Qualitative Analytical Chemistry

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Contents

Preface

Determining the composition of inorganic compounds and development of the required classical analytical methods greatly influenced the birth of modern chemistry. This process is connected to famous scientists like Jöns Jacob Berzelius (1779-1848), Friedrich Wöhler (1800-1882) and Carl Remigius Fresenius (1818-1897). About the importance of chemical analytical methods, Fresenius stated: '*It is easy to understand that every development at the area of chemistry is more or less directly connected with the new or improved analytical methods. The methodology of chemical analysis is a big scientific achievement and it is of great value.*' Creation of analytical chemistry as single coherent field happened at the second half of the 19th century. Fresenius, who was originally a pharmacist, initiated this by writing a comprehensive book for chemists who worked on analysis (*Anleitung zur Qualitativen Chemischen Analyse*, 1841) and by founding the first journal specialized to analytical chemistry (*Zeitschrift für Analytische Chemie*). At the end of the 19th century, classical analytical chemistry possessed lots of experimental results and sophisticated methods. However, it still remained a descriptive science, without physicochemical explanation of the chemical observations. Wilhelm Ostwald (1853-1932) changed this in 1894 by publishing his breakthrough work (*Die Wissenschaftlichen Grundlagen der Analytischen Chemie*). This book was based on the results of Svante Arrhenius (1859-1927), Jacobus Henricus van't Hoff (1852-1911) and Ostwald himself. It interpreted analytically useful phenomena like precipitation or solution phase reactions on the theoretical basis of physical chemistry, creating the current form of classical analytical chemistry.

There are important questions from both teachers and students. What could be the aims and benefits of Qualitative Analytical Chemistry course and the connected curriculum at the beginning of the 21st century? Is the knowledge contained within classical inorganic analytical chemical methods modern enough? Taking into consideration the already crowded schedule, is there enough time to acquire this knowledge?

It is true that analytical methods underwent exponential development in the last century. High performance analytical methodologies were created on the basis of electrochemistry, spectroscopy, X-ray crystallography, X-ray fluorescence, neutron activation, mass spectrometry and nuclear magnetic resonance. Separation methods progressed tremendously. Development of microanalytical sensors built on semiconductor chips (lab-on-a chip) became a hot area at the 2000s.

However, breaking the well-established order of courses is not advised, because up-to-date knowledge can be obtained only in a stepwise manner, through acquiring the theoretical and practical basics of classical analysis. Factual knowledge offered by qualitative inorganic chemical analysis is also important, especially in the case of pharmacists. Lots of inorganic compounds have biological activity, for example they are often toxic. These compounds can be found in official pharmacopoeia either because of their therapeutic use or as important, possible impurities. Their identification with simple methods is important in the identification of raw materials arriving to a pharmacy and in pharmaceutical quality assurance.

Importantly, acquiring factual knowledge is not the only goal of higher education. Improving logical thinking and problem solving skills are aimed too. Teaching and learning inorganic qualitative analysis helps to achieve these goal in various ways. Thanks to its thoroughly elaborated methods, students can learn how to observe carefully and how to make conclusions. They also obtain knowledge about the appearance and behaviour of different compounds, and can improve their general laboratory skills.

This curriculum was written in order to help students achieving these goals by discussing lots of analytical chemical reactions, summarizing the theoretical background of qualitative chemical analysis and providing a practical guide for the laboratory work.

In order to understand which pharmacist quantitative analysis competencies are developed by this course, a table has been made (Table I) on the appropriate knowledge elements, the skills created with their help (ability), the attitude elements needed to perform the task and the autonomy of the student in this area after completing the course.

Table I: Competencies of Qualitative Analytical Chemistry

Knowledge	Ability	Attitude	Autonomy and responsibility
He / she knows and understands the classification of cations.	He / she is able to accurately determine a given cation based on the classification and their characteristic reactions.	He / she knows and observes that the preparation for the laboratory practice includes a detailed knowledge of the accident and fire prevention instructions.	Based on his / her chemical knowledge, he / she decides on the detection of any contaminant in the sample mixture.
He / she knows the determination algorithm by which a given cation can be identified.		He / she observes the rule that analytical chemistry requires cleanness and reagents and equipment have to be kept clean.	As he / she knows the critical points of quantitative analysis he / she performs measurements independently or he /she can supervises the work of an chemical assistant.
He / she knows and understands the classification of anions.	He / she is able to accurately determine a given anion based on the classification and their characteristic reactions.	He / she knows that Pasteur pipettes (droppers) of reagents should not contact with the test tube or the unknown solution, because it contaminates the reagent.	
He / she knows the determination algorithm by which a given anion can be identified.	He / she is able to co-detection of compounds of cations and anions.	He / she knows that compounds containing concentrated acids or bases, heavy metals or toxic components (e.g. cyanide ion) have to be spilled into the appropriate containers, not into the sink.	
He / she knows the methodology by which the components of a ternary mixture can be determined.	He / she is able to apply the complex analysis separation technique to identify 3 or more different ions in one system.	He / she interprets the separation of cations / anions on the basis of drug analysis.	

1. Basics of qualitative analyis

1.1. Concepts

Our tests are focused on the qualitative analysis of inorganic ions. The aim of qualitative analysis is identification of the components present in the unknown compound. In contrast, quantitative analysis is interested in the exact amounts of known components. This means that quantitative analysis can be performed only after identification of the components via qualitative analysis. Of course, these branches of analysis are not always separated completely. For example, observations during qualitative analysis always contain some quantitative information. Different analytical reactions have different sensitivity to the target compound. Sensitivity is the smallest concentration required for identifying the target compound with a given reaction. Usually, it is characterized quantitatively by the concentration limit:

$$\text{concentracion limit} = \frac{\text{detection limit } (\mu g)}{\text{volume limit } (ml)}$$

The concentration limit can be measured in *ppm* (*pars pro million*) too. 1 ppm means that mass of the target compound is one millionth of the mass of the sample. In the case of diluted solutions ($\rho \approx 1$ g/ml) the value of the concentration limit in µg/ml and in ppm are practically the same. Dilution limit (10^6/concentration limit) is used too.

