2+}, Fe^{3+}, Cu^{2+} interference of Ni^{2+} determination.*	reagent **(or Dimethylglioxime - in lab fume hood)** to 2-4 drops of $NiSO_4$ solution. Reaction may be realized in the form of drop test on paper filter.		

1.6. THE FOUTH GROUP OF CATIONS

1.6.1. Action of group reagent HCl

Content	**Description**	**Observation**	**Explanation**
The diluted *HCl* and soluble chlorides deposits Ag^+ and Pb^{2+} in form of white precipitates of AgCl and $PbCl_2$, not soluble in diluted HNO_3 and H_2SO_4.	Take 2 tubes. Add 2-3 drops of $AgNO_3$ **(reagent - in lab fume hood)** in the first tube; 2-3 drops $Pb(NO_3)_2$ in the second tube. Add the same quantity of diluted HCl. Formed precipitates of AgCl and $PbCl_2$ divide into 4 tubes each. Study their solubility in hot	1st tube __________ colour of sediment 2d tube __________ colour of sediment 3d tube __________ ________________ 4th tube __________ ________________	$AgNO_3 + HCl = AgCl\downarrow + HNO_3$; $Ag^+ + Cl^- = AgCl\downarrow$; $Pb(NO_3)_2 + 2HCl = PbCl_2\downarrow + 2HNO_3$; $Pb^{2+} + 2Cl^- = PbCl_2\downarrow$; $PbCl_2\downarrow \xrightarrow{t°C} Pb^{2+} + 2Cl^-$ (dissolving in boiling water); $AgCl\downarrow + 2NH_3{\cdot}H_2O = [Ag(NH_3)_2]Cl + 2H_2O$ (dissolving in concentrated ammonia); $AgCl\downarrow + 2NH_3{\cdot}H_2O = [Ag(NH_3)_2]^{2+} + Cl^- + 2H_2O$; $AgCl\downarrow + (NH_4)_2CO_3 = [Ag(NH_3)_2]Cl$

	H_2O, concentrated $NH_3{\cdot}H_2O$ **(reagent - in lab fume hood)**, concentrated $(NH_4)_2CO_3$ **(reagent - in lab fume hood**, concentrated HCl **(reagent - in lab fume hood).** $PbCl_2$ in contrast to AgCl dissolves well in hot DW. This technique is used for the separation of AgCl and $PbCl_2$ precipitates.	5th tube ___________ ________________ 6th tube ___________ ________________ 7th tube ___________ ________________ 8th tube ___________ ________________	$+2H_2O+CO_2\uparrow$ (dissolving in concentrated ammonia carbonate); $AgCl\downarrow+2NH_4^{+}+CO_3^{2-} =[Ag(NH_3)_2]^{+} + Cl^{-} + 2H_2O +CO_2\uparrow$; $AgCl\downarrow +HCl = H[AgCl_2]$; $AgCl\downarrow+H^{+} +Cl^{-} = H^{+} + [AgCl_2]^{-}$; $PbCl_2\downarrow + 2HCl = H_2[PbCl_4]$; $PbCl_2\downarrow+2H^{+}+2Cl^{-}=2H^{+} + [PbCl_4]^{2-}$.

1.6.2. Characteristic reactions of Silver cations Ag^+

Content	Description	Observation	Explanation
1. Water ammonia *$NH_3{\cdot}H_2O$* precipitates silver cation in form of Ag_2O, which is dissolved in excess of reactant. Reaction *is selective.*	Add by drops water ammonia solution to 1-2 drops of $AgNO_3$ solution till precipitate formation. Observe dissolving of turbidity at adding of excess of $NH_3{\cdot}H_2O$.		$AgNO_3 + NH_3{\cdot}H_2O = AgOH\downarrow + NH_4NO_3$; $Ag^{+} + NH_3{\cdot}H_2O = AgOH\downarrow + NH_4^{+}$; $2AgOH\downarrow = Ag_2O\downarrow + H_2O$; $Ag_2O\downarrow + 4NH_3{\cdot}H_2O = 2[Ag(NH_3)_2]OH + 3H_2O$; $Ag_2O\downarrow + 4\ NH_3{\cdot}H_2O = 2[Ag(NH_3)_2]^{+} + 2OH^{-} + 3H_2O$.

1.6.3. Characteristic reactions of Lead cations Pb^{2+}

Content	Description	Observation	Explanation
1. Potassium Iodide *KI* isolates sediment PbI_2. The compound is colourless when dissolved in hot water, but crystallizes on cooling as thin but visibly larger bright yellow flakes, that settle slowly through the liquid — a visual effect often described as "golden rain". This reaction is called sometimes “golden rain”. Conditions of re-crystallization: pH less than 7, fast cooling. The test *is selective.*	Add 1-3 KI drops to 2 drops of $Pb(NO_3)_2$, acidified by 1-2 drops of CH_3COOH. Add 5-7 mL DW to precipitate and boil mixture in a water bath. After complete dissolving of precipitate, cool mixture quickly at stream of tap water. For acceleration of re-crystallization rub tube sides of glass stick.		$Pb(NO_3)_2 + 2KI = PbI_2\downarrow + 2KNO_3$; $Pb^{2+} + 2I^- = PbI_2\downarrow$.
2. Potassium Chromate (Dichromate) *K_2CrO_4 ($K_2Cr_2O_7$)* gives yellow precipitate $PbCrO_4$ with Pb^{2+} ions. This sediment doesn’t dissolve in acetic and hydrochloric acids, but solutes in alkali and nitrate acid. Conditions: pH less than 7 (in presence of acetic acid), absence of reducing agents, reduced Cr^{6+} to Cr^{3+} (for example, Fe^{2+}) Reaction *is*	Add 1-2 drops of K_2CrO_4 or $K_2Cr_2O_7$ solution to 1-2 drops of $Pb(NO_3)_2$ solution.		$Pb(NO_3)_2 + K_2CrO_4 = PbCrO_4\downarrow + 2KNO_3$; $Pb^{2+} + CrO_4^{2-} = PbCrO_4\downarrow$.

selective, in presence of Ag^+ brick-red sediment Ag_2CrO_4 or dark-red $Ag_2Cr_2O_7$ is precipitated.			
3. Diluted Sulfate Acid *H_2SO_4* and soluble sulfates precipitate Pb^{2+} cation in the form of crystalline precipitate $PbSO_4$. Sediment doesn't dissolve in excess of diluted H_2SO_4, but dissolves in alkalis, ammonia acetate, conc. H_2SO_4 and HCl. Conditions: pH<7, because $PbSO_4$ dissolves in alkalis, absence of Ca^{2+} and Sr^{2+} ions in examined solution. *Reaction is selective.*	Add 1-2 drops of diluted H_2SO_4 to 2-3 drops of $Pb(NO_3)_2$.		$Pb(NO_3)_2+H_2SO_4 = PbSO_4\downarrow +2HNO_3$; $Pb^{2+} + SO_4^{2-} + PbSO_4$.

1.7. REACTIONS OF THE ANIONS

The methods available for the detection of anions are not as systematic as those which have been described in the previous chapter 1 for cations. No really satisfactory scheme has yet been proposed which permits of the separation of the common anions into major groups, and the subsequent unequivocal separation of each group into its independent constituents. In must, however, be mentioned that it possible to separate the anions into major groups dependent upon the solubility of their silver salts, or their barium salts. These however, can only be regarded as useful in giving an indication of the limitations of the method ad for the confirmation of the results obtained by the simpler procedures to be described below.

Classification of anions

Group	I	II	III
Anions included	SO_4^{2-}; SO_3^{2}; CO_3^{2-}; PO_4^{3-}; SiO_3^{2-}; BO_2^- (or $B_4O_7^{2-}$); MoO_4^{2-}	Cl^-, Br^-, I^-	NO_3^-, NO_2^-, CH_3COO^-
Group reagent	$BaCl_2$ in neutral or weakly alkaline medium.	$AgNO_3$ in the presence of diluted HNO_3.	No group reagent, practically all salts are soluble in water.
Properties of precipitates	Barium salts are insoluble in H_2O but soluble in diluted acids (excepting $BaSO_4$).	Silver salts are insoluble in H_2O and HNO_3.	Barium and silver salts dissolve in water.

1.7.1. The first group of anions

BaCl₂ as group reagent deposits the first group anions in the form of white precipitates $BaSO_4$, $BaSO_3$, $BaCO_3$, $Ba_3(PO_4)_2$, $Ba(BO_2)_2$ or BaB_4O_7, $BaSiO_3$, $BaMoO_4$. All precipitates are soluble in Hydrochloric HCl and Nitrate HNO_3 acids, excluding $BaSO_4$. Precipitates $Ba_3(PO_4)_2$, $BaCO_3$ and $Ba(BO_2)_2$ solve in acetic acid CH_3COOH. For example,

$Na_2SO_4 + BaCl_2 = BaSO_4\downarrow + 2NaCl$;

$Na_2SO_3 + BaCl_2 = BaSO_3\downarrow + 2NaCl$;

$2Na_3PO_4 + 3BaCl_2 = Ba_3(PO_4)_2\downarrow + 6NaCl$;

$Na_2B_4O_7 + 2BaCl_2 + H_2O = 2Ba(BO_2)_2\downarrow + 2NaCl + 2HCl$;

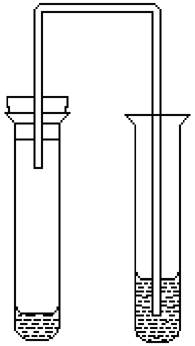
$Na_2CO_3 + BaCl_2 = BaCO_3\downarrow + 2NaCl$;

$Na_2SiO_3 + BaCl_2 = BaSiO_3\downarrow + 2NaCl$;

$(NH_4)_2MoO_4 + BaCl_2 = BaMoO_4\downarrow + 2NH_4Cl$.

Content	Description	Observation	Explanation
Characteristic reactions of Sulfate anions SO_4^{2-}			
1. $BaCl_2$ **(group reagent)** in neutral medium deposits SO_4^{2-} in form of precipitate $BaSO_4$, insoluble in acids and alkali.	Add 1-2 drops of $BaCl_2$ solution to 2-3 drops of Na_2SO_4. Divide the sediment on two test tubes. Add 10-15 HCl drops to the first one, and 5-10 NaOH drops to the second one.		$Na_2SO_4 + BaCl_2 = BaSO_4\downarrow + 2NaCl$; $SO_4^{2-} + Ba^{2+} = BaSO_4\downarrow$; $BaSO_4\downarrow + HCl \rightarrow$ no react; $BaSO_4\downarrow + NaOH \rightarrow$ no react.
2. **Soluble Lead salt** ***(i.e., $Pb(NO_3)_2$)*** precipitates SO_4^{2-} anions in the form of $PbSO_4$, insoluble in acids, but soluble in alkali (in contrast to $BaSO_4$).	Add 1-2 drops of $Pb(NO_3)_2$ to 2-3 drops of Na_2SO_4. Add by drops of NaOH until obtained precipitate is dissolved completely.		$Na_2SO_4 + Pb(NO_3)_2 = PbSO_4\downarrow + 2NaNO_3$; $SO_4^{2-} + Pb^{2+} = PbSO_4\downarrow$; $PbSO_4\downarrow + 4NaOH$ (excess) $= Na_2[Pb(OH)_4] + Na_2SO_4$; $PbSO_4\downarrow + 4OH^- = [Pb(OH)_4]^{2-} + SO_4^{2-}$.
Characteristic reactions of Sulfite anions SO_3^{2-}			
1. $BaCl_2$ **(group reagent)** in neutral medium gives precipitate $BaSO_3$, soluble in strong mineral acids (excluding H_2SO_4). For example, the precipitate dissolves in dilute HCl, when SO_2 (has odour of burning matches) evolves.	Add 1-2 drops of $BaCl_2$ solution to 2-3 drops of Na_2SO_3. Divide the sediment on two test tubes. Add 10-15 HCl drops to the first one, and 5-10 NaOH drops to the second one.		$Na_2SO_3 + BaCl_2 = BaSO_3\downarrow + 2NaCl$; $SO_3^{2-} + Ba^{2+} = BaSO_3\downarrow$ $BaSO_3\downarrow + 2HCl \rightarrow BaCl_2 + SO_2\uparrow + H_2O$; $BaSO_3\downarrow + 2H^+ \rightarrow Ba^{2+} + SO_2\uparrow + H_2O$. $BaSO_3\downarrow + NaOH \rightarrow$ no react

2. Dilute hydrochloric acid *HCl* or dilute sulfate acid *H_2SO_4*: decomposition, more rapidly at warming, with the evolution of sulfur oxide(IV) SO_2: The gas may be identified by its suffocating odour of burning sulfur, or by the green colouration, due to the formation of chromium(III) ions, produced when a filter paper, moistened with acidified potassium dichromate solution, is held over the mouth of the test-tube.	Place 8-10 drops of fresh-prepared solution of Sodium Sulfite Na_2SO_3 upon test-tube, add 8-10 drops of HCl. Identify the gas using described method.		$Na_2SO_3 + 2HCl = SO_2\uparrow + 2NaCl + H_2O$; $SO_3^{2-} + 2H^+ = H_2SO_3$; $H_2SO_3 \rightarrow SO_2\uparrow + H_2O$; $3SO_2 + K_2Cr_2O_7 + H_2SO_4 = Cr_2(SO_4)_3 + K_2SO_4 + H_2O$; $3SO_2 + Cr_2O_7^{2-} + 2H^+ = 2Cr^{3+} + 3SO_4^{2-} + H_2O$.
3. Lime water *$Ca(OH)_2$*. This test is carried out by adding dilute hydrochloric acid to the solid sulfite, and bubbling the evolved gas through lime water; a white precipitate of calcium sulfite $CaSO_3$ is formed.	This test is best carried out in the apparatus shown in fig. The solid Na_2SO_3 (near 0,05-0,1 g) is placed in the test-tube or small distilling flask (10-25 mL capacity), dilute hydrochloric acid added, and the cork immediately replaced. The gas which is evolved (warming may be necessary) is passed into lime water **(reagent - in lab fume hood)** contained in the test-		$Na_2SO_3 + Ca(OH)_2 = CaSO_3\downarrow + 2NaOH$; $SO_3^{2-} + Ca^{2+} = CaSO_3\downarrow$

	tube; the production of a turbidity indicates the presence of a sulfite. 		
4. Strong oxidation agents (*$KMnO_4$ or free I_2 solution*). Potassium permanganate solution, acidified with dilute sulfate acid before the testing, reacts with Sulfite solution with discolouration, owing to reduction to Mn^{2+} ions. If to use free iodine solution, visual effect of reaction is to discolouration of solution owing to transformation of free I_2 to colourless iodide-ions.	Add 2 drops of Potassium permanganate upon test-tube, acidify by adding of 2-3 drops of H_2SO_4 and add 5-6 drops of fresh-prepared solution of Na_2SO_3. To repeat the previous test with iodine (iodine water) solution.		$2KMnO_4+5Na_2SO_3+8H_2SO_4= 2MnSO_4 +5Na_2SO_4 +K_2SO_4 + 8H_2O$; $5SO_3^{2-} + 2MnO_4^- + 6H^+ = 2Mn^{2+} + 5SO_4^{2-} + 3H_2O$; or $2Na_2SO_3 + I_2 = Na_2S_2O_6 + 2NaI$; $2SO_3^{2-} + I_2 = S_2O_6^{2-} + 2I^-$.

Characteristic reactions of Carbonate anions CO_3^{2-}			
1. *$BaCl_2$* (group reagent). Obtained precipitate $BaCO_3$, soluble in HCl with gas bubbles of CO_2 (no odour) isolation indicates the presence of CO_3^{2-} ions in solution.	Add 2-3 drops of Na_2CO_3 to 2-3 drops of $BaCl_2$. Dilute the obtained sediment in HCl.		$Na_2CO_3 + BaCl_2 = BaCO_3\downarrow + 2NaCl$; $CO_3^{2-} + Ba^{2+} = BaCO_3\downarrow$; $BaCO_3\downarrow + 2HCl = BaCl_2 + CO_2\uparrow + H_2O$; $BaCO_3\downarrow + 2H^+ = Ba^{2+} + CO_2\uparrow + H_2O$.
2. Mineral acids *(H_2SO_4, HCl, HNO_3 etc.)*, and **acetic acid *CH_3COOH*** decompose carbonates with gassing of CO_2.	Add 1-2 mL of HCl to 10-15 drops of Na_2CO_3.		$Na_2CO_3 + 2HCl = CO_2\uparrow + 2NaCl + H_2O$; $CO_3^{2-} + 2H^+ = CO_2\uparrow + H_2O$;
Characteristic reactions of Phosphate anions PO_4^{3-}			
***1.* *$BaCl_2$* (group reagent)** in neutral medium sediments PO_4^{3-} in form of precipitate $Ba_3(PO_4)_2$, soluble in strong acids (except H_2SO_4).	Add 2-3 drops of Na_2HPO_4 to 2-3 drops of $BaCl_2$. Dissolve the obtained precipitate by adding 10-15 drops of HCl.		$2Na_2HPO_4 + 3BaCl_2 = Ba_3(PO_4)_2\downarrow + 4NaCl + 2HCl$; $2HPO_4^{2-} + 3Ba^{2+} = Ba_3(PO_4)_2\downarrow + 2H^+$; $Ba_3(PO_4)_2\downarrow + 6HCl = 3BaCl_2 + 2H_3PO_4$; $Ba_3(PO_4)_2\downarrow + 6H^+ = 3Ba^{2+} + 2H_3PO_4$.
2. Magnesia mixture *($MgCl_2$ in presence of buffer mixture $NH_3{\cdot}H_2O + NH_4Cl$)* reacts with phosphates forming white crystalline precipitate	Add to test tube 2-3 drops of $MgCl_2$ and NH_4Cl solutions, add to prepared mixture 2-3 drops of $(NH_4)_2HPO_4$		$Na_2HPO_4 + MgCl_2 + NH_3{\cdot}H_2O = MgNH_4PO_4\downarrow + 2NaCl + H_2O$; $HPO_4^{2-} + Mg^{2+} + NH_3{\cdot}H_2O = MgNH_4PO_4\downarrow + H_2O$.

$MgNH_4PO_4$.	solution. Shuffle mixture and add solution of $NH_3 \cdot H_2O$ for alkali reaction of medium (use litmus).		
3. Molybdenum liquid (*the mixture of $(NH_4)_2MoO_4$ and HNO_3).* As the result of reaction the yellow crystalline precipitate $(NH_4)_3H_4[P(Mo_2O_7)_6]$ is formed.	Add 5-8 drops of Molybdenum liquid to 2-3 drops of Phosphate solution. Boil mixture.		$Na_2HPO_4+12(NH_4)_2MoO_4+23HNO_3=(NH_4)_3H_4[P(Mo_2O_7)_6]\downarrow+2NaNO_3+21NH_4NO_3+10H_2O$; $HPO_4^{2-}+3NH_4^{+}+12MoO_4^{2-}+23H^{+}==(NH_4)_3H_4[P(Mo_2O_7)_6]\downarrow+10H_2O$.
Characteristic reactions of Borate anions $B_4O_7^{2-}$ (BO_2^-)			
1. *$BaCl_2$* (group reagent) precipitates Barium metaborate $Ba(BO_2)_2$ from concentrated solution of borates.	Add 5-6 drops of $BaCl_2$ to 10-15 drops of $Na_2B_4O_7$ **(reagent - in lab fume hood).** Dissolve the precipitate by adding hydrochloric acid HCl by drops.		$Na_2B_4O_7 + 2BaCl_2 + H_2O = 2Ba(BO_2)_2\downarrow + 2NaCl + 2HCl$; $B_4O_7^{2-} + 2Ba^{2+} + H_2O = 2Ba(BO_2)_2\downarrow + 2H^{+}$; $Ba(BO_2)_2\downarrow + 2HCl + 2H_2O = BaCl_2 + 2H_3BO_3$; $Ba(BO_2)_2\downarrow + 2H^{+} + 2H_2O = Ba^{2+} + 2H_3BO_3$.
2. Silver nitrate *$AgNO_3$* precipitates Silver Metaborate from moderate concentrated solutions. In very diluted	Add 1-2 drops of Silver Nitrate solution to 10-15 drops of $Na_2B_4O_7$ **(reagent - in lab fume**		$Na_2B_4O_7 + 2AgNO_3 + 3H_2O = 2AgBO_2\downarrow + 2H_3BO_3 + 2NaNO_3$. $B_4O_7^{2-} + 2Ag^{+} + 3H_2O = 2AgBO_2\downarrow + 2H_3BO_3$.

solutions at cool and in more concentrated ones at heating it forms brown precipitate of Silver Oxide $2AgBO_2+3H_2O=Ag_2O\downarrow+2H_3BO_3$.	**hood).** Observe slow formation of precipitate.		
3. Flame test. Bringing of volatile Boron compounds (Methyl Ether $(CH_3O)_3B$ or Ethyl Ether $(C_2H_5O)_3B$ or free Borate acid) in colourless flame, it is observed specific colouring of flame.	0,5-1 mL of $Na_2B_4O_7$ **(reagent - in lab fume hood)** add in small evaporating dish and heat to dry residue on electric stove. Add 10-15 drops of concentrated Sulfate acid to dry residue (**Carefully! reagent - in lab fume hood**), 1-2 mL of ethyl alcohol **(reagent - in lab fume hood)** and set fire to surface of mixture in the plate.		$Na_2B_4O_7 + H_2SO_4$ (conc.) $+ 5H_2O = 4H_3BO_3 + Na_2SO_4$; $B_4O_7^{2-} + 2H^+ + 5H_2O = 4H_3BO_3$; $H_3BO_3 + 3C_2H_5OH = B(OC_2H_5)_3 + 3H_2O$; $2B(OC_2H_5)_3 + 18O_2 \xrightarrow{t} B_2O_3 + 12CO_2 + 15H_2O$.
Characteristic reactions of Molybdate anions MoO_4^{2-}			
1. *$BaCl_2$* (group reagent) precipitates Barium Molybdate $BaMoO_4$ from concentrated solution of molybdates.	Add 1-2 drops of Silver Nitrate solution to 10-15 drops of Na_2MoO_4 **(reagent - in lab fume hood).** Weight a few		$Na_2MoO_4 + BaCl_2 = BaMoO_4\downarrow + 2NaCl$; $MoO_4^{2-} + Ba^{2+} = BaMoO_4\downarrow$.

	minutes. Observe slow formation of precipitate.		
2. Ammonium Thiocyanide (Rodanide) ***NH_4SCN*** forms complex rodanides with molybdates. Ions Fe^{3+} interferes to this reaction. Fe^{3+} ions are masked by reducing to Fe^{2+} added reducing agents, for example, Sn^{2+} compounds. The last reagents in the same time reduce Mo^{6+} to Mo^{5+}.	Acidify 1 mL of Sodium Molybdate Na_2MoO_4 solution **(reagent - in lab fume hood)** by 0,5 mL of HCl, add 1-2 mL of saturated solution of Tin(II) chloride $SnCl_2$ **(reagent - in lab fume hood)** and add 5-6 drops of 10% NH_4SCN **(in lab fume hood).**		$2Na_2MoO_4 + SnCl_2 + 10NH_4SCN + 12HCl = 2Na_2[MoO(SCN)_5] + SnCl_4 + 10NH_4Cl + 6H_2O$; $2\ MoO_4^{2-} + Sn^{2+} + 10SCN^- + 12H^+ = 2[MoO(SCN)_5]^{2-} + Sn^{4+} + 6H_2O$.
3. Hydrogen Peroxide ***H_2O_2*** in presence of concentrated ammonia $NH_3 \cdot H_2O$ gives Permolybdate red coloured solution. Colour is unstable, may be observed during 10-30 sec after Peroxide was added.	Add 1 mL of concentrated Ammonia **(in lab fume hood)** to 1-2 mL of Na_2MoO_4 solution **(in lab fume hood).** Add by drops 10% Hydrogen Peroxide H_2O_2 **(in lab fume hood)**.		$Na_2MoO_4 + 2\ NH_3 \cdot H_2O \leftrightarrow (NH_4)_2MoO_4 + 2NaOH$; $(NH_4)_2MoO_4 + H_2O_2 = (NH_4)_2[MoO_5] + H_2O$ $MoO_4^{2-} + H_2O_2 \leftrightarrow [MoO_5]^{2-} + H_2O$ $Mo^{6+} - 2e \rightarrow Mo^{8+} \quad \vert\ 1$ $2O^{1-} + 2e \rightarrow 2O^{2-} \quad \vert\ 1$
Characteristic reactions of Silicate anions SiO_3^{2-}			
1. ***$BaCl_2$*** **(group reagent)** gives Barium Silicate $BaSiO_3$ precipitate from concentrated	Add 5-6 drops of $BaCl_2$ to 10-15 drops of Na_2SiO_3 **(reagent - in lab**		$Na_2SiO_3 + BaCl_2 = BaSiO_3\downarrow + 2NaCl$; $SiO_3^{2-} + Ba^{2+} = BaSiO_3\downarrow$.

solution of soluble silicates.	**fume hood).** Wait a few minutes.		
2. Diluted acids *(HCl, H_2SO_4)* isolate voluminous gelatinous precipitate of silicate acids from concentrated silicate solutions. At certain conditions (high concentration of silicate, slowly adding of mineral acid) this precipitate coagulates completely and don't pour out from tube. If HCl was added quickly to diluted solution of silicate, silicate acids form colloid solution and don't precipitate for a long time.	Add slowly by drops concentrated HCl (**in lab fume hood).** to 15-20 drops of Na_2SiO_3 **(in lab fume hood)**.		$Na_2SiO_3 + 2HCl = H_2SiO_3\downarrow + 2NaCl$; $SiO_3^{2-} + 2H^+ = H_2SiO_3\downarrow$.
3. Silver nitrate *$AgNO_3$* isolates yellow precipitate of Silver Silicate Ag_2SiO_3 from concentrated silicate solutions.	Add slowly by drops $AgNO_3$ solution **(in lab fume hood)** to 5-10 drops of concentrated Na_2SiO_3 **(in lab fume hood).**		$Na_2SiO_3 + 2AgNO_3 = Ag_2SiO_3\downarrow + 2NaNO_3$; $SiO_3^{2-} + 2Ag^+ = Ag_2SiO_3\downarrow + 2NO_3^-$.
4. Ammonium Salts (for example, *NH_4Cl*) isolate gelatinous precipitate of silicate acids more completely, than mineral acids. Silicate acids	Add 3-6 drops of concentrated NH_4Cl **(in lab fume hood)** solution to 5-10 drops of Na_2SiO_3 solution **(in lab fume**		$Na_2SiO_3 + 2NH_4Cl + 2H_2O = H_2SiO_3\downarrow + 2\ NH_3 \cdot H_2O + 2NaCl$; $SiO_3^{2-} + 2NH_4^+ + 2H_2O = H_2SiO_3\downarrow + 2\ NH_3 \cdot H_2O$.

precipitate more quickly at heating.	**hood)**, heat mixture in a water bath.		

1.7.2. The second group of anions

Content	Description	Observation	Explanation
Characteristic reactions of Chloride anions Cl^-			
1. Silver Nitrate *$AgNO_3$* in presence of HNO_3 reacts with Cl^- forming precipitate AgCl, which is dissolved in water ammonia $NH_3·H_2O$. Reaction is accompanied by the formation of soluble complex compound diamminosilver chloride $[Ag(NH_3)_2]Cl$.	Add 1-2 drops of $AgNO_3$ solution **(in lab fume hood)** to 2-3 drops of HNO_3 and 1-2 drops of NaCl solution. Add concentrated $NH_3·H_2O$ **(in lab fume hood)** to the precipitate up to complete dissolving. Add by drops solution of HNO_3 up to precipitate formation (turbidity).		$NaCl + AgNO_3 = AgCl\downarrow + NaNO_3$; $Cl^- + Ag^+ = AgCl\downarrow$; $AgCl\downarrow + 2NH_3·H_2O = [Ag(NH_3)_2]Cl + 2H_2O$; $AgCl\downarrow + 2NH_3·H_2O = [Ag(NH_3)_2]^+ + Cl^- + 2H_2O$; $[Ag(NH_3)_2]Cl + 2HNO_3 = AgCl\downarrow + 2NH_4NO_3$; $[Ag(NH_3)_2]^+ + Cl^- + 2H^+ = AgCl\downarrow + 2NH_4^+$.
Characteristic reactions of Bromide anions Br^-			
1. Silver Nitrate *$AgNO_3$* in presence of HNO_3 gives with Br^- precipitate AgBr, which is slightly soluble in $NH_3·H_2O$ in	Add 1-2 drops of $AgNO_3$ solution **(in lab fume hood)** to 2-3 drops of HNO_3 and 2-3 drops of		$KBr + AgNO_3 = AgBr\downarrow + KNO_3$; $Br^- + Ag^+ = AgBr\downarrow$.