Notably, experiments can only determine whether the concentration of a compound exceeds the concentration limit or not. They cannot exclude the possibility that the compound is present below the concentration limit. Because sensitivity is influenced by various factors depending on the type of reaction, the analytical method had to be chosen according to the required concentration limit of detection.

From the viewpoint of analytical chemistry, only those reactions are useful where ions or ion groups which produce observable change with the reagent are known. If the reaction results in observable or unique change only with a certain ion, the reaction is specific. If the reaction produces observable change with a small well-defined group of ions, the reaction is selective. From a quantitative view of point, selectivity and specificity are connected with the ratios of sensitivities. If the reagent reacts with a wide range of ions, it is called group reagent (and the reaction is a group reaction).

Selectivity of an analytical reaction can be improved without physically removing the interfering ions with separation methods. These techniques are called masking and they transform interfering ions to inert (non-interfering) ones by appropriate reactions (e.g. precipitation or formation of stable complexes).

Instrumental methods of qualitative analysis are omitted from this curriculum, experiments will be performed with classic methods and simple equipment. As a result, the reactions used to identify components should produce changes which are easily observable with human senses like precipitation, dissolution of a precipitate, gas formation or change in the colour of the solution or precipitate. In the case of precipitation, important details are its colour, consistence, as well as the time and temperature required for precipitation. In the case of gas evolution, the intensity of the process and the smell of the formed gas can be important.

1.2. Role of dissolution

Although qualitative analytical tests can be performed with solids or aqueous solutions, most reactions are done in aqueous phase with ionic reagents. The role of the solvent is very important, since during dissolution the reagents and the unknown compound dissociate and become solvated. Thanks to its highly polar nature and hydrogen bonded structure, water readily dissolves ionic compounds and highly polar molecules.

Often, dissolution only involves secondary bonds (physical dissolution). When dissolution involves primary bonds (chemical dissolution), covalent bonds are rearranged during the process and water serves as both solvent and reactant (for example, aqua ion formation or dissolution of anhydrides, acids, or bases). As a consequence of the above facts, the studied ions are solvated in water and take part in chemical reactions independently. This enables considerable generalization and simplification: instead of examining the chemical properties of every possible cation – anion pair, it is enough to discover and systematize behaviour of individual cations and anions in qualitative analysis.

1.3. Stoichiometry and chemical equations

Thanks to the atomic structure of matter and the law of conservation of mass, the reactants react with each other during a chemical reaction in well-defined ratios. These ratios are called the stoichiometry of the reaction. Chemical reactions are described with chemical equations where reactants are on the left side while products are on the right side. Reactants and products are represented with their chemical or structural formulas. The coefficients deduced from stoichiometric ratios are on the left side of the formulas.

Chemical equations should obey the law of conservation of mass and the law of conservation of charge. If the enthalpy of the reaction and the state of the compounds are also shown, the reaction equation also obeys the conservation of energy (in qualitative analysis this is not important). As a result of the above laws, the overall charge and the amounts of elements should be the same at the left and the right sides of the equation. This enables balancing chemical equations in a stoichiometrically correct way.

Some reactions used in qualitative analysis are the results of complex reaction systems. In these cases, determining the overall stoichiometry is not always possible. In the case of such non-stoichiometric reactions, the chemical equation only shows the reactants and the products (without coefficients).

Important observations are often noted in the chemical equation with symbols. Underlined products are precipitates and gas state is noted with an upward pointing arrow (↑). When analytical chemical equations are written, incorporating every component is usually not necessary. In most cases, the counterions are not participating in the reaction so showing relevant reactants and products is enough. For example, precipitation of silver chloride from silver nitrate solution with sodium chloride reagent can be written with all components or without the inert counterions:

$$AgNO_3 + NaCl = \underline{AgCl} + NaNO_3$$

$$Ag^+ + Cl^- = \underline{AgCl}$$

2. Classification of reactions

2.1. Acid-base reactions

Theories concerning acid-base reactions developed considerably since the foundation of analytical chemistry. The first approach by Arrhenius stated that every compound which produces protons (H^+ ions) in water is acid, while every compound which produces hydroxide ions (OH^-) in water is base. This meant that acidity and basicity are absolute properties and acid-base reactions can only be interpreted in aqueous solutions. However, acid-base reactions can occur in non-aqueous media, or even in gas phase. It was also realized that acidity and basicity are relative properties, and it is more useful to interpret what happens between particular reaction partners. These principles are incorporated into Brønsted-Lowry theory, which states that the essence of acid-base reactions is proton exchange and it interprets acidity and basicity in interactions only. In a particular reaction, acid is the particle (molecule, ion) which loses proton (proton donor) while base is the particle which accepts proton (proton acceptor).

$$\mathrm{HA} + \mathrm{B} \rightleftharpoons \mathrm{A}^{\ominus} + \mathrm{BH}^{\oplus}$$

$$\mathrm{acid}_1 + \mathrm{base}_1 \rightleftharpoons \mathrm{base}_2 + \mathrm{acid}_2$$

The best example of this principle is self-dissociation, which can greatly influence the outcome of reactions in the case of different solvents (especially water).

$$\mathrm{H_2O} + \mathrm{H_2O} \rightleftharpoons \mathrm{OH}^{\ominus} + \mathrm{H_3O}^{\oplus}$$

The above reaction equations show that acid-base reactions are treated as chemical equilibriums. The strength of the acid is defined by the equilibrium constant of its proton exchange reaction with water (acid dissociation constant or acidity constant, K_a):

$$\mathrm{HA} + \mathrm{H_2O} \rightleftharpoons \mathrm{A}^{\ominus} + \mathrm{H_3O}^{\oplus}$$

$$K_a = \frac{[\mathrm{A}^-]\cdot[\mathrm{H_3O}^+]}{[\mathrm{HA}]}$$

In the special case of self-dissociation of water, the corresponding acidity constant is known as self-ionization constant or water ion-product constant ($K_w = [H_3O^+]\cdot[OH^-]$) which is 10^{-14} at room temperature. The basicity constant of the anion A^- is the water ion-product constant divided by the acidity constant of HA. In practice, the negative of their base 10 logarithms ($pK_a = -\log K_a$, $pK_b = -\log K_b$) are used to characterize acids and bases (see Annexes).

The concentration of protons (or hydroxide ions) in a solution is usually quite important in analysis. Usually, the pH value is measured, which is the negative of the base 10 logarithm of proton concentration. Accurate determination of pH value requires an electrochemical cell (glass electrode) but in qualitative analysis, use of pH indicators like litmus is usually enough. Determination of the pH of the solutions of weak or strong acids or bases at a given concentration with the above equations is a simple mathematical task, further details can be found in recommended literature.

The Lewis theory of acid-base reactions is also important. It states that bases are electron pair donors, while acids are coordinatively unsaturated molecules or ions which can accept electron pairs. In this theory, proton exchange is a special case of reactions involving nonbonding electron pairs. (Bases accept protons with the help of their nonbonding electron pairs.) The Lewis theory is very useful in the case of complex formation reactions.

2.2. Complex formation reactions

Complex formation reactions involve creation of coordinative covalent bonds (dative bonds) between the reaction partners. This requires an electron pair acceptor (Lewis acid) and one or more electron pair donors (Lewis bases) to participate in the reaction. Importantly, electron transfer (which is characteristic to redox reactions) does not happen. Usually, the Lewis acid partner is a transition metal ion, while the Lewis base partner which has nonbonding electron pair can be either a molecule or an ion. In most cases, in the middle of the complex ion is the metal ion. It is called coordination centre, while the ions and molecules coordinated (bonded) to it are called ligands. The number of ligands bonded to the central metal ion is the coordination number. Multidentate ligands have more than one nonbonding electron pair which can participate in coordination. Interaction of such ligands with metal ions creates cyclic complexes called chelates. The overall charge of the complex ion (the sum of the charges of the central metal ion and the ligands) can be negative, positive or even neutral.

Formation of complex ions is an equilibrium process which proceeds in a stepwise manner. In every step, an additional ligand (L) bonds to the metal centre (M) which can be repeated until the final coordination number (n) is achieved.

$$M + X \rightleftharpoons MX$$

$$MX + X \rightleftharpoons MX_2$$

$$\cdots$$

$$MX_{n-1} + X \rightleftharpoons MX_n$$

Equilibrium constants can be written for the formation of every complex ion above (stepwise constants), but characterizing the stability of the final complex is enough in qualitative analysis. This can be accomplished with the cumulative constant (β) which can be expressed as the product of stepwise constants (see Annexes).

$$M + nX \rightleftharpoons MX_n$$

$$\beta = \frac{[MX_n]}{[M]\cdot[X]^n}$$

The nomenclature of complexes is summarized below:

• Order of components: negatively charged ligands are named first, followed by neutral ligands and finally the central metal ion.

• Negatively charged ligands gain *–o* suffix (for example, hydroxo, cyano, thiosulfato). Coordinated water is called *aqua*, while coordinated ammonia is called *ammine*.

• The number of a particular ligand is indicated by the Greek prefixes *mono-*, *di-*, *tri-*, *tetra-*, *penta-*, *hexa-* etc.

• In the case of complex ions with negative overall charge, the Latin name of the central metal ion is used with *–ate* suffix. In the case of other complexes, the English name of the central metal ion is used without any suffixes.

• The oxidation number of the metal centre is shown by Roman numeral in parentheses after naming the metal.

2.3. Redox reactions

Redox reactions involve electron transfer. One reaction partner loses electrons (oxidation) while the other one accepts it (reduction). In the case of disproportionation, both reaction partners are the same compound (e.g. $H_2O_2 + H_2O_2 = 2\ H_2O + O_2$). In the case of comproportionation, the oxidized product and the reduced product are the same compound (e.g. $Cu + [Cu(NH_3)_4]^{2+} = 2\ [Cu(NH_3)_2]^{+}$). The degree of oxidation is described by the oxidation state. In the case of monatomic ions, the oxidation state is equal to the charge of the ion (for example, oxidation state of Cl^- is -1). In the case of more complex systems, the situation is slightly different. For each covalent bond, the bonding electron pair is assigned solely to the more electronegative bonding atom. The resulting hypothetical charges of the atoms are their oxidation numbers. As a result of electronegativities, oxidation state of oxygen in its compounds is always -2 (except in peroxides where it is -1), oxidation state of hydrogen in its compounds is always +1 (except in metal hydrides). These help a lot to figure out other oxidation numbers. For example, the oxidation state of nitrogen is -3 in ammonia (NH_3), while +5 in the nitrate ion (NO_3^-).

From the viewpoint of qualitative analysis, the extent of the oxidizing or reducing capabilities of reagents are important. These are measured with electrochemical cells.

One half-cell of the electrochemical cell consists of an appropriate electrode (usually platinum) and the solution of the studied redox reagent as electrolyte. The other half-cell is a reference electrode. The two half-cells are connected by a salt bridge. This setup separates the oxidation and the reduction half-reactions in space (they happen on different electrodes): the anode is the electrode where oxidation happens, while the cathode is the electrode where reduction takes place. The electric potential between the electrodes is the difference of their electrode potentials: $U = E_{cathode} - E_{anode}$. By definition, the reference electrode is the standard hydrogen electrode where hydrogen gas and protons are in equilibrium with each other. Also by definition, the potential of this electrode is zero. With a standard hydrogen electrode as anode, electric potentials of other redox systems can be determined.

$$\mathrm{ox} + n\,e^{\ominus} \rightleftharpoons \mathrm{red}$$

$$2\,H^{\oplus} + 2\,e^{\ominus} \rightleftharpoons H_2$$

It is important that the electrode potential depends on the redox system itself and the concentrations of the oxidized and reduced forms. The electrode potential can be calculated by the Nernst equation:

$$E = E_0 + \frac{0.25\ \mathrm{mV}}{n}\ \ln\frac{[\mathrm{ox}]}{[\mathrm{red}]}$$

E_0 is the standard redox potential of the redox system in question, which can be measured when [ox] and [red] are both 1 mol/dm^3. If the reduced form is solid (for example, elemental metal), its concentration is constant and can be incorporated into E_0.