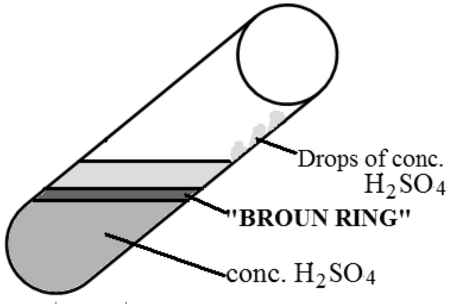
unlike AgCl.	KBr solution. Add concentrated $NH_3 \cdot H_2O$ **(in lab fume hood).** Study solubility of sediment in concentrated ammonia.		
2. Chloric water Cl_2 (*the solution of Cl_2 in H_2O*). Cl_2 reacts with bromides displacing free bromine Br_2 from its salts. The isolated Bromine Br_2 is better dissolved in benzene than in H_2O and benzene layer is colouring yellow.	Add 5-6 drops of benzene C_6H_6 **(in lab fume hood)** and 4-5 drops of chloric water **(in lab fume hood)** to 6-8 drops of KBr. Shake the mixture. Wait a few seconds till separating of water and benzene layers.		$2KBr + Cl_2 \rightarrow Br_2 + 2KCl$; $2Br^- + Cl_2 \rightarrow Br_2 + 2Cl^-$.
Characteristic reactions of Iodide anions I^-			
1. Silver Nitrate *$AgNO_3$* in presence of HNO_3 reacts with I^- given precipitate AgI, which is slightly soluble in $NH_3 \cdot H_2O$ in unlike AgCl.	Add 1-2 drops of $AgNO_3$ solution **(in lab fume hood)** to 2-3 drops of HNO_3 and KI solution. Add concentrated $NH_3 \cdot H_2O$ **(in lab fume hood).** Study solubility of sediment in concentrated ammonia.		$KI + AgNO_3 = AgI\downarrow + KNO_3$; $I^- + Ag^+ = AgI\downarrow$.

2. Chloric water Cl_2 (*it is the solution of Cl_2 in H_2O*). Cl_2 reacts with iodides displacing free Iodine I_2 from its salts. The isolated I_2 is better dissolved in benzene than in H_2O and benzene layer is colouring pink or crimson. In excess of chloric water colour may vanish due to oxidation of free I_2 to iodate(V) acid HIO_3: $I_2+5Cl_2+6H_2O = 2HIO_3+10HCl$	Add 5-6 drops of benzene C_6H_6 **(in lab fume hood)** and 4-5 drops of chloric water **(in lab fume hood)** to 6-8 drops of KI. Shake the mixture. Wait a few seconds till separating of water and benzene layers.		$2KI + Cl_2 \rightarrow I_2 + 2KCl$; $2I^- + Cl_2 \rightarrow I_2 + 2Cl^-$.
3. Copper salts (for example, Copper Sulfate *$CuSO_4$*) react with I^- given milk-white precipitate CuI. Mixture has brown colour due to free Iodine I_2.	Mix 5-6 drops of KI and 1-2 drops of $CuSO_4$. Add 2-4 drops $Na_2S_2O_3$ until discolouration of mixture. Note on the colour of CuI precipitate.		$2CuSO_4 + 4KI = 2CuI\downarrow + I_2 + 2K_2SO_4$; $2Cu^{2+} + 4I^- = 2CuI\downarrow + I_2$. $\begin{array}{l\|l} Cu^{2+} + 1e \rightarrow Cu^{1+} & 2 \\ 2I^- - 2e \rightarrow I_2 & 1 \end{array}$

1.7.3. The third group of anions

Content	Description	Observation	Explanation
Characteristic reactions of Nitrite anions NO_2^-			
1. Potassium Iodide *(KI)* is oxidized in acetous medium by nitrite ions up to free I_2. Presence of free Iodine may be	Add 1 drop of fresh-prepared starch, 2 drops of CH_3COOH, 1 drop of KI, and 2-3 drops of		$2KNO_2 + 2KI + 4CH_3COOH =$ $= I_2+2NO+4CH_3COOK+2H_2O$ $\begin{array}{l\|l} N^{3+} +1_e \rightarrow N^{2+} & 2 \\ 2I^- - 2_e \rightarrow I_2 & 1 \end{array}$

determined by adding of starch. Starch is very sensitive and specific indicator for Iodine.	NaNO$_2$ or KNO$_2$).		$2NO_2^- + 2I^- + 4CH_3COOH = I_2 + 2NO + 4CH_3COO^- + 2H_2O$.
2. Potassium Permanganate (*KMnO$_4$*). In acid medium KMnO$_4$ oxidizes the nitrite ions up to nitrate ions. The colour of KMnO$_4$ disappears and the solution becomes colourless.	Add 1-2 drops of Potassium Permanganate KMnO$_4$, 1-2 drops of H$_2$SO$_4$ to 2-3 drops of Sodium or Potassium Nitrite (NaNO$_2$ or KNO$_2$).		$5KNO_2 + 2KMnO_4 + 3H_2SO_4 = 5KNO_3 + 2MnSO_4 + K_2SO_4 + 3H_2O$ $\left.\begin{array}{l} N^{3+} - 2e \rightarrow N^{5+} \\ Mn^{7+} + 5e \rightarrow Mn^{2+} \end{array}\right\vert \begin{array}{l} 5 \\ 2 \end{array}$ $5NO_2^- + 2MnO_4^- + 6H^+ = 5NO_3^- + 2Mn^{2+} + 3H_2O$.
3. Strong acids decompose Nitrites gives gaseous reddish-brown NO$_2$ (sometimes named “foxtail”).	Add 2-3 drops of Sulfate acid H$_2$SO$_4$ to 2-3 drops of Sodium or Potassium Nitrite (NaNO$_2$ or KNO$_2$). Heat the mixture in a water bath.		$2NaNO_2 + H_2SO_4 = Na_2SO_4 + 2HNO_2$; $2NO_2^- + 2H^+ = 2HNO_2$; $2HNO_2 = NO_2\uparrow + NO\uparrow + H_2O$.
Characteristic reactions of Nitrate anions NO$_3^-$			
1. Iron(II) Sulfate *(FeSO$_4$)* (in excess) in presence of concentrated sulfate acid H$_2$SO$_4$ gives complex compound [Fe(NO)]SO$_4$. The reaction is called **"brown ring".** Note that the presence of	Add 4-5 drops of saturated solution FeSO$_4$ **(in lab fume hood)** to 4-5 drops of NaNO$_3$, shake mixture. The **concentrated** H$_2$SO$_4$ **(in lab fume hood)** should be **CAREFULLY (Be**		$2NaN^{5+}O_3 + 6Fe^{2+}SO_4 + 4H_2SO_4 = 3Fe_2^{3+}(SO_4)_3 + 2N^{2+}O + Na_2SO_4 + 4H_2O$ $\left.\begin{array}{l} 2Fe^{2+} - 2\bar{e} \rightarrow 2Fe^{3+} \\ N^{5+} + 3\bar{e} \rightarrow N^{2+} \end{array}\right\vert \begin{array}{l} 3 \\ 2 \end{array}$ $NO + FeSO_4 = [Fe(NO)]SO_4$

nitrite ions will interfere with this test.	**attentive! Dangerous)** slowly adding by drops at the test-tube wall (in bending state). **Do not mix the solution!** Slowly lift test-tube in vertical state. A brown ring will form at the junction of the two layers, indicating the presence of the nitrate ion.		
Characteristic reactions of Acetate anions CH_3COO^-			
1. Strong acids. At HCl or H_2SO_4 action to acetates free acetic acid is isolated which can be identified by odour.	Add 3-4 drops of H_2SO_4 to 5-6 drops of Sodium Acetate CH_3COONa, heat the mixture in a water bath.		$2CH_3COONa + H_2SO_4 = Na_2SO_4 + 2CH_3COOH\uparrow$; $CH_3COO^- + H^+ = CH_3COOH\uparrow$.
2. Iron(III) Chloride *(FeCl₃)* with solution of Acetate gives reddish-brown solution of Iron(III) Acetate. When this solution was diluted and heated, the precipitate of basic salt deposited in the result of hydrolysis intensification.	Add 1-2 drops of $FeCl_3$ solution to 5-6 drops of CH_3COONa. Add 4-6 mL of DW and heat mixture in a water bath until forming of gelatinous precipitate.		$FeCl_3 + 3CH_3COONa = Fe(CH_3COO)_3 + 3NaCl$; $Fe(CH_3COO)_3 + 2H_2O = Fe(OH)_2CH_3COO\downarrow + 2CH_3COOH$.

1.8. PROTOCOL CATIONS MIXTURE OF ANALYSIS

Content of operation	Observation	Conclusion
1. Pre-definition		
A. Colour of solution *Previous hypothesis about presence or absence of coloured ions (Fe^{2+}, Fe^{3+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+}) in examined mixture*	Your result	
B. Odour *Previous hypothesis about presence or absence of NH_4^+ ions*	Your result	
C. pH of solution *Previous hypothesis about presence or absence of ions of weak bases (NH_4^+, Fe^{2+}, Fe^{3+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+}, Al^{3+}, Zn^{2+}, Mg^{2+}) in the case of pH less than 7.*	Your result	
2. Fractional analysis		
1. Test of NH_4^+: To 6-10 drops of the examined mixture add 10 drops of 20% NaOH **(in lab fume hood)** and the obtained solution heat in a water bath. If ammonia odour fixes or wet litmus paper turns blue, this is **NH_4^+.**	Your result	*Presence or absence **NH_4^+** in examined mixture*
2. Test of Na^+: To 3-4 drops of the examined mixture add 2 drops of DW and 3-5 drops of Zinc-Uranyl-Acetate $Zn(UO_2)_3(CH_3COO)_8$ **(in lab fume hood)**. Isolation of light-green precipitate means that **Na^+** presents in a mixture.	Your result	*Presence or absence **Na^+** in examined mixture*

3. Test of Fe^{2+}: To 4 drops of the examined mixture add 2 drops CH_3COOH (pH~5) and 3 drops of $K_3[Fe(CN)_6]$. Isolation of dark-blue precipitate means that Fe^{2+} presents in a mixture.	Your result	*Presence or absence Fe^{2+} in examined mixture*
4. Test of Fe^{3+}: To 4-5 drops of the examined mixture add 1-2 drops of HCl and 2-3 drops of $K_4[Fe(CN)_6]$. Isolation of blue precipitate means that Fe^{3+} presents in a mixture.	Your result	*Presence or absence Fe^{3+} in examined mixture*
5. Test of Cu^{2+}: To 12-15 drops of the examined mixture add 10-12 drops of concentrated $NH_3 \cdot H_2O$ **(in lab fume hood)**. Wait 2-3 min. If was observed cornflower color of upper layer of tube content, it means that examined mixture contains Cu^{2+} cations.	Your result	*Presence or absence Cu^{2+} in examined mixture*
6. Test of Co^{2+}: Select *Variant A* or *Variant B* depends on result, obtained of p. 4. **Variant A. In presence** of Fe^{3+} (see p. 4): to 6-8 drops of the examined mixture add a few grains of solid NaF; mix content to its complete dissolving. Then add 2-3 drops of NH_4SCN solution, saturated in acetone **(in lab fume hood)** (if the solution is red, one should add NaF till the red colour disappears). If the blue colour solution is observed - there is Co^{2+}. **Variant B. In absence** of Fe^{3+} (see p. 4): Add 6-8 drops of the examined mixture to 2-3 drops of NH_4SCN solution saturated in acetone **(in lab fume hood)**. If observes blue colour of solution, then there is Co^{2+}**.**	Your result	*Presence or absence Co^{2+} in examined mixture*

7. Test of Mn^{2+}: To 5-6 drops of the examined mixture add 10 drops of HNO_3 and a few grains of $NaBiO_3$ **(in lab fume hood)**. Wait 1 min. If magenta colour is observed – there is **Mn^{2+}**.	Your result	____________________ *Presence or absence **Mn^{2+}** in examined mixture or observe trace quantities of this ion*
8. Test of Ni^{2+}: Select *Variants A, or B, or C, or D, or E* according to results of pp. 3, 4, 5 and 6. **Variant A.** It is realized **in absence Fe^{3+} and Cu^{2+}**: To 6-8 drops of the examined mixture add 10-15 drops of concentrated $NH_3 \cdot H_2O$ **(in lab fume hood)**, shuffle tube content and add 2-3 drops of Dimethylglioxime $C_4H_8N_2O_2$ (Chugaev's reagent) **(in lab fume hood)**; if crimson coloured sediment formed, then there is **Ni^{2+}.** **Variant B.** It is realized **in presence of Fe^{3+}**: To 6-8 drops of the examined mixture add a few grains of NaF up to complete solving, and then 10-12 drops of concentrated $NH_3 \cdot H_2O$ **(in lab fume hood)** and 2-3 drops of Dimethylglioxime **(in lab fume hood)**; if crimson precipitate observed, then there is **Ni^{2+}**. **Variant C.** It is realized **in presence of Cu^{2+}**: To 6-8 drops of the examined mixture in centrifuge tube add 3-4 drops of diluted CH_3COOH and then 5-6 drops of KI solution and the precipitate is separated by centrifuge. Add to brown supernatant liquid by drops $Na_2S_2O_3$ till the solution gets colourless. Then one should add 10-15 drops of concentrated $NH_3 \cdot H_2O$ **(in lab fume hood)** and 2-3 drops of Dimethylglioxime **(in lab fume hood).** If crimson coloured sediment observed, then there is **Ni^{2+}**.	Your result	____________________ *Presence or absence **Ni^{2+}** in examined mixture or observe trace quantities of this ion*