E_0 can be used to compare redox properties because it is independent from concentrations (see Annexes). Positive E_0 values indicate that the reagent readily accepts electrons from the electrode, it has oxidizing properties. Higher E_0 values indicate stronger oxidants. On the other hand, negative E_0 values indicate that the reagent wants to give electrons (it has reducing properties). A reagent with higher E_0 can oxidize another reagent with lower E_0. However, pH can greatly influence reactions which involve H^+ ions. For example, arsenate ions oxidize iodide ions yielding arsenite ions and elemental iodine in acidic environment; while arsenite is oxidized by iodine yielding arsenate and iodide ions in basic environment.

$$AsO_4^{3-} + 2\,I^- + 2\,H^+ \longrightarrow AsO_3^{3-} + I_2 + H_2O$$

$$AsO_3^{3-} + I_2 + 2\,OH^- \longrightarrow AsO_4^{3-} + 2\,I^- + H_2O$$

2.4. Reactions involving precipitation

Reactions involving precipitation are quite commonly used in qualitative analysis. Although acid-base reactions, complex formation reactions and redox reactions can result in precipitation too, differentiation of reactions involving precipitation form other reactions is justified by the fact that precipitation (and the reverse process, dissolution of solids) can be discussed as an independent chemical equilibrium. In order to dissolve a solid, solvation by the solvent have to compete successfully with the forces (primary or secondary bonds) holding together the solid. If the crystal lattice is held together by sufficiently covalent interactions or the crystal is composed of hydrophobic neutral molecules, solvation by the strongly polar water is disfavoured and no dissolution occurs. During analytical reactions, usually solutions of ionic compounds are reacted with each other. In the case of weakly soluble cation-anion pars, the low solubility is a result of the considerable covalent character of the ionic bond (except cases like CaF_2 where the very high lattice energy cannot be compensated by hydratation). From the viewpoint of nucleation, this process can be viewed as creation of a network of dative covalent bonds resulting in a scarcely water-soluble three-dimensional lattice.

The solid precipitate is in equilibrium with the dissolved, solvated ions. For a general A_mB_n precipitate:

$$A_mB_n(sz) \rightleftharpoons m\,A(aq) + n\,B(aq)$$

$$K_{sp} = [A]^m \cdot [B]^n$$

$$S = \left(\frac{K_S}{m^m \cdot n^n}\right)^{\frac{1}{m+n}}$$

In the proper equilibrium constant, the denominator of the right side would be the concentration of the solid A_mB_n. However, since this is constant, it can be merged into the equilibrium constant, creating the solubility product K_{sp}. With the help of K_{sp}, we can calculate the concentration of a saturated solution of A_mB_n (solubility, S). The negative of the base 10 logarithm of K_{sp} (pK_{sp}) is used too.

During precipitation, the solution is in equilibrium with crystals of different sizes. Thanks to surface energy effects, particle size has a pronounced effect on the value of K_{sp}: in the case of smaller particles, K_{sp} is higher. This means that in a solution which is in equilibrium with larger (some μm sized) crystals (saturated solution), smaller crystals can still dissolve. As a result, small particles are redissolved, and concentration of the solution is maintained by precipitation of the excess compound into large particles, growing them further (Ostwald ripening). Ostwald ripening can be accompanied by recrystallization into a more stable polymorph. These phenomena are called digestion or precipitate aging. Precipitates can bind other ions on their surface which influences their physical behaviour. When quantitative separation is desired, these adsorbed ions have to be removed with washing.

Precipitation is usually performed with excess precipitating agent (precipitant) to ensure that the common ion of the precipitate and the precipitating agent is in excess. The presence of excess common ion decreases solubility:

$$S = \frac{1}{m}\left(\frac{K_S}{L^n}\right)^{\frac{1}{m}}$$

In the above formula, *L* is the concentration of the common ion, *m* is its stoichiometric coefficient while *n* is the stoichiometric coefficient of the counterion.

Dissolution of precipitates has comparable importance to precipitation in qualitative analysis. Generally, dissolution of precipitates requires shifting the precipitation equilibrium to the right side. This can be achieved by an appropriate reagent, which reacts with an ion of the precipitate, greatly decreasing its concentration. In the case of sufficiently basic anions, protonation is a straightforward way to dissolve the precipitate (good examples are the dissolutions of various hydroxide precipitates under acidic conditions). Decreasing cation concentration can be accomplished by adding a complexing agent which forms a sufficiently stable cation-ligand complex (for example, dissolution of AgCl by transformation of Ag^+ into its ammine complex). It the solubility product is extremely low, a quantitative and irreversible reaction is needed to dissolve the precipitate. For example, dissolution of some metal sulphides require concentrated nitric acid which oxidizes sulphide ions to elemental sulphur, decreasing concentration of S^{2-} to almost zero.

3. Methods

3.1. Importance of sample amount

The methods used in qualitative analysis can be classified according to the necessary amount of sample (Table 1).

Table 1. Classification of qualitative analytical methods based on the required amount of sample

Method	Amount of sample
Macro analysis	100 mg
Semi-micro analysis	10 mg
Micro analysis	1 mg
Ultra-micro analysis	0.1 mg

During the qualitative analysis laboratory practice of pharmacist students, which focuses on the basics, use of semi-micro size is ideal. It is economic (sparing chemicals, solvents, energy and equipment), but reactions at this scale are still noticeable (even by inexperienced people). During laboratory work, students have to learn economic, environmentally friendly ways of working, including performing reactions at semi-micro size.