Variant D. It is realized **in presence of Fe^{3+} and Cu^{2+}** at the same time. To 6-8 drops of the examined mixture in centrifuge tube add 3-4 drops of diluted CH_3COOH and then 5-6 drops of KI solution and the precipitate is separated by centrifuge. Add to brown supernatant liquid by 5-10 drops of $Na_2S_2O_3$.Then a few grains of NaF up to complete solving, and then 10-12 drops of concentrated $NH_3 \cdot H_2O$ **(in lab fume hood)** and 2-3 drops of Dimethylglioxime **(in lab fume hood)**; if crimson precipitate observed, then there is **Ni^{2+}**. **Variant E.** It is realized **in presence of Fe^{2+}**, it is oxidized by 2-3 drops of the 6% solution of H_2O_2 **(in lab fume hood)** to Fe^{3+}, and then add a few grains of NaF up to complete solving, and then 10-12 drops of concentrated $NH_3 \cdot H_2O$ **(in lab fume hood)** and 2-3 drops of Dimethylglioxime **(in lab fume hood)**; if crimson coloured sediment, then there is **Ni^{2+}**.		
3. Systematic analysis		
9. Test for K^+: Select Variant A or Variant B according to results of pp. 1, 5. **Variant A** realizes **in absence of NH_4^+ and Cu^{2+}:** To 1-2 mL of examined mixture (in centrifugal test-tube) add 1-2 mL of saturated solution of Na_2CO_3 **(in lab fume hood)**; the mixture is centifugated, supernatant liquid is tested for fullness of sediment. Then one should add 1-2 drops of CH_3COOH to pH = 6, to the obtained solution one adds 5-6 drops of $Na_3[Co(NO_2)_6]$ **(in lab fume hood)**; if there is yellow-orange precipitate - then there is **K^+.**		

Variant B. It is realized **in presence of NH_4^+, but absence of Cu^{2+}:** To 2-3 mL of the examined mixture (in centrifugal test-tube) add by drops 2-3 mL of saturated solution of Na_2CO_3 **(in lab fume hood)**; the mixture is centifugated. The filtrate is transported in the crucible, evaporate liquid, and then calcinate in muffle during 1,5 hours at 700-800 °C. A few crystals of dry residue transport in test-tube, add 10 drops of DW and 1-2 drops of Nessler's reactant **(in lab fume hood)**. If no reddish precipitate, **NH_4^+** was removed completely. Residue is dissolved in 1-2 mL of DW. Then add 1-2 drops CH_3COOH to pH=6, 5-6 drops of $Na_3[Co(NO_2)_6]$ **(in lab fume hood)**; if there is yellow-orange precipitate - there is **K^+.** **Variant C.** It is realized **in absence of NH_4^+, but presence of Cu^{2+}:** To 1-2 mL of the examined mixture in centrifugal test-tube add 7-10 drops of solution of NaI **(in lab fume hood)**, and the precipitate obtained is separated using centrifuge (don't forget test of fullness of precipitation!). The supernatant solution has to be decanted in test-tube. Then $Na_2S_2O_3$ is added till the solution gets colourless. Add 1-2 mL of saturated solution of Na_2CO_3 **(in lab fume hood)**. The mixture is centifugated; supernatant liquid is tested for fullness of sedimentation. Then one should add 1-2 drops of CH_3COOH to pH = 6, to the obtained solution one adds 5-6 drops of $Na_3[Co(NO_2)_6]$ **(in lab fume hood)**; if there is yellow-orange precipitate - then there is **K^+.**	*Your result*	*Presence or absence* K^+ *in examined mixture*

10. Separation and tests of the 4th group cations (Ag^+ and Pb^{2+}): To 2 drops of the examined mixture add 2 drops of HCl. - If **no precipitate**, there is no Ag^+ and/or Pb^{2+} in examined mixture. **Go to p. 11.** If precipitate was observed, the order of operation is the next. To 2-3 mL of the examined mixture in centrifugal tube add 2-3 mL of 10% HCl **(in lab fume hood)**; the sediment obtained is separated using centrifuge (don't forget test of fullness of precipitation). The upper liquid **is decanted in separate labeled tube and stores it for the next analysis (Filtrate 1).** Solid residue **– Precipitate 1** in centrifuge test-tube is rinsed with 2-3 mL of hot DW and is centrifuged again (for separating of $PbCl_2$ soluble in hot water), which gives us **the Filtrate 2** and the **Precipitate 2.** The Filtrate 2 is decanted into the clean test-tube; then add 3-4 drops KI. If forms yellow precipitate, then there is **Pb^{2+}.** If **the Precipitate 2** didn't dissolved completely in hot water, it should be processed by adding 1-2 mL of concentrated $NH_3 \cdot H_2O$ solution **(in lab fume hood),** and centrifuged again. **The Filtrate 3** is decanted in a clean test-tube; then add HNO_3 solution to pH = 3-4 (using the universal litmus indicator). If the turbidity or bulky white precipitate observes, then there is **Ag^+**.	Your result	*Presence or absence **Ag^+ and/or Pb^{2+}** in examined mixture*

11. Separation and tests of cations Ca^{2+} and Sr^{2+}: Select Variant A or B according to result of p. 10. **Variant A – if no detected the presence of the 4th group cations (Ag^{+} and/or Pb^{2+}).** To 5-10 drops of examined mixture add 5-6 drops of 20% H_2SO_4 **(in lab fume hood)** and 2-3 drops of acetone (or alcohol) **(in lab fume hood)**. If there is precipitate, then there is **Ca^{2+} and/or Sr^{2+}**. If the solution remains clean, then there is **no Ca^{2+} and Sr^{2+}. Go to p. 12.** **Test of Ca^{2+}.** In centrifuge test tube add 1-2 mL of 20% H_2SO_4 **(in lab fume hood)** and 5-10 drops of acetone **(in lab fume hood)** to 2-3 mL of the examined mixture. Content of test-tube should be mixed and heated in a water bath for 3-4 min. (to 70-80°C). The mixture is cooled down, and centrifuged, obtained **the Precipitate 4** and **the Filtrate 4** (**store it in the separate labeled tube for the next analysis**). To **the Precipitate 4** in centrifuge test-tube add 2-3 mL of concentrated $(NH_4)_2SO_4$ solution **(in lab fume hood)** and then heat it in the water bath 3-5 min. If the precipitate didn't dissolve completely, then it should be centrifuged again. Decant **the Filtrate 5** in clean test-tube, add by drops $NH_3 \cdot H_2O$ to pH ~ 5-6 (by universal litmus indicator) and add 5-6 drops of $(NH_4)_2C_2O_4$. If there is white precipitate, then there is **Ca^{2+}**. **Test of Sr^{2+}**: Add in test-tube 1-2 mL of saturated $(NH_4)_2SO_4$ solution **(in lab fume hood)** and heat 1-2 min. in a water bath, and then add 10-12 drops of the examined mixture. If there is white precipitate, it means that **Sr^{2+}** presents in the mixture.	*Your result*	*Present or absent **Ca^{2+} and/or Sr^{2+}** in examined mixture*

Variant B. It is realized in presence of the 4th group cations (Ag$^+$ and/or Pb^{2+}) like the **Variant A**, there is one difference only – examined mixture is replaced of the **Filtrate 1** (was obtained in p. 11 and was stored in labeled tube) .		
12. Separation and tests of cations Al^{3+} and Zn^{2+}: Select Variant **A**, **B**, or **C** depends on results of p. **7, 10** and **11**. **Variant A.** If detected **the absence** of **Mn^{2+}** (see p. **7**), **absence the 4th group cations (Ag$^+$ and Pb^{2+})** (see p. **10), absence cations Ca^{2+} and Sr^{2+}** (see p. **11).** In centrifuge test tube mix 2-3 mL of examined mixture and 1-2 mL of 10% NaOH **(in lab fume hood),** heat in a water bath for 2-3 min. After cooling this mixture it should be centrifuged**,** and obtained **The Precipitate 6** (don't use in the next operations) and **The Filtrate 6.** Decant Filtrate 6 in two test-tubes. **Test of Al^{3+}**: To **the Filtrate 6** in the first test tube add a few crystals of solid NH4Cl till getting the saturated solution. Heat a test tube in a water bath (for 2-3 min.). If white gelatinous precipitate Al(OH)$_3$ was observed, it means that **Al^{3+}** was contained in mixture. **Test of Zn^{2+}**: To **the Filtrate 6** in the second test tube add by drops HCl (to pH~5 by universal litmus paper) and 5-6 drops of K$_3$[Fe(CN)$_6$]. If there is yellow-and-orange precipitate, then there is **Zn^{2+}**.	*Your result*	____________________ ____________________ *Presence or absence* ***Al^{3+} and/or Zn^{2+}*** *in examined mixture*

Variant B. If detected **the presence** of **Mn^{2+}** (see p. **7**), but **absence the 4th group cations (Ag^{+} and Pb^{2+})** (see p. **10)**, and **absence cations Ca^{2+} and Sr^{2+}** (see p. **11).** In centrifuge test tube mix 2-3 mL of examined mixture, 5-6 drops of 6% H_2O_2 **(in lab fume hood),** and 1-2 mL of 10% NaOH **(in lab fume hood),** heat in a water bath for 2-3 min. Cool this mixture, centrifuge, and obtained **The Precipitate 6** (don't use in the next operations) and **The Filtrate 6.** Decant Filtrate 6 in two test-tubes. Continue as Variant A – tests of Al^{3+} and Zn^{2+}. **Variant C.** It is realized **in the presence of Mn^{2+}** (see p. **7**), **presence of the 4th group (Ag^{+} and/or Pb^{2+}**) (see p. **10), but absence of Ca^{2+} and/or Sr^{2+}.** In centrifuge test tube mix 1-2 mL of **the Filtrate 1**, 5-6 drops of 6% H_2O_2 **(in lab fume hood),** and 1-2 mL of 10% NaOH **(in lab fume hood),** heat in a water bath for 2-3 min. After cooling this mixture it should be centrifuged, and obtained **The Precipitate 6** (keep away) and **The Filtrate 6.** Decant Filtrate 6 in two test-tubes. Continue as Variant A – tests of Al^{3+} and Zn^{2+}. **Variant D.** It is realized **in the presence of Mn^{2+}** (see p. **7**), **presence of the 4th group (Ag^{+} and/or Pb^{2+}**) (see p. **10), and presence of Ca^{2+} and/or Sr^{2+}.** In centrifuge test tube mix 1-2 mL of **the Filtrate 4**, 5-6 drops of 6% H_2O_2 **(in lab fume hood),** and 1-2 mL of 10% NaOH **(in lab fume hood),** heat in a water bath for 2-3 min. After cooling this mixture it should be centrifuged, and obtained **The Precipitate 6** (keep away) and **The Filtrate 6.** Decant Filtrate 6 in two test-tubes. Continue as Variant A – tests of Al^{3+} and Zn^{2+}.		

Variant E. It is realized **in the absence of Mn^{2+}** (see p. **7**), **presence of the 4th group (Ag^{+} and/or Pb^{2+}**) (see p. **10), and absence of Ca^{2+} and/or Sr^{2+}.** In centrifuge test tube mix 1-2 mL of **the Filtrate 1** and 1-2 mL of 10% NaOH **(in lab fume hood),** heat in a water bath for 2-3 min. After cooling this mixture it should be centrifuged**,** and obtained **The Precipitate 6** (don't use in the next operations) and **The Filtrate 6.** Decant Filtrate 6 in two test-tubes. Continue as Variant A – tests of Al^{3+} and Zn^{2+}. **Variant F.** It is realized **in the absence of Mn^{2+}** (see p. **7**), **absence of the 4th group (Ag^{+} and/or Pb^{2+}**) (see p. **10), but presence of Ca^{2+} and/or Sr^{2+}.** In centrifuge test tube mix 1-2 mL of **the Filtrate 4** and 1-2 mL of 10% NaOH **(in lab fume hood),** heat in a water bath for 2-3 min. After cooling this mixture it should be centrifuged**,** and obtained **The Precipitate 6** (don't use in the next operations) and **The Filtrate 6.** Decant Filtrate 6 in two test-tubes. Continue as Variant A – tests of Al^{3+} and Zn^{2+}. **Variant G.** It is realized **in the presence of Mn^{2+}** (see p. **7**), **absence of the 4th group (Ag^{+} and/or Pb^{2+}**) (see p. **10), and presence of Ca^{2+} and/or Sr^{2+}.** In centrifuge test tube mix 1-2 mL of **the Filtrate 4,** 5-6 drops of 6% H_2O_2 **(in lab fume hood),** and 1-2 mL of 10% NaOH **(in lab fume hood),** heat in a water bath for 2-3 min. After cooling this mixture it should be centrifuged**,** and obtained **The Precipitate 6** (don't use in the next operations) and **The Filtrate 6.** Decant Filtrate 6 in two test-tubes. Continue as Variant A – tests of Al^{3+} and Zn^{2+}.		

Variant G. It is realized **in the absence of Mn**$^{2+}$ (see p. **7**), **presence of the 4th group (Ag**$^{+}$ **and/or Pb**$^{2+}$) (see p. **10), and presence of Ca**$^{2+}$ **and/or Sr**$^{2+}$**.** In centrifuge test tube mix 1-2 mL of **the Filtrate 4,** and 1-2 mL of 10% NaOH **(in lab fume hood),** heat in a water bath for 2-3 min. After cooling this mixture it should be centrifuged**,** and obtained **The Precipitate 6** (don't use in the next operations) and **The Filtrate 6.** Decant Filtrate 6 in two test-tubes. Continue as Variant A – tests of Al^{3+} and Zn^{2+}.		
13. Separation and analysis of cation Mg^{2+}**:** Select Variant A or B depends on the result of p. **5.** **Variant A:** It is realized **in the presence of Cu**$^{2+}$ (see p. **5**) in the examined mixture. In centrifuge test-tube add 8-10 drops of NaI **(in lab fume hood)** to 1-2 mL of the examined mixture The sediment obtained should be centrifuged: there is the precipitate (don't use in the next operations) and **The filtrate 7.** Decant **the Filtrate 7** in a centrifuge test-tube, add by drops of $Na_2S_2O_3$ till the solution gets colourless, then one should of the 5-6 drops of solution NH_4Cl, 5-6 drops of concentrated $NH_3 \cdot H_2O$ **(in lab fume hood)** and 15-20 drops of concentrated $(NH_4)_2CO_3$ **(in lab fume hood)** . The mixture is heated in a water bath 2-3 min, cooled after that, and centrifuged. The precipitate (don't use in the next operations) and **the Filtrate 8** are obtained. To the **Filtrate 8** is decanted in a test-tube, add 5-6 drops of Na_2HPO_4. Formation of white precipitate indicates the presence of **Mg** $^{2+}$ ions.	*Your result*	____________________ ____________________ *Presence or absence* ***Mg***$^{2+}$ *in examined mixture*

Variant B: It is realized **in the absence of Cu^{2+}** (see p. **5**): to 1-2 mL of the examined mixture add 5-6 drops of concentrated $NH_3 \cdot H_2O$ **(in lab fume hood)** and 15-20 drops of concentrated $(NH_4)_2CO_3$ **(in lab fume hood.** The mixture is heated in a water bath 2-3 min, cooled after that, and centrifuged. The precipitate (don't use in the next operations) and **the Filtrate 7** are obtained. To the **Filtrate 7** is decanted in a test-tube, add 5-6 drops of Na_2HPO_4. Formation of white precipitate indicates the presence of **Mg** $^{2+}$ ions.		
CONCLUSION: Examined mixture contains cations ____________________________________. ***(list of detected cations)***		

1.9. QUALITATIVE ANALYSIS OF THE INORGANIC SUBSTANCES

1.9.1 A soluble salt

Unknown substance is considered as the salt soluble in water, and it consists of one cation and one anion. Tests of cations and anions are executed till the first positive reaction.

Qualitative analysis of unknown substance consists of series of operations:

A. Pre-definition;
B. Examination of cation component;
C. Examination of anion component.

A. Pre-definition

Describe *colour*:

Colourless – research object probably doesn't include coloured cations (Fe^{2+}, Mn^{2+}, Fe^{3+}, Cu^{2+}, Co^{2+}, Ni^{2+});

Fe^{2+} – light-green, light-grey;
Mn^{2+} – slightly pink;
Cu^{2+} – dark blue, blue, green-and-blue;
Co^{2+} – pink, violet;
Ni^{2+} – light green;
Fe^{3+} – yellow-and-brown;

and *relative size* of particles (coarse-crystalline or powder).

Draw attention to *odour* of substance. Ammonium- and acetate-contained salts have a characteristic odour.

Dissolving of unknown salt

The tests for dissolving of the substance are started from the processing of some quantity of its grains by salt, which are taken for the analysis, are easily dissolved in DW or in diluted nitrate acid HNO_3.

The first testing object, proposed for analysis, is soluble in water or is the solution (in the case of high hygroscopic).

a) If the received sample is the solid substance, so 0,15-0,2 g of substance is dissolved in 6-8 mL of DW (if necessary the solution is heated in a water bath);

b) If the received sample is the solution, so it should be diluted: 3-4 mL of DW is added to 1 mL of solution.

A pH of received solution is examined using universal litmus paper. Acidic reaction of solution indicates that the sample can be the salt of weak base and strong acid (for example, $AlCl_3$, NH_4Cl, $Zn(NO_3)_2$). Alkaline reaction of the solution gives the salts formed of weak acid and strong base (for example, Na_2CO_3, K_3PO_4, CH_3COONa). The neutral reaction of the solution indicates that the examined substance is the salt of strong acid and strong base or weak acid and weak base (for example, KCl, Na_2SO_4, $CaCl_2$, CH_3COONH_4).

B. Determination of cations

1. Test for the presence of the 4th cations group

Add the group reagent HCl to separate portion of the examined solution. If precipitate was observed so the cation belongs to the 4th group – Ag^+ or Pb^{2+}.

Test of Ag^+ – to precipitate, obtained at HCl acting, add concentrated $NH_3{\cdot}H_2O$ ***(in lab fume hood)***. If precipitate dissolved completely, add nitrate acid HNO_3 by drops till turbidity;

Test of Pb^{2+} – with KI and subsequent re-crystallization of "gold rain".

2. Test for the presence of the 3d and 2d cations groups

Add the group reagent $(NH_4)_2HPO_4$ to separate portion of the solution. If precipitate was formed so the cation can belong to 3d or 2d group. In this case add some drops of concentrated $NH_3{\cdot}H_2O$ ***(in lab fume hood)*** to the isolated precipitate. If we see that:

- The precipitate dissolved, so the cation belongs to the 3d group;
- The precipitate is not dissolved so the cation belongs to the 2d group.

Variant A. The precipitate is dissolved - cation of the 3d group; the reactions are performed in separate portions of the solution:

Test of Cu^{2+} – with $NH_3{\cdot}H_2O$ (excess) ***(in lab fume hood)***;

Test of Zn^{2+} – with $K_3[Fe(CN)_6]$;

Test of Co^{2+} – with NH_4SCN in acetone ***(in lab fume hood)***;

Test of Ni^{2+} – with of Dimethylglioxime (Chugaev's reagent) $C_4H_8N_2O_2$ ***(in lab fume hood)***.

Variant B. If the precipitate is not dissolved – the 2d cations group:

Test of Fe^{2+} – with $K_3[Fe(CN)_6]$;

Test of Fe^{3+} – with $K_4[Fe(CN)_6]$ or NH_4SCN;

Test of Mn^{2+} – with $NaBiO_3$ ***(in lab fume hood)*** + HNO_3;

Test of Al^{3+} – with NaOH and crystalline NH_4Cl at heating;

Test of Ca^{2+} – with $(NH_4)_2C_2O_4$;

Test of Sr^{2+} – with gypsum water (saturated water solution of $CaSO_4$) ***(in lab fume hood)***;

Test of Mg^{2+} – with Na_2HPO_4 in presence of $NH_3{\cdot}H_2O$ + NH_4Cl.

3. Determination of the 1st cations group

The sequence and conditions of reaction performance should be followed:

Test of NH_4^+ – with NaOH at heating;

Test of K^+ – with $Na_3[Co(NO_2)_6]$ ***(in lab fume hood)***; or $NaHC_4H_4O_6$;

Test of Na^+ – with Zinc-Uranyl-Acetate $Zn(UO_2)_3(CH_3COO)_8$ ***(in lab fume hood)***.

C. Determination of anions

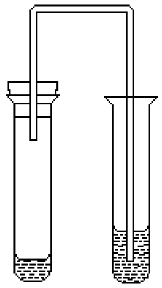
It is concluded that series of anions can be present in solution after the definition of cation, taking into account that unknown substance is soluble in water.

1. Determination of the 1st anions group

Add $BaCl_2$ group reagent to the separate portion of examined solution. If the precipitate is formed so the anion is of the first group. Remember, that anions $B_4O_7^{2-}$, SiO_3^{2-}, MoO_4^{2-} form precipitates only from concentrated solutions.

Test of SO_4^{2-} – HCl acts to precipitation. If the precipitate is not dissolved so SO_4^{2-} is present in examined substance.

Test of CO_3^{2-} – as the result of HCl action to precipitate, the last is dissolved with bubbles gassing. To be sure of CO_3^{2-} to pass gas through acidified weak solution of $KMnO_4$ used test system



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If permanganate solution keeps light-crimson, CO_3^{2-} is present.

Test of SO_3^{2-} – as the result of HCl action to precipitation, the last is dissolved with bubbles gassing. To be sure of SO_3^{2-} to pass gas through acidified weak solution of $KMnO_4$ used gas test system (see above). If permanganate solution decolourized, SO_3^{2-} is present.

Test of PO_4^{3-} – as the result of HCl action, the precipitate is dissolved without gas isolation. It can be supposed that there is PO_4^{3-}. Then perform the reaction of PO_4^{3-} determination with molybdenum liquid ***(in lab fume hood)*** at heating in the separate portion of examined solution.

Even if the result of $BaCl_2$ action the precipitate is not observed, examine the presence of $B_4O_7^{2-}$, SiO_3^{2-}, MoO_4^{2-}.

Test of $B_4O_7^{2-}$ – flame test with H_2SO_4 (conc.) (**CAREFFULLY!**) ***(in lab fume hood)*** and alcohol ***(in lab fume hood);***

Test of SiO_3^{2-} – with concentrated NH_4Cl solution ***(in lab fume hood)***;

Test of MoO_4^{2-} – with 10% H_2O_2 ***(in lab fume hood)*** in presence of concentrated ammonia $NH_3 \cdot H_2O$ ***(in lab fume hood)***.

If all tests are negative, so there is *no the first group* of anions and the search should be continued in the second group of anions.

2. Determination of the 2^{d} *anions group*

Add $AgNO_3$ group reagent ***(in lab fume hood)*** to the separate portion of examined solution in presence of HNO_3. If the precipitate of white (yellow-white) colour is formed so anion of the 2^{d} group is present.

Test of Cl^- – if the precipitate, obtained on the action of group reagent is dissolved in $NH_3 \cdot H_2O$ and as the result of HNO_3 adding the precipitate becomes turbid so there is Cl^- ion.

Test of Br^- *and* I^- – chloric water Cl_2 ***(in lab fume hood)*** and benzene C_6H_6 ***(in lab fume hood)*** add to the examined solution. If benzene layer becomes yellow, Br^- is present, crimson – I^- is present.

If no sediment as the result of group reagent action – *no the second group* of anions, the search should be continued in the third anion group.

3. Determination of the 3^{d} *anions group*

Perform the determination reactions in separate portions of examined solution:

Test of NO_3^- – with saturated $FeSO_4$ ***(in lab fume hood)*** + concentrated H_2SO_4 ***(in lab fume hood)***;

Test of NO_2^- – with KI + CH_3COOH;

Test of CH_3COO^- – with HCl at heating.

On the basis of obtained results the report on unknown substance analysis should be prepared and the formula of salt should be given (below).

PROTOCOL OF ANALYSIS
SUBSTANCE # 1 (Soluble salt)

Stage of analysis	Content of operation	Observation	Conclusion
1. Predefinition	Colour of solid salt, hygroscopicity		
	Odour		
	Solubility in water		
	pH of water solution		
2. Determination of cations	**Test for the presence of the 4th cations group:** + *HCl* *Test of* Ag^+ ____ *Test of* Pb^{2+} ____		
	Test for the presence of the 3d and 2d cations groups (if necessary): + $(NH_4)_2HPO_4$+ $NH_4Cl+NH_3 \cdot H_2O$; + $NH_3 \cdot H_2O$ (in excess) *Test of* Cu^{2+} ______________________________________ *Test of* Zn^{2+} ______________________________________ *Test of* Co^{2+} ______________________________________ *Test of* Ni^{2+} ______________________________________		

	Text of Fe^{2+} ________________________________ Test of Fe^{3+} ________________________________ Test of Mn^{2+} ________________________________ Test of Al^{3+} ________________________________ Test of Ca^{2+} ________________________________ Test of Sr^{2+} ________________________________ Test of Mg^{2+} ________________________________		
	Test of the presence of the 1st cations group (if necessary): Test of NH_4^+ ________________________________ Test of K^+ ________________________________ Test of Na^+ ________________________________		
3. Determination of anions	**Test of the 1st anions group:** + $BaCl_2$ Test of SO_4^{2-} ________________________________ Test of CO_3^{2-} ________________________________ Test of PO_4^{3-} ________________________________ Test of $B_4O_7^{2-}$________________________________		

	Test of SiO_3^{2-} ____ *Test of* MoO_4^{2-} _______________________________________		
	Test of the 2d anions group (if necessary): *Test of* Cl^- ____ *Test of* Br^- *or* I^- _____________________________________		
	Test of the 3d group of anions (if necessary): *Test of* NO_3^- ____ *Test of* NO_2^- ____ *Test of* CH_3COO^- ____________________________________		
CONCLUSION: Formula of salt is ___________________________			

1.9.2 Insoluble substances

Unknown substance may be insoluble in water.

In the first case, the previous step of analysis – to dissolve of unknown substance.

It may be free metals, oxides, basic salts, carbonates, phosphates. Given such substances will be considered to consist of one cation and one anion. Tests of cations and anions are executed till the first positive reaction. The most of such compounds are dissolving in acids or alkalis.

Test of solubility includes examining of the next solvents:

- Boiled DW (for example, $PbCl_2$ is more soluble in hot water, that in cool water);
- Diluted acetic acid CH_3COOH – dissolves the carbonates (**with gassing of CO_2**), oxides, hydroxides;
- Diluted nitrate acid HNO_3 – for dissolving of free heavy metals, oxides, basic salts, phosphates, and hydroxides;
- Concentrated nitrate acid HNO_3 – for dissolving of free heavy metals, oxides and hydroxides;
- “Aqua regia” – mixture of concentrated HCl and concentrated HNO_3 (in volume ratio 3:1) – for dissolving of the most insoluble compounds.

The next order of analysis is the same described above. **Remember, that prepared solution would be acidic, if we dissolved the unknown substance in weak or strong acid**. For tests of cations and anions it is necessary to regulate pH of examined solution to add corresponding agents (for example, diluted NaOH by drops till required medium). Of course, anion of acid, used for dissolving, will present in examined solution.

For tests of cations and anions it is necessary to regulate pH of examined solution to add corresponding agents. Remember, that components of analytes used for regulation of pH will be detected in examined solution.

The next order of analysis is the same one as described in p. 1.9.1.

PROTOCOL OF ANALYSIS
SUBSTANCE # 2 (Insoluble)

Stage of analysis	Content of operation	Observation	Conclusion
1. Predefinition	Colour of Substance		
	Solubility in: ■ Boiled DW; ■ Diluted acetic acid CH_3COOH; ■ Diluted nitrate acid HNO_3; ■ Concentrated nitrate acid HNO_3; ■ “Aqua regia” Observation of gassing		
	pH of obtained solution		
2. Determination of cations	Test for the presence of the 4^d cations group: *Test of Ag*$^+$ ____ ____ Test for the presence of the 3^d and 2^d cations groups (if necessary): *Test of Cu*$^{2+}$ ____ ____ ____ ____		

	____ ____ ____ ____		
3. Determination of anions	**Test of the 1st anions group:** *Test of* SO_4^{2-} ____ ____ ____		
	Test of the 2d anions group (if necessary): *Test of* Cl^- _________________________________ ____		
	Test of the 3d anions group (if necessary): *Test of* NO_3^- ________________________________ ____ ____		
CONCLUSION: Formula of substance is ________________________			

EXAMPLES OF CONTROL TASKS FOR QUALITATIVE ANALYSIS

1. Write the equation of the chemical reaction of group reagent $(NH_4)_2HPO_4$ (in the presence of ammonia $NH_3{\cdot}H_2O$) and soluble Strontium soluble salt (for example, $Sr(NO_3)_2$) in molecular from. Write the equation of the dissolving of obtained sediment in the Acetic acid CH_3COOH.

2. Propose the reagent for the separation of cations:

Zn^{2+}, Na^{+}
↓ Added Reagent ________
Solution:___ Cation   Sediment:___ (chemical formula)

Write the molecular equation of the precipitation reaction.