Test tube reactions will be performed in semi-micro test tubes with some ml volume. Importantly, test tubes should not be filled with more than 1/3 of their volume. This enables safe handling during heating and shaking, and reactions at this scale are easily observable. Reagents should be added dropwise to samples, with thorough shaking after every dose and we have to leave enough time to study changes.

During redissolution of precipitates, it is enough to use the minimum amount of precipitate whose dissolution is easily visible. Use of higher amount of precipitate may require more reagent than the free volume of the semi-micro test tube. In such cases, outcome of the reaction will not be satisfactory.

3.2. Sample preparation and sample dissolution

Grainy samples are ground with mortar and pestle until a homogenous powder is obtained which is stored in a closed container until further use. Most reactions will be performed in solutions, making the dissolution process crucial. At first, dissolution should be attempted with distilled water. If the sample does not dissolve, the second attempt should be diluted hydrochloric acid (with or without warming). Use of sulfuric acid is not recommended because numerous metal sulphates (e.g. $PbSO_4$, alkaline earth sulphates) are precipitates. If neither distilled water nor diluted HCl is capable of dissolving the sample, try to use concentrated hydrochloric acid (with or without warming). In the case of failure, nitric acid (HNO_3) or aqua regia (3:1 mixture of conc. HCl and conc. NHO_3) should be applied. Warm, concentrated nitric acid is a strong oxidant, which can facilitate dissolution (although in the case of sulphides, it can yield elemental sulphur precipitate). In the case of aqua regia, the oxidative property of nitric acid is combined with the complex formation ability of chloride ions. If dissolution succeed only with strong acids or with the oxidative nitric acid, the dissolved sample should be evaporated to dryness to get rid of impurities (which may interfere the analysis) originating from the reagents.

When the above oxidative and strongly acidic conditions cannot dissolve the sample, dissolution should be attempted with aqueous NaOH, NH_3 or cyanide solutions. Through complex formation, these can dissolve numerous compounds which are insoluble in water or strong acids. The other option is fusion (see later).

3.3. Separation

In the case of samples with more components, qualitative analysis requires physical separation of the ions. This can be selective dissolution, precipitation, separation in gas phase and chromatographic methods. The latter one is beyond the scope of this curriculum.

Separation of samples containing water-soluble and insoluble components can be achieved by selective dissolution of the soluble components with water. Generally, if selective dissolution is possible, the order shown in **Section 3.2** (*Sample preparation and sample dissolution*) should be checked and from the appropriate solvents the mildest one should be chosen.

The most common separation strategy is selective precipitation followed by filtration. In order to succeed, the solubility product of the products formed from the precipitating agent with the ions which have to be separated should be different enough. Often, selectivity can be improved by applying complexing agents (see masking) or fine-tuning the pH. It should be noted that precipitation can result in very small particles, creating finely dispersed or even colloidal systems. Finely dispersed precipitates also have a tendency to adsorb ions from the solution, creating a surface electrical double layer which stabilizes them against aggregation and further slows down sedimentation.

The easiest way to separate the solution and the precipitate, decantation, can be applied only for precipitates which sediment readily. After sedimentation is complete, the supernatant is simply poured off (it can be kept or discarded). The precipitate is then washed with some ml water, which is then decanted. Washing is repeated at least two times. In the case of slowly sedimenting systems, centrifugation can accelerate the process.

If the separation of the solution and the precipitate should be quantitative or the solution phase is required too, filtration is applied. Filtration should be performed with a funnel and a Büchner flask or vacuum flask.

First, filter paper is placed into the funnel. Then it is wetted and the suspension carefully poured along a glass rod to the filter. Filtration can be accelerated by applying vacuum. The precipitate collected on the filter is then washed with pure solvent unless stated otherwise. Notably, finely dispersed precipitates can pass through filter paper. In such cases, heating can promote aggregation of the precipitate, which makes filtration easier. Use of filter paper with smaller pores can help too.

3.4. Heating of samples

Samples are usually heated with Bunsen burners. In these, the gas flows up in a tube with open slots in its side which admits air into the gas stream. The amount of air can be regulated by changing the size of the open slots. The gas burns at the top of the tube once ignited. (Before ignition, make sure that the gas pipe is attached tightly.) The properties of the resulting flame depend on the ratio of gas and air. When the slots are closed (pure gas burns), the resulting flame is cooler, brighter, yellow and produces soot. When the ideal gas-air ratio is used, the resulting flame is almost colourless, less luminous and it is hotter (the highest temperature is achieved in the upper third of the flame, it is 800-1200 °C). Between uses, the slots should be closed to produce the much more visible yellow flame or the burner should be turned off to avoid accidents. Prolonged use warms the burner considerably. Hot Bunsen burners are prone to flashback (flame propagation down the tube), making them a fire risk.

Some samples are heated in water bath, which enables mild heating or drying. Because the water bath is heated electrically, the general electrical safety rules should be followed.

The usual method for evaporation of samples is starts with placing the sample into a porcelain or platinum dish. Then, the dish is placed on a wire gauze and carefully heated with Bunsen burner. In special cases, evaporation should be performed under milder conditions (water bath).

3.5. Solid-state reactions and reactions involving fusing and fluxing

During qualitative analysis, some samples are insoluble and cannot be studied in solution. Also, some reactions have to be performed with solid samples. From the numerous existing methods (see recommended literature), only those are mentioned which may be used during this laboratory practice.

Fusing and fluxing. Some samples cannot be dissolved in any of the dissolving agents. In such cases, a flux is added to the solid sample and the mixture is fused in porcelain or platinum dish or crucible at high temperatures followed by cooling down the resulting mixture. Under these conditions, double displacement reaction happens and the sample is transformed into a water-soluble form. Depending on the acid-base properties of the studied sample, different fluxes are used: acidic flux (for example, potassium disulphate) for basic substances, and basic flux (for example, a mixture of sodium and potassium carbonate) for acidic samples. If redox reaction is required during fusion, nitrates can be used as oxidants while activated charcoal can be used for reduction.

$$BaSO_4 + Na_2CO_3 = BaCO_3 + Na_2SO_4$$

The above example shows basic fusion of $BaSO_4$, an extremely insoluble compound. Na_2CO_3 and Na_2SO_4 are water-soluble, while $BaCO_3$ can be dissolved in weak acids.