3. Note on the characteristic analytical test of Molybdate MoO_4^{2-} anions:

A	Action of Hydrogen peroxide H_2O_2 and water ammonia $NH_3{\cdot}H_2O$	**C**	Action of Silver nitrate $AgNO_3$ and the following dissolving of isolated sediment in water ammonia $NH_3{\cdot}H_2O$
B	Action of $FeSO_4$ (saturated) and H_2SO_4 (concentrated)	**D**	Action of Potassium Permanganate $KMnO_4$ in presence of H_2SO_4 (diluted)

4. Write reaction of $FeCl_3$ and yellow blood salt in molecular form and calculate the sum of coefficients in this reaction (*remember, that absence of coefficient before formula means figure 1)*

5. Note the correspondence of the anions and their group reagents:

A	$BaCl_2$ (at pH-7)	**1**	NO_3^-
B	$AgNO_3$ (at pH=2)	**2**	CH_3COO^-
C	No group reagent	**3**	I^-
		4	CO_3^{2-}
		5	Cl^-
		6	PO_4^{3-}

6. Note on the highest pure analyte grade of a reagent:

A	Extra Pure grade	**C**	Guaranteed Reagent (GR)
B	Ultra pure grade	**D**	Technical grade

7. Minimum value of concentration limit of qualitative analytical reaction must be not less than

A	1:1000
B	1:100000
C	1:10
D	1:1000000

8. NaOH may be the selective analytical reagent for such group of cations:

A	Ions of alkali metals;
B	Ions of alkali-earth metals;
C	Ions of amphoteric metals;
D	Ions of d-elements.

9. What reactant may be used for separation of Ca^{2+} and Co^{2+} cations?

A	NaOH;
B	$(NH_4)_2CO_3$ (concentrated);
C	NH_4Cl (concentrated);
D	$NH_3 \cdot H_2O$ (in excess).

10. Put in the sentence a missing word: *Qualitative reaction of* SiO_3^{2-} *anion with* NH_4Cl *(saturated solution) is accompanied by visual effect of ____________ sediment.*

11. Determine correspondence of the cations and their groups according to phosphate classification:

A	1st	**1**	Ca^{2+}
B	2d (A)	**2**	Cu^{2+}
C	2d (B)	**3**	NH_4^+
D	3d	**4**	Fe^{2+}
E	4th	**5**	Fe^{3+}
		6	Co^{2+}
		7	Mg^{2+}
		8	K^+
		9	Ag^+

CHAPTER 2. QUNTITATIVE ANALYSIS

2.1. Lab work - Precipitate gravimetry (mass analysis). Determination of Barium content in Hydrated Barium Chloride

REAGENTS

1. Sulfate acid H_2SO_4, 2N solution;
2. Hydrochloric acid HCl, 2N solution;
3. DW.

GLASSWARE

1. Watch glass, 80-90 mm diameter;
2. Two beakers, volume 230-300 mL;
3. Wash bottle;
4. Glass stick;
5. Glass funnel;
6. Porcelain crucible, 30-35 mm diameter;
7. Dessicator;
8. Filter paper (Whatman Blue Ribbon filter paper. Ashless standard filter paper for very fine precipitates (class 2d acc. to DIN 53 135);
9. Scissors;
10. Spatula;
11. Crucible tongs.

EQUIPMENT

1. Analytical balances;
2. Electric oven;
3. Lab dry box;
4. Muffle.

BACKGROUND

The historical method of choice for sulfate in waters and wastewaters is the gravimetry with barium:

$$Ba^{2+} + SO_4^{2-} = BaSO_4 \text{ (precipitate)}$$

1. Barium sulfate precipitates quantitatively by adding excess of ion Ba^{2+} under acidic conditions; low pH is required to avoid the co-precipitation of barium carbonates and/or phosphates.

2. The formation of high purity and non-filterable crystals implies to allow reaction to continue for at least 2 hours at temperature over 80-90 ^{o}C. This process (digestion of the precipitate) minimizes the formation of filterable $BaSO_4$ crystals from the initial colloidal particles.

3. Filter the precipitate by decantation on a filter paper and the resulting solid mass is washed and dried in an oven for 1 hour at 800 ^{o}C.

This calcination procedure (1 hour at 800-900 ºC) should be performed on the porcelain crucible used for this operation.

4. Finally it is weighed at room temperature (keep it into a dessicator).

Determination of barium as $BaSO_4$. The precipitate is not carried out by slow addition of precipitant to the analyte containing solution. Such a procedure tends to produce conditions of super-saturation and a consequent rapid formation of small, relatively impure solid particles results. This effect cannot be entirely eliminated and is a source of error. The homogeneous precipitation techniques are able to avoid this erroneous effect; the precipitating reagent is generated slowly and homogeneously in presence of hydrochloric acid in boiling aqueous solution.

Procedure:

1. Determine mass of examined salt, using analytical balance.

Note on the W_1 = _______________ g (your result).

2. Weigh empty clean calcinated during 30 min. porcelain crucible **(do not forget number of crucible!)**

Note on the $W_{crucible}$ = ___________g (your result);

Number of crucible (or sign) ______________.

3. Weighted mass of salt is transported to the 350-300 mL beaker, after then solid salt is dissolved by hot DW. Total volume of water in beaker must be not more 100-150 mL. Add 3 mL of 2N HCl for acidification of solution.

4. Prepare solution of precipitate agent in the other 100-150 mL beaker, added 4-5 mL of 2N H_2SO_4 and 25-50 mL of hot DW and stir up mixture.

5. Solutions of $BaCl_2$ and H_2SO_4 warm up practically to boiling state (to 80-90 °C). Very slowly (during at least 15 min.), by drops add solution of H_2SO_4 to solution of Barium salt, stirring well permanently by glass stick.

6. Let beaker with mixture settle for 24 hours at room temperature and protected from dust by paper list, **note on the surname of student**.

7. Test the fullness of precipitation adding 2-3 drops of 1N H_2SO_4 into beaker with precipitate. If no turbidity, it’s OK.

8. Decant transpired upper layer (mother liquid) from beaker on paper filter, contained in funnel. Wash precipitate in beaker of 2-3 portions of hot DW (30-50 mL each portion).

9. Transport the precipitate from beaker to filter completely. Wash it 2-3 times of DW on filter.

10. Test the filtrate of absence of Cl^- with $AgNO_3$. If your filtrate remains clear, dispose of the filtrate in the appropriate waste container.

8. Dry filter with precipitate at 110 ºC during 0,5-1 hour.

9. Ash filter with precipitate by heating in gas burner.

10. Then calcinate the precipitate with the aid of porcelain crucible in muffle at 800 °C during 30-35 min.

11. Cool crucible to room temperature in a dessicator.

12. Weigh crucible with calcinated precipitate.

Note on the W_2 = ____________ g (your result).

13. Calculate content of barium in examined example of Barium chloride:

$$\mathbf{Z = \% Ba =} \frac{0{,}5884(W_2 - W_{crucible}) \times 100\%}{W_1} = \text{---------------------------} =$$

________%.

Check the result of the analysis in the teacher.

Calculate absolute and relative errors of analysis:

Absolute error:

Δ = |%Ba experimental (your result) - %Ba true (given by teacher)| =

___________-______________= _______.

Relative error:

$$\sigma = \frac{\Delta}{\%\text{Ba true}} \times 100\%. = \text{\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_}.$$

Remember, that relative error of gravimetry is not more 2%.

2.2. Laboratory work – Volumetric neutralization method. Determination of alkali concentration in solution

REAGENTS

1. Titrated solution of borax $Na_2B_4O_7$ (0,1000N);
2. Concentrated HCl solution (~38-40 w/w %);
3. Methyl orange indicator (solution);
4. DW.

GLASSWARE

1. 2-3 Erlenmeyer flasks, volume 250-300 mL;
2. 50 mL Burette fastened on a ring stand;
3. 20 mL Pipette;
4. 10 mL graduate cylinder;
5. Burette clamp;
6. Glass or plastic funnel (diameter 20-30 mm);
7. Wash bottle.

BACKGROUND

In the narrow sense in chemistry, neutralization means that equal amount of acids and bases in a solution react to produce salt and water. In the neutralization reaction between a strong acid and base in a solution, salt, which is produced, ionized almost perfectly so that hydrogen ions and hydroxide ions form water. Therefore, when acids and bases are equal, the hydrogen ion concentration ionizes to de-mineralized water (pH=7), which is neutral.

In chemical reactions, the various reacting substances always react in definite amounts. Taking the neutralization:

$$\underset{1\text{ mole}}{HCl} + \underset{1\text{ mole}}{NaOH} \rightarrow NaCl + H_2O$$

So, according to Law of equivalents 1 mole of HCl (36,5 g) will react exactly with 1 mole of NaOH (40,0 g).

Suppose we have two standard solutions: one of these (HCl) has a concentration of 1 M while the other (NaOH) also has a concentration of 1 M. Then, it follows that 1000 cm^3 of that NaOH solution will react exactly with 1000 mL of the HCl solution, since these volumes contain **equimolar amounts** (the same number of moles) of the reactants. In fact, since definite amounts of acid and base are involved, we know that for the neutralization:

$$\text{Acid} + \text{base} \rightarrow \text{salt} + \text{water};$$

$$\text{Amount of acid} = \text{amount of base};$$

$$\frac{\text{Volume of acid (mL)} \times \text{Normality of acid (g-eq/L)}}{1000} = \frac{\text{Volume of base (mL)} \times \text{Normality of base (g-eq/L)}}{1000}.$$

The above relationship is the basis for acid-base titrations. If we know one concentration accurately, as well as the two volumes, which neutralize each other exactly, we can easily calculate the unknown concentration.

Working solutions of neutralization method

Solutions of acids and alkalis are working solutions of method of neutralization. Solutions of H_2SO_4, HNO_3 and NaOH, KOH are used more frequent. Dissolution of exact mass of the analytically pure substance (AR) in the definite volume of solution is the most exact method of preparation of titration working solutions. But it is practically impossible in the case of the indicated acids and alkalis, because they do not respond to requests to the initial matters and solutions and their exact initial concentration is unknown. Therefore working solutions are prepared with approximate concentration in the method of neutralization, and then their exact concentration is determined by initial solutions with the prepared concentration.

More frequent for determination of exact concentration of acids is used a **borax $Na_2B_4O_7 \cdot 10H_2O$** or waterless salt **$Na_2B_4O_7$** as a primary standard and oxalic acid **$H_2C_2O_4 \cdot 2H_2O$** is applied for determination of exact concentration of alkalis.

Preparation of HCl working solution. Order of preparation of solution:

- Take 4,5-5,0 mL concentrated Hydrochloric acid by the measured cylinder or conical measuring test tube;
- To carry it to glass jar on 0,5 L;
- To rinse a cylinder by DW and outpour this water in glass jar;
- To dilute acid in glass approximately to 0,5 L by DW;
- To close glass by a cork, to mix a reagent carefully;
- To sign the last name of student and name of reagent.

DETERMINATION OF NORMALITY OF HCl WORKING SOLUTION (Secondary standard)

Procedure:

1. Before the beginning of work to wash carefully all glassware.
2. To wash burette by HCl solution.
3. To wash pipette by borax solution.
4. Using funnel to fill a burette by HCl solution and obtain absence of air bubbles in the tap of burette.
5. To take off funnel and show out the level of liquid in a burette to the zero mark.
6. To take aliquot of borax solution by a pipette in washed by distilled water Erlenmeyer flask.
7. To add 1-2 drops of methyl orange indicator to borax solution in a flask; solution will becomes yellow.
8. To put a flask with borax solution under a burette and a sheet of white paper under flask.

9. To doze HCl solution slowly with constantly mixing a liquid in a retort by smooth circular motions.

10. It is necessary to catch a moment when yellow colour of solution in a flask will change on a pink from one drop of HCl.

11. To mark volume of HCl solution, used for titration.

12. To repeat titration of a new portion of borax solution.

TO MEMORIZE: any titration analyses must be conducted minimum three times (it is called parallel determinations). Thus the data about the volume of titrant which was used for titration are used for computations if they differ no more than on 0,1 mL. If three results have divergence more than 0,1 mL it is needed to conduct the fourth titration and etc. (until the absence of divergence).

Results fix in the table 1.

Table 1. Determination of accurate concentration of Hydrochloric acid solution used primary standard – borax

# of titration	Normality of borax solution, g-eq/L	Volume of borax in titration, mL (*equal to volume of pipette*)	Volume of HCl used for titration, mL	Normality of HCl, g-eq/L
1.	0,1000	20,0	*Your result*	0,__ __ __ __
2.	0,1000	20,0	*Your result*	
3.	0,1000	20,0	*Your result*	

$$N(HCl) = \frac{N(borax) \cdot V(borax)}{V(HCl\ for\ titration,\ average)} = \text{-----------------------------}$$

$$= 0,\_\_\ \_\_\ \_\_\ \_\_\ \text{g-eq/L}.$$

For calculation of normality of HCl solution applies average volume from two parallel titrations which differ no more than on 0,1 mL. The value of normality is calculated within **a fourth sign** after a comma. A result must be added to the table 1 (to calculate for the average value of the acid volume that was used for titration).

DETERMINATION OF ALKALI SOLUTION NORMALITY

REAGENTS

1. HCl solution with definite normal concentration (see table 1);
2. Methyl orange indicator.

GLASSWARE: alike in a previous section.

Procedure: it is similar to the previous section, but instead of borax solution must be taken alkali solution. Results write in the table 2.

Table 2. Determination of equivalent concentration of NaOH

# of titration	Normality of HCl solution, g-eq/L	Volume of HCl in titration, mL	Volume of NaOH for determination, mL (*equal to volume of pipette*)	Normality of NaOH, g-eq/L
1.	From previous table, last column 0,__ __ __ __	*Your result*	20,0	0,__ __ __ __
2.		*Your result*	20,0	
3.		*Your result*	20,0	

$$N(NaOH) = \frac{N(HCl) \cdot V(HCl\ for\ titration,\ average)}{V(NaOH)} = \text{-----------------------} =$$

0,__ __ __ __ g-eq/L.

Check the result of the analysis in the teacher.

Calculate absolute and relative errors of analysis:

Absolute error:

Δ=N(NaOH) experimental (your result) - N(NaOH) true (given by teacher)|
= _____________- _____________= ______.

Relative error:

$$\sigma = \frac{\Delta}{N(NaOH\ true)} \times 100\%. = \text{\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_}.$$

Remember, that relative error of volumetry is not more 1%.

2.3. Lab work – Oxidation-reduction (RedOx) titration (RedOxmetry). Determination of Iron(II) content in Mohr's salt

REAGENTS

1. Primary standard of oxalate acid $H_2C_2O_4$ solution (0,0500 N);
2. Working solution Potassium Permanganate $KMnO_4$, approximately 0,05N;
3. 2N Sulfate acid H_2SO_4 solution;
4. DW.

GLASSWARE

1. 2-3 Erlenmeyer (titration conical) flasks, volume 250-300 mL;
2. 50 mL Burette fastened on a ring stand;
3. 20 mL Pipette;
4. Laboratory tilt measure (10 mL);
5. Burette clamp;
6. Lab electric oven;
7. Glass or plastic funnel (diameter20-30 mm);
8. Wash bottle.

DETERMINATION OF CONCENTRATION OF $KMnO_4$ WORKING SOLUTION

BACHGROUND

Reaction based on method:

$5\ H_2C_2O_4 \cdot 2H_2O + 2\ KMnO_4 + 3\ H_2SO_4 = 10\ CO_2 + 2\ MnSO_4 + K_2SO_4 + 18\ H_2O$;

$Mn^{7+} + 5e \rightarrow Mn^{2+}$ | 2 oxidation agent;
$2C^{3+} - 2e \rightarrow 2C^{4+}$ | 5 reducing agent.

If precise concentration of oxalate acid is known and reacted volumes of permanganate and oxalate acid solutions, the precise concentration of $KMnO_4$ may be calculated according Law of Equivalents:

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

Procedure

1. Clean pipette, burette and Erlenmeyer flasks, as described above.

2. Add 20 mL of oxalate acid solution from measuring pipette to 250-300 mL Erlenmeyer flask. Acidify this solution adding 20 mL of 2N H_2SO_4 using tilt measure. Add near 40 mL of DW. Heat prepared solution to 70-80 °C. **BE CAREFUL, NOT BOIL SOLUTION** (because oxalic acid decomposes at 100 °C)!

3. Using a burette, slowly add the $KMnO_4$ solution to hot solution in flack. $KMnO_4$ acts as its own indicator. That is, at the start of the titration the deep violet colour of MnO_4^- will be lost because it is changing to Mn^{2+}, but as soon as there is no more oxalate acid in the solution for the MnO_4^- to react with, the MnO_4^- will remain in the reaction solution. The slightly pink colour of the dilute solution MnO_4^- indicates the end of the reaction. This colour must safe during at least 1 min. This is known as the "end point" or equivalence point of the titration.

4. The procedure of titration repeats two times or more. The results of so-called parallel titrations must distinguish one from other not more than 0,1 mL .

Results of experiment present in the form of table 3.

Table 3. Determination of accurate concentration of Permanganate solution used primary standard – oxalate acid

# of titration	Normality of oxalate acid $H_2C_2O_4$ solution, g-eq/L	Volume of oxalate acid $H_2C_2O_4$ solution in titration, mL (*volume of pipette*)	Volume of $KMnO_4$ used for titration, mL	Normality of $KMnO_4$, g-eq/L
1.	0,0500	20,0	*Your result*	0,__ __ __ __
2.	0,0500	20,0	*Your result*	
3.	0,0500	20,0	*Your result*	

Accurate concentration of permanganate solution is equal to:

$$N(KMnO_4) = \frac{N(H_2C_2O_4)\cdot V(H_2C_2O_4)}{V(KMnO_4)} = =$$

$$= \frac{0{,}0500\,\text{g-eq/L}\cdot 20\,\text{mL}}{\text{your result\_\_\_\_\_\_\_\_ mL}} = 0{,}\_\_\ \_\_\ \_\_\ \_\_\ \text{g-eq/L}.$$

DETERMINATION OF IRON(II) CONCENTRATION IN THE MOHR’S SALT SOLUTION

Mohr’s salt is a double salt - Iron(II)-Ammonium sulphate hexahydrate ($Fe(NH_4)_2(SO_4)_2\cdot 6H_2O$) included ions of Fe(II). The last one may reacts with potassium permanganate in acidic medium:

$10\ Fe(NH_4)_2(SO_4)_2\cdot 6H_2O + 2\ KMnO_4 + 8\ H_2SO_4 = 5\ Fe_2(SO_4)_3 + 2\ MnSO_4 + 10\ (NH_4)_2SO_4 + K_2SO_4 + 68\ H_2O$;

$Mn^{7+} + 5\bar{e} \rightarrow Mn^{2+}$ | 2 oxidation agent;

$2Fe^{2+} - 2\bar{e} \rightarrow 2Fe^{3+}$ | 5 reducing agent.

This reaction isn’t heating, because ion Fe (II) may oxidizes by air oxygen transformed to Fe (III) with rising of temperature.

Procedure

1. Add 20 mL of Mohr’s salt solution (**according to your variant of task)** with unknown concentration used measuring pipette to 250-300 mL Erlenmeyer flask. Acidify this solution adding 20 mL of 2N H_2SO_4 using

graduated cylinder. Add near 40 mL of DW. **BE CAREFUL, DON'T HEAT SOLUTION**!

2. Using a burette, slowly add the $KMnO_4$ solution to hot solution in flack. The slightly pink colour of the dilute solution MnO_4^- (stable 1 min. at least) indicates the end of the reaction. This colour must safe during at least 1 min. The procedure of titration repeats two times or more as described above.

Results of experiment present in the form of table 4:

Table 4. Determination of Iron(II) concentration in Mohr's salt solution

# of titration	Normality of $KMnO_4$ solution, g-eq/L	Volume of $KMnO_4$ in titration, mL	Volume of Mohr's salt solution for determination, mL (*volume of pipette*)	Equivalent concentration (normality) of Fe^{2+} in examined solution, g-eq/L
1.	From previous table, last column 0,__ __ __ ___	*Your result*	20,0	0,__ __ __ __
2.		*Your result*	20,0	
3.		*Your result*	20,0	

Calculate the concentration of Fe^{+2} present in the Mohr's salt solution:

$$N\,(Fe^{2+}) = \frac{N(KMnO_4)\cdot V(KMnO_4\ avarage)}{V(Mohr's\ salt\ solution)} = \frac{\rule{6cm}{0.4pt}}{20mL} =$$

$$= 0,\_\,\_\,\_\,\_\ g\text{-}eq/L.$$

Check the result of the analysis in the teacher.

Calculate absolute and relative errors of analysis:

Absolute error:

Δ = N(Fe^{2+} experimental (your result) – N(Fe^{2+}) true (given by teacher)| =

____________–_______________= ________.

Relative error:

$$\boldsymbol{\sigma} = \frac{\Delta}{N(Fe^{2+} true)} \times 100\%. = \underline{\hspace{8cm}}.$$

Remember, that relative error of volumetry is not more 1%.

2.4. Laboratory work – Iodometry. Determination of Copper(II) Content in Copper Vitriol

REAGENTS

1. 0,0500N Standard Thiosulfate $Na_2S_2O_3$;
2. 2N acetate acid CH_3COOH solution;
3. 10% Potassium Iodide KI solution;
4. Starch, fresh-prepared solution;
5. DW.

GLASSWARE

1. Watch glass, diameter 70-80 mm;
2. 100 mL Measuring flack;
2. 2-3 Erlenmeyer flasks, volume 250-300 mL;
3. 50 mL Burette fastened on a ring stand;
4. 20 mL Pipette;
5. Laboratory tilt measure (10 mL);
6. 5 mL cylinder;
7. Burette clamp;
8. Spatula;
9. Glass or plastic funnel (diameter20-30 mm);
10. Wash bottle.

EQUIPMENT

Analytical balance.

BACKGROUND

Iodometric determination of copper is based on the oxidation of iodides to iodine by copper (II) ions, which get reduced to Cu^+. Reaction taking place in the solution is:

$$2Cu^{2+} + 4I^- \rightarrow 2CuI\downarrow + I_2$$

and produced equivalent amount of iodine can be titrated with Thiosulfate solution:

$$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-.$$

Finally, united process may be presented as:

$$2Cu^{2+} + 2S_2O_3^{2-} + 2I^- \rightarrow 2CuI\downarrow + S_4O_6^{2-}, \text{ or}$$

$$2CuSO_4 + 2Na_2S_2O_3 + 2KI \rightarrow 2CuI\downarrow + Na_2S_4O_6 + K_2SO_4 + Na_2SO_4.$$

For the best results reaction should take place in the slightly acidic solution (pH near 4-5), adding a few drops of acetate acid. Solution should be free of other substances that can oxidize iodides to iodine (for example, Fe^{3+} or nitrites).

Procedure

1. Weight out accurately near 1,3 g of the analyzed salt.

Note on the W_1 = 1, ___ ___ ___ g.

2. Transport the probe in 100 mL measuring flack, dissolve in DW. Add 10-15 drops of 2N Acetate acid CH_3COOH. Make up volume of solution to 100 mL. Shake well.

3. Pipette 20,0 mL of this solution into a 250 mL titration conical flack, add 10 mL of 10% KI solution (using tilt measure);

4. Place the conic flack into dark place for 5-10 min;

5. Titrate swirling the flask the liberated iodine with standard 0,0500N sodium thiosulphate until a pale yellow colour of mixture;

6. Add 1 mL of fresh prepared starch solution – indicator;

7. Titrate swirling the flask, until blue colour disappears.

6. Repeat the titration. Results write in table 5.

Table 5. Determination of Copper(II) content in Copper Vitriol

# of titration	Normality of $Na_2S_2O_3$ solution, g-eq/L	Volume of $Na_2S_2O_3$ in titration, mL	Volume of copper(II) solution for determination, mL (*volume of pipette*)	Copper(II) content in Copper Vitriol, wt. %
1.	0,0500	*Your result*	20,0	___ ___,___ ___
2.	0,0500	*Your result*	20,0	
3.	0,0500	*Your result*	20,0	

$$\text{Wt.}\,\%\,\text{Cu} = \frac{N(Na_2S_2O_3)\cdot V(Na_2S_2O_3\ \text{for titration, average})\cdot E(Cu)\cdot V(\text{flack})\cdot 100\%}{V(\text{pipette})\cdot 1000\cdot W_1} =$$

$$\frac{0{,}0500\cdot V(Na_2S_2O_3\ \text{for titration, average})\cdot 63{,}543\cdot 100\cdot 100}{20{,}0\cdot 1000\cdot W_1}$$

$$= \frac{1{,}58858\cdot V(Na_2S_2O_3\ \text{for titration})}{W_1} = \frac{1{,}58858\cdot\_\_\_\_\_}{\_\_\_\_\_}\ \_\_\_,\_\_\_\ \%.$$

Check the result of the analysis in the teacher.

Calculate absolute and relative errors of analysis:

Absolute error:

Δ = |%$Cu_{experimental}$ (your result) - %Cu_{true} (given by teacher)| =
= ___________- __________ = _______.

Relative error:

$$\boldsymbol{\sigma} = \frac{\Delta}{\%\ \text{Cu true}}\times 100\%. = \_\_\_\_\_\_\_\_\_\_\_\_\%.$$

Remember, that relative error of volumetry is not more 1%.

2.5. Laboratory work – Complexonometry. Determination of Calcium concentration in solution

REAGENTS

1. Primary standard -0,0500N Zinc Sulfate solution $ZnSO_4$;
2. Working solution Trilon B, approximately 0,05N;
3. Ammonia buffer solution (pH=10);
4. Eriochrome black T indicator, solid, 1% (w/w) in Sodium Chloride;
5. DW.

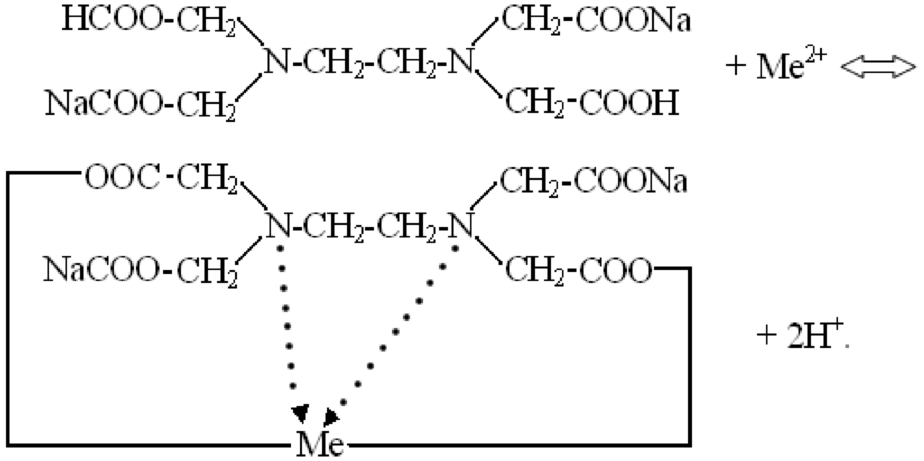
GLASSWARE

1. 2-3 Erlenmeyer flasks, volume 250-300 mL;
2. 50 mL Burette fastened on a ring stand;
3. 20 mL Pipette;
4. 10 mL cylinder;
5. Burette clamp;
6. Glass or plastic funnel (diameter20-30 mm);
7. Wash bottle.

BACKGROUND

The most important one in titrimetric analysis has a complexing of metals ions with halide- or pseudo-halide ions (SCN^-, CN^-), and with group of polyamine carboxylic acids (chelators).

The most commonly used regent for this method Trilon B may forms a very stable complex compound with a great number of cations (alkali-earth metals, copper, zinc, iron, manganese etc.) according to the reaction:



Different cations form stable complexes with Trilon B depending on their nature. For example, triple-charged cations form stable complexes when pH very low (1-3), while cations of alkaline earth metals – at pH 10.

Determination of titration endpoint is realized using special metallochromic indicators. They are a weak complexing agents made own colour and formed colour complexing compounds with metal cations. Last ones have a weak stability. One of such indicators is an Eriochrome black T. Its own colour in solution - sky-blue, when colour of his complexes with metals – wine-red. In general, schemes of titration processes are:

$$\mathrm{Me^{n+}} + \underset{\textit{Sky-blue solution}}{\mathrm{Ind}} \leftrightarrow \underset{\textit{Wine-red solution}}{\mathrm{MeInd^{n+}}}$$

$$\underset{\textit{Wine-red solution}}{\mathrm{MeInd^{n+}}} + \underset{\textit{Colourless solution}}{\mathrm{EDTA}} \leftrightarrow \underset{\textit{Colourless solution}}{\mathrm{MeEDTA}} + \underset{\textit{Sky-blue solution}}{\mathrm{Ind}}$$

DETERMINATION OF NORMALITY OF TRILON B WORKING SOLUTION (Secondary standard)

Procedure:

1. Before the beginning of work to wash carefully all glassware.

2. To wash burette by Trilon B solution.

3. To wash pipette by Zinc Sulfate $ZnSO_4$ solution.

4. Using funnel to fill a burette by Trilon B solution and to remove of air bubbles from the tap of burette.

5. To take off funnel and show out the level of liquid in a burette to the zero mark.

6. To take aliquot of Zinc Sulfate $ZnSO_4$ solution by a pipette in washed by DW Erlenmeyer flask.

7. To add 5 mL Ammonia buffer (use 10 mL cylinder), and a few grains of Eriochrome black T indicator to Zinc Sulfate $ZnSO_4$ solution in a flask; solution will becomes red-wine.