Cobalt nitrate test. Heating of cobalt compounds exposed to air yields black cobalt(III) oxide. If other metal oxides are present too, mixed oxides can be formed with characteristic colours (Table 2), such as Rinmann's green (in the presence of Zn^{2+}) or Thénard's blue (in the presence of Al^{3+}).

Table 2. Colours during cobalt nitrate tests

Element	Colour
aluminium	blue
zinc	green
magnesium	pink
titanium	yellowish green
silicon	blue
tin	bluish green

In order to perform this test, a stripe of filter paper is wetted with the unknown solution and dried. Then, it is wetted with some drops of cobalt nitrate solution and dried again. Finally, it is burned to ash in the upper third of the colourless flame (oxidizing flame) of a Bunsen burner. If the test was successful, the coloured mixed oxide is present along with black cobalt(III) oxide. Warning: if too much cobalt salt is used, the resulting cobalt(III) oxide can completely suppress the colour of the mixed oxide (especially in the case of Thénard’s blue).

Borax bead test. Anhydrous borax ($N_2B_4O_7$) melts at 740 °C. Cooling down the molten material yields a transparent, glass-like solid. Incorporation of metal ions into this boron trioxide glass gives it characteristic colour. To perform this test, a loop is created at the end of an iron or platinum wire and heated in flame. When it is hot, it is dipped into powdered borax, then heated again in flame to produce a small, glassy borax bead. Then, the bead is immersed into a diluted solution of the studied metal ion and heated again. The resulting colour depends two factors. The first is the metal ion present. The second is the flame used for heating: the colder reducing part of the flame and the hotter oxidizing part of the flame can yield different colours. Because heating with the upper third of the flame (oxidizing flame) is easier to reproduce, Table 3 only shows colours achieved in this way.

Table 3. Colours observed during borax bead tests when oxidizing flame is used

Element	Colour
iron	pale yellow
cobalt	blue
nickel	reddish brown
manganese	reddish purple
copper	bluish green
chromium	green

Methods of thermal analysis. The solid sample is heated in porcelain or platinum dish or crucible at high temperatures, observe whether colour change, sublimation or gas evolution happens. For example, identification of ammonium ions from multicomponent samples requires starting the analysis with heating a part of the sample because most group reagents contain ammonium ions. (Most ammonium salts lose NH_3 gas upon heating.) Heating should be performed carefully and gradually, because some salts can decompose explosively. (During the discussion of ions, this curriculum mentions if the salts of that ion are explosive.) Also, heating of mercury salts should be avoided. It can cause sublimation of the mercury salt or formation and evaporation of elemental mercury, resulting in safety (toxicity) issues. Thermal decomposition of compounds can be followed by continuously measuring their mass and the temperature during heating. This process, called thermogravimetric analysis, is an instrumental analytical method and it is not important in qualitative analysis.

3.6. Flame coloration (flame test)

At the temperature of the hotter, non-luminous Bunsen flame (800-1200 °C) some compounds dissociate into their atoms whose weakly bound outer electrons are excited. The excitation energy is released in the form of electromagnetic waves at the range of visible light, colouring the flame. Because the energy levels of electrons are quantized, only photons with certain frequencies (colours) are emitted which are characteristic to the emitting atom (Table 4).

Table 4. Colours observed during flame coloration

Element	Colour
sodium	intense(!) orange
potassium	pale(!) purple
lithium	red
calcium	brick red
strontium	deep red
barium	pale green (often yellowish green)
copper	green
boron	green

Flame coloration is mainly used to identify alkali and alkaline earth metals in their volatile salts. In the case of multicomponent samples, it should be taken into account that the intensity of flame coloration is not the same for every element. For example, the very intense orange coloration of sodium can conceal the pale purple coloration of potassium. In these cases, viewing the flame through a colour filter may enable detection of the weaker emission. For example, the orange light produced by sodium can be subtracted by viewing the flame through cobalt glass or copper(II) sulphate solution.

Flame coloration can be performed with the solid sample or with its solution. Solid samples are transferred to a loop of a platinum wire and heated with the flame of a Bunsen burner. The burner should be tilted to avoid sample drops falling into it, and the wire should by cleaned by heating before use. In the case of dissolved samples, zinc and hydrochloric acid is added to the sample. The forming hydrogen gas brings small droplets of the solution into the air above it, and the flame of the burner is directed into this area. Never drop the solid or dissolved sample directly into the Bunsen burner because it makes flame coloration harder to observe and leads to quick corrosion of the burner.

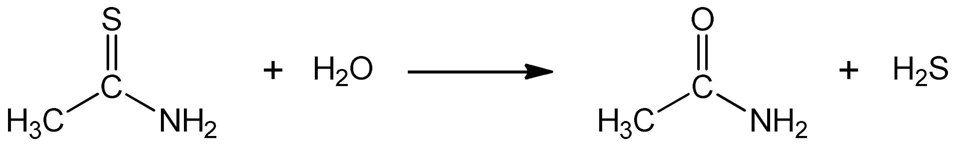
3.7. Reagents

Table 5 shows the most common reagents of qualitative analysis.

Table 5. Concentrations of the most common reagents used in qualitative analysis

Reagent in aqueous solution	Concentration
sulphur hydrogen (or thioacetamide)	saturated
ammonium sulphide	1 M
ammonium polysulphide	1 M
sodium hydroxide	2 M
ammonium carbonate	1 M
ammonium hydroxide	2 M
conc. ammonium hydroxide	15 M
silver nitrate	0.1 M
barium chloride	0.25 M
potassium iodide	2 M
acetic acid	2 M
hydrochlorid acid	2 M
conc. hydrochlorid acid	12 M
nitric acid	2 M
conc. nitric acid	16 M
sulphuric acid	1 M
conc. sulphuric acid	18 M

Importantly, because sulphur hydrogen gas is poisonous, its saturated solution should be used with great care and only in the necessary amount. If the reaction requires direct addition of H_2S gas to the reaction mixture, the reaction have to be performed under a fume hood. Instead of aqueous sulphur hydrogen solution, we can use thioacetamide solution which contains sulphide ions thanks to *in situ* hydrolysis of the reagent. This enables working in a safer way.