9. To titrate adding Trilon B solution slowly swirling the flask.

10. To fix volume of Trilon B used for titration, in the moment when colour of mixture in the flask changes from wine-red to blue after adding of one drop of titrant.

11. To repeat titration for a new portion of Zinc Sulfate $ZnSO_4$ solution.

Results of experiment present in the form of table 6:

Table 6. Determination of accurate concentration of Trilon B solution used primary standard – Zinc Sulfate $ZnSO_4$

# of titration	Normality of Zinc Sulfate $ZnSO_4$, g-eq/L	Volume of $ZnSO_4$ in titration, mL *(equal to volume of pipette)*	Volume of Trilon B used for titration, mL	Normality of Trilon B, g-eq/L
1.	0,______	20,0	*Your result*	0,__ __ __ __
2.	0,______	20,0	*Your result*	
3.	0,______	20,0	*Your result*	

$$N(\text{Trilon B}) = \frac{N(ZnSO_4)\cdot V(ZnSO_4)}{V(\text{Trilon B for titration, average})} =$$

$$\frac{\_\_\_\_\_\_\_\_\cdot 20{,}0}{\_\_\_\_\_\_} =$$

$$= 0{,}\_\_\ \_\_\ \_\_\ \_\_ \text{ g-eq/L.}$$

DETERMINATION OF NORMALITY OF CALCIUM Ca^{2+} SOLUTION

REAGENTS

1. Trilon B solution with definite normal concentration (see table 6);
2. Ammonia buffer solution (pH=10);
3. Eriochrome black T indicator, solid, 1% (w/w) in Sodium Chloride;
4. DW.

GLASSWARE: alike in a previous section.

Procedure

It is similar to the previous section, but instead of Zinc Sulfate $ZnSO_4$ solution must be taken Calcium Ca^{2+} solution.

Results write in the table 7.

Table 7. Determination of Calcium Ca^{2+} concentration in solution

# of titration	Normality of Trilon B solution, g-eq/L	Volume of Trilon B in titration, mL	Volume of Calcium solution for determination, mL *(equal to volume of pipette)*	Normality of Ca^{2+} of solution, g-eq/L
1.	From previous table, last column 0,__ __ __ __	*Your result*	20,0	0,__ __ __ __
2.		*Your result*	20,0	
3.		*Your result*	20,0	

$$N(Ca^{2+}) = \frac{N(\text{Trilon B}) \cdot V(\text{Trilon B for titration, average})}{V(\text{Ca soluiton})} =$$

$$\frac{\_\_\_\_\_\_\_\_\_\_ \cdot \_\_\_\_\_\_\_\_\_\_}{20{,}0} =$$

= 0,__ __ __ __ g-eq/L.

Check the result of the analysis in the teacher.

Calculate absolute and relative errors of analysis:

Absolute error:

$\Delta = N(Ca^{2+})_{\text{experimental}}$ (your result) - $N(Ca^{2+})_{\text{true}}$ (given by teacher)| =

= ________- _________=_________.

Relative error:

$$\sigma = \frac{\Delta}{N(Ca^{2+}\ \text{true})} \times 100\%. = \_\_\_\_\_\_\_\_\_\_\_\_\_\_.$$

Remember, that relative error of volumetry is not more 1%.

EXAMPLES OF CONTROL TESTS FOR QUANTITATIVE ANALYSIS

1. Calculate ionic strength I of solution contained 17,43 g K_2SO_4 (M=174,26 g/mol) per 1 L.

A	0, 10 mol/L	**B**	0,20 mol/L	**C**	0,30 mol/L	**D**	0,50 mol/L

2. Calculate gravimetric factor *f* for the quantitative determination of Magnesium content in the form MgO (M=40,31 g/mol), if the weighted form of the sediment is $Mg_2P_2O_7$ (M=222,57 g/mol).

3. Note on the absorption indicator for RedOx volumetric method:

A	Eriochrome black T	C	Methyl orange
B	Starch	D	Phenolphthalein

4. Calculate ppt (‰) concentration of solution contains 0,01 g of solute per 50 g of solution.

A	0, 200	**B**	1,000	**C**	0,500	**D**	0,001

5. Calculate pH of 10 N hydrochloride acid HCl (to consider as a strong acid, dissociated completely):

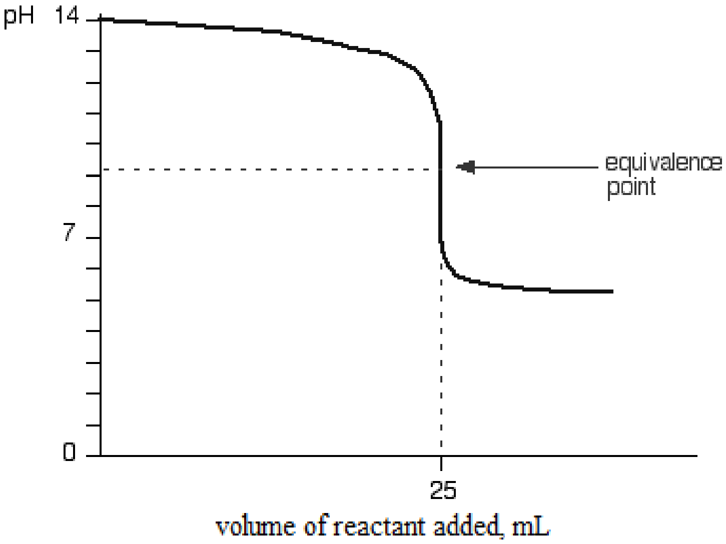
A	1	**B**	10	**C**	0	**D**	-1

6. Put a missing word: *A standard solution is a solution containing a precisely known _______of an element or a substance i.e., a known ___________ of solute is dissolved to make a specific volume.*

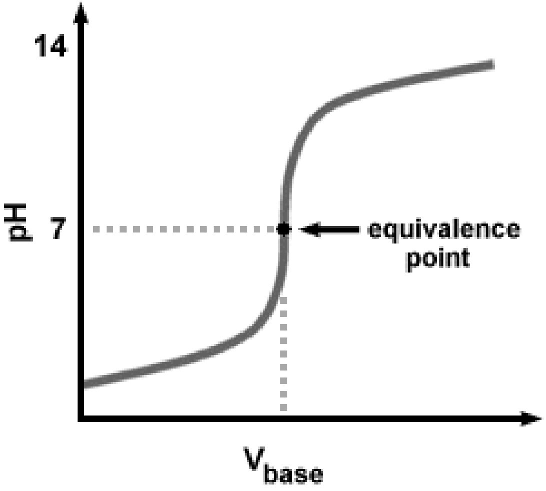
7. Calculate mass of $FeSO_4{\cdot}7H_2O$ (MW=278,01 g/mol) for the Iron gravimetric determination on the form of Fe_2S_3 (MW=207,89 g/mol) according to the Tananaev's recommendation.

8. Sample of lime (m_{sample} = 0,8960 g) was dissolved in the nitrate acid and total volume of obtained solution was 200 mL ($V_{measuring\ flack}$). Aliquot of this solution (20 mL, $V_{pipette}$) was titrated triply by 0,0505N Trilon B and obtained the next results: 14,6; 13,6; 13,5 mL. Calculate Calcium content (w/w %) in this sample.

9. Figure below demonstrates the curve of titration of ______(*weak or strong*) ______ (*acid or base*) by _________ (*weak or strong*) ____________ (*acid or base*) (*put the missing words*).



10. Refer to the titration curve below for questions:



- The titration curve shown above describes the:

A. Titration of a strong base. **C**. Titration of a strong acid.
B. Titration of a weak acid. **D**. Titration of a weak base.

- The equivalence point occurs at:

A. 7,50 mL titrant added. **C.** 15,0 mL titrant added.
B. 30,0 mL titrant added. **D.** 22,5 mL titrant added.

- The titrant is a

A. Strong acid. **C.** Weak acid.
B. Strong base. **D.** Weak base.

11. Note on the figure of Fixanale :


A

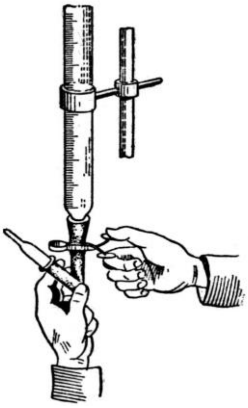

B


C


D


E

12. What is aim of the next previous operation of titration (see picture)?



13. Calculate the pH of a 0,1 M Na_2CO_3 (pK_1 = 6,52; pK_2 = 10,22) and 0,1 M NaOH.

14. Determine the types of sediments in gravimetric analysis:

A	Crystalline	1	CoS
B	Amorphous	2	$SrSO_4$
		3	$Fe(OH)_2$
		4	$MgNH_4PO_4$

15. Determine the active concentrations ($a = \gamma \cdot c$) of 0,01 M Cl^- solution and 0,0001 M Al^{3+} solution in soil solution where ionic power of solution is equals to 0,0005 (See APPENDIX).

APPENDIX Ionic activity coefficients at different ionic strength of solution

Ionic strength I, mol/L	Activity coefficients γ for ions with charge Z_i			
	1+ or 1-	2+ or 2-	3+ or 3-	4+ or 4-
0,0001	0,99	0,95	0,90	0,83
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
0,005	0,92	0,72	0,51	0,30
0,01	0,89	0,63	0,39	0,18
0,02	0,87	0,57	0,28	0,12
0,05	0,84	0,50	0,21	0,06
0,1	0,81	0,44	0,16	0,04

16. What is the solubility (M) of $SrSO_4$ in a solution that already contains 0.0600 M SO_4^{2-}? The K_{sp} for $SrSO_4$ is $3,2 \cdot 10^{-7}$ (*Effect of common ion*).

17. Calculate equivalent weight of a $K_2Cr_2O_7$ (M=294,10 g/mol) for RedOx titration in acidic medium.

18. Calculate equivalent weight of a H_3PO_4 (M=97,99 g/mol) for neutralization reaction: $H_3PO_4 + NaOH = NaH_2PO_4 + H_2O$.

19. Calculate volume (in mL) of 50% Sulfate acid solution (density d=1,40 g/cm^3) for preparation of 5 L 0,01 N solution (Molar weight (H_2SO_4) = 98 g/mol).

20. Calculate molarity of HCl solution of the Titre 0,01 g/mL.

21. Calculate pH of a 0,1N NH_4Cl solution (pK ($NH_3 \cdot H_2O$)=4,77)

22. Calculate pH of a 10N hydrochloric acid HCl (to consider as a strong acid, dissociated completely)

23. Calculate the pH of a 0,1 M H_3PO_4 (pK_1=1,96; pK_2=6,70; pK_3=12,44).

24. Calculate the pH of a 0,01 M NaClO (pK_{acid} = 7,50).

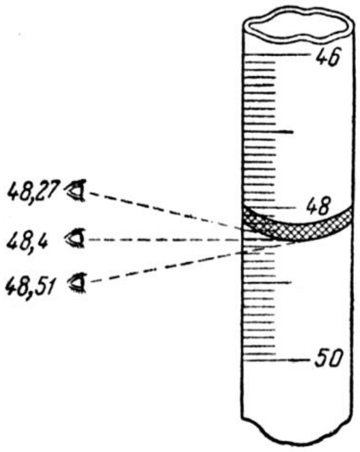
25. Calculate the pH of a 1 M Na_2CO_3 (pK_1 = 6,52; pK_2 = 10,22).

26. Calculate ppm concentration of solution contains 0,05 g of solute per 1000 g of solution.

27. Calculate solubility (in mol/L and g/L) of $Ni(OH)_2$ (SP=$1,6 \cdot 10^{-14}$, MW=92,71 g/mol) in solution of 0,1N KOH (*Be attentive: effect of the common ion into solubility*).

28. Calculate Copper (AW=63,548 g/mol) percent content in 1,0000 g malachite sample, if for iodometric titration 20 mL solution taken of 200 mL measuring flack was used 15,0 mL 0,0500N $Na_2S_2O_3$.

29. Note on the true result of titration (see a figure below)



30. Calculate the RedOx system potential E, included 0,1 M $FeCl_3$ and 0,01 M $FeCl_2$ (E° (Fe^{3+}/Fe^{2+}) = +0,771 V.

31. Calculate the RedOx system potential E, included 0,1 M $KMnO_4$ and 0,01 M $MnSO_4$ at pH=1 (E° (MnO_4^-/Mn^{2+}) = +1,51 V.

32. Calculate E of the RedOx system, included zinc electrode, immersed into 1 M $ZnSO_4$ if E° (Zn^{2+}/Zn^0) = - 0,764 V.

33. Equivalent mass of Ce^{3+} cation (AW=140,12 g/mol) in reaction with Trilon B is, g-eq/g:

A	70,06	**B**	46,83	**C**	140,12	**D**	187,32

34. Determine the order of steps of iodometric analysis.

A	To add excess of KI to analysing solution
B	To add indicator starch
C	To titrate by thiosulphate solution to slightly yellow colour of solution
D	To stand flack with analysing solution and a certain reactant in dark place (near 15 min).
E	To titrate by thiosulphate solution to decolourizing of solution

35. Calculate theoretical percent content (w/w) of Magnesium (AW=24,31 g/mol) in epsomite $MgSO_4 \cdot 7H_2O$ (MW= 246,48 g/mol).

MY RATING TABLE

THEORETICAL QUIZZES	Points	EXPERIMENTAL TASKS	Points
Module test 1. Qualitative analysis of cations		1. Analysis of cations mixture.	
Module test 2. Qualitative analysis of substances		2. Analysis of a soluble salt	
		3. Analysis of insoluble substance	
Module test 3. Heterogeneous equilibrium. Gravimetry		4. Gravimetric determination of Barium content in Hydrated Barium Chloride	
Module test 4. Homogeneous equilibrium. Volumetry.		5.Volumetric determination of alkali solution normality	
		6. Permanganatometric determination of Iron(II) concentration in the solution of Mohr’s salt	
		7. Iodometric determination of Copper(II) content in Copper Vitriol	
		8. Complexonometric determination of normality of Calcium Ca^{2+} solution	