4. Working in the laboratory

4.1. General instructions

You should begin the experiment only if you are well prepared and understand the purpose of the experiment and every operation involved in the work. The preparation for the laboratory practice includes a detailed knowledge of the accident and fire prevention instructions. Importantly, laboratory notes have to be written about the current laboratory practice before the practice starts. This should be accomplished with the help of this curriculum and helps students to prepare for the practice. It also facilitates efficient and target-oriented working, and helps avoiding dangers which originate from the lack of knowledge or attention. During laboratory work, observations should be written into the laboratory notes (preferably at the time of the observation, not later). It is important to record every observation (including negative ones) because changes in the purity or concentration of the reagents can result in (slightly) different behaviour compared to the contents of the curriculum.

The most important thing in analytical chemistry is maintaining cleanness. Reagents and equipment have to be kept clean. Glassware have to be cleaned at the end of the laboratory practice. Semi-micro test tubes are washed with tap water first, followed by distilled water. Wet test tubes are put into a test tube rack where they slowly dry. Impurities strongly adhered to the wall of the test tube are removed mechanically with a test tube brush. Do not use cleaning brushes that are so worn that the spine hits the glass.

Pasteur pipettes (droppers) of reagents should not contact with the test tube or the unknown solution, because it contaminates the reagent. Return the dropper to its reagent bottle immediately after use, do not leave it on the table.

Order should be maintained on the tables. Before tests, decide which reagents are required and their order. Put unnecessary reagents in their places. Without order, it is easy to topple equipment and/or contaminate your samples. Maintaining order is especially important if you are working with toxic, corrosive or flammable reagents. Also, accidents can be avoided by paying attention to Bunsen burners.

We should spare reagents and equipment is it is possible. In semi-micro size, experiments require some tenth of millilitres of sample and some drops of reagents. Using more is unnecessary and not economic. The flame of the Bunsen burner should not be bigger than required because it consumes gas unnecessarily and it can cause accidents. Impure test tube should be cleaned, not discarded.

Spilling reaction products (precipitates or solutions) have to be performed with great care. Compounds containing concentrated acids or bases, heavy metals or toxic components (e.g. cyanide ion) have to be spilled into the appropriate containers, not into the sink.

4.2. Accident and fire prevention instructions in the laboratory

1. Eating, drinking and smoking in the laboratory are forbidden. Coats, bags, etc. must be left outside the laboratory in the places indicated. Only the materials and equipment that will be used are allowed on the laboratory bench. No materials must ever be taken out of the laboratory.
2. Order must be maintained in the laboratory so that the equipment and other objects do not disturb the work. The laboratory bench and the hood must be kept clean. Before work, students should be informed about the places of the main gas tap, the main electricity switch and the escape routes.
3. A laboratory coat and safety glasses must always be worn during the entire practical. Gloves must be worn when dangerous or poisonous materials are handled. Avoid contact with every form (sample, reagent, solution) of chemicals. If any chemical comes into contact accidentally with your skin, the affected area must be wiped with a dry cloth and then washed with plenty of water. The order of the two actions is especially important when concentrated acid contacted with your skin. Tasting chemicals or pipetting them by mouth is forbidden. After eye contact with a chemical, rinse the opened eye for several minutes under running water, then neutralize the area with the solutions maintained for such accidents. (Sodium carbonate or borax solution for acids, acetic acid or boric acid solution for bases. Do NOT use solutions from the laboratory shelves for this purpose.)
4. Glass apparatus should be carefully examined before use; any which is cracked, chipped or flawed must be changed.
5. Concentrated acids are diluted by pouring the acid into water (the reversed way is dangerous). Be aware that neutralization of concentrated acids or bases is accompanied by serious warming so the reaction vessel cannot be heat-sensitive.
6. Attempts to remove water mechanically from freshly washed test tubes (e.g. shaking) are forbidden. If the washing was not perfect, the droplets from the test tube can contain residual acid. After evaporation of water, the now concentrated acid can damage the area where the droplet landed (for example, skin, eye or clothes).

7. When a test tube is to be heated, it must be filled to only at most one third of its volume. Do NOT wear protective gloves during heating with a Bunsen burner because the flame melts rubber gloves, causing serious injuries requiring professional medical care. Heating have to be applied gently, and the test tube have to be tilted slightly. To avoid local overheating, gently but continuously shake and/or rotate the test tube. The opening of the tube must not point towards yourself of other people in the laboratory, because when the liquid starts to boil, the resulting bubbles can shoot heated liquid out of the test tube like a cannon. Use of test tube holder is recommended (practiced experimenters are capable of holding the test tube at its upper third with their hand without burning themselves).

8. Usually, there is not any visible difference between hot and cold laboratory equipment. Previously heated dishes and crucibles have to be left on a wire gauze to cool down.

9. During fusing and fluxing, be aware of spluttering of the reaction mixture. After fusing, dissolution have to be done carefully and only after the sample cooled down.

10. All experiments in which toxic or acidic fumes or vapours are formed must be carried out under a fume hood. Only our hands should be inside the fume hood and the reaction should be observed though the glass door of the hood.

11. A minor fire on the laboratory bench can be extinguished by covering it with a fire blanket or coat. In the event of a more serious fire, the main gas taps must be closed and electrical switches must be switched off, the people inside the laboratory and firefighters must be notified and a fire extinguisher must be used to extinguish the fire. In the case of a flashback (flame propagation down the tube), gas tap of the Bunsen burner must be closed immediately. Do not use fire extinguisher on burning personnel, use a fire blanket of the shower above the doors instead. Extinguishing electric fires with water is forbidden!

12. In the event of an accident, the instructor must be notified immediately.

5. Groups of cations

5.1. Cation group Ia

5.1.1. Reactions of Silver(I)-ion

Silver is a chemical element, a transition metal with the symbol Ag and it exhibits the highest electrical conductivity, thermal conductivity, and reflectivity of any metal. Silver compounds are used in photography (AgBr), for the preparation of explosives (AgCNO), small silver iodide crystals are used in cloud seeding to cause rain. Pure silver metal is used as a food colouring (E174), traditional Pakistani and Indian dishes sometimes include decorative silver foil known as *vark*, and in other cultures, silver *dragée* are used to decorate cakes. In medicine, silver and silver compounds have very important properties such as antibacterial and antifungal effects. Taking advantage of antibacterial property, silver is also used for water sanitisation and colloidal silver is similarly used to disinfect closed swimming pools. The solid $AgNO_3$ is used for the removing of the wart and for the treatment of slowly healing wounds. Contact to the skin, metal silver is formed from the $AgNO_3$, which discolours the skin and the released nitric acid has a scathing effect.

The silver ion is colourless, and $AgNO_3$ (0.05 M) solution can be used to study the reactions of silver.

1. Dissolving of silver metal

The silver metal can be dissolved by heating with cc. nitric acid. During the reaction, the formation of the brownish nitrogen-dioxide can be observed.

$$3Ag + NO_3^- + 4H^+ = 3Ag^+ + NO\uparrow + 2H_2O$$

$$2NO + O_2 = 2NO_2 \qquad \boxed{\textbf{brown}}$$

2. Group reaction

By adding hydrogen-chloride, silver-ion gives white precipitate. The solid is sensitive for the light.

$$Ag^+ + Cl^- = \underline{AgCl} \qquad \boxed{\textbf{white}}$$

3. Reactions with halogenides

The silver-ion gives light sensitive precipitations with other halogenides. The original colour of the precipitates is getting dark depending on the atomic number of the halogen.

$$Ag^+ + Br^- = \underline{AgBr} \qquad \boxed{\text{yellow-white}}$$

$$Ag^+ + I^- = \underline{AgI} \qquad \boxed{\text{yellow}}$$

The silver-halogenides can be dissolved by complex-formations. The complex-forming agents can be ammonia, thiosulphate-ion and cyanide-ion.

$$AgCl + 2NH_3 = [Ag(NH_3)_2]^+ + Cl^-$$

$$AgCl + 2S_2O_3^{2-} = [Ag(S_2O_3)_2]^{3-} + Cl^-$$

$$AgCl + 2CN^- = [Ag(CN)_2]^- + Cl^-$$

Before dissolution, the AgCl must be washed acid-free, in acidic solution poisonous hydrogen cyanide is evolved from the cyanide. Diamine-silver complex cannot be kept for longer time on desk, because the spontaneously formed silver-nitride (Ag_3N) can cause explosion! Diamine-silver can be transformed back to the halogenide precipitate by adding nitric acid. If the medium is acidic, the decomposition of thiosulphate-ion is also take place (see group reaction of thiosulphate-ion).

The complex-formation ability of halogenide precipitates are changing (based on the atomic number of the halogen) according to the following table:

	NH_3	$S_2O_3^{2-}$	CN^-
AgCl	+	+	+
AgBr	+!	+	+
AgI	-	+!	+

+ dissolves easily; +! dissolves by heating; - does not dissolve

4. Precipitation with hydrogen-sulphide

The reaction of group Ia with hydrogen-sulphide can be interpreted as a second group-reaction, because even in acidic conditions, sulphide precipitation is forming.

$$2Ag^+ + S^{2-} = \underline{Ag_2S} \qquad \boxed{\textbf{black}}$$

The sulphide precipitation can be dissolved by using cc. nitric acid, while the sulphide-ion will be reduced to elemental sulphur.

$$3Ag_2S + 2NO_3^- + 8H^+ = 6Ag^+ + 2NO\uparrow + 3\underline{S} + 4H_2O$$

5. Reaction with sodium-hydroxide and ammonium-hydroxide

By adding NaOH, brownish silver-oxide precipitation is forming, that in the excess of the reagent does not dissolve, because silver-ion does not form hydroxo-complex. The immediately forming oxide precipitation is characteristic for noble metals.

$$2Ag^+ + 2OH^- = \underline{Ag_2O} + H_2O \qquad \boxed{\textbf{brown}}$$

The oxide precipitation is also forming with ammonium-hydroxide that in the excess of the reagent, by the formation of diamin-complex dissolves.

$$Ag_2O + 4NH_3 + H_2O = 2[Ag(NH_3)_2]^+ + 2OH^-$$

6. Reaction with chromate-ion

By adding chromate-ion, red-brown silver-chromate precipitation is forming. The precipitation dissolves with orange colouration in diluted nitric-acid, because during this time dichromate is forming, and the equilibrium is shifted toward the dissolution. In the ammonia, the precipitation is dissolving parallel with the formation of the yellow chromate-ion.

$$2Ag^+ + CrO_4^{2-} = \underline{Ag_2CrO_4} \qquad \boxed{\textbf{red-brown}}$$

$$2Ag_2CrO_4 + 2H^+ = 4Ag^+ + Cr_2O_7^{2-} + H_2O \qquad \boxed{\textbf{orange solution}}$$

$$Ag_2CrO_4 + 4NH_3 = 2[Ag(NH_3)_2]^+ + CrO_4^{2-} \qquad \boxed{\textbf{yellow solution}}$$

7. Precipitation with arsenate- and arsenite-ions

The silver-ion precipitates characteristic coloured compounds with the oxoanions of arsenate and arsenite. This latter reaction can be applied to determine the oxidation state of the arsene in question.

$$3Ag^{+} + AsO_3^{3-} = \underline{Ag_3AsO_3} \qquad \boxed{\text{yellow}}$$

$$3Ag^{+} + AsO_4^{3-} = \underline{Ag_3AsO_4} \qquad \boxed{\text{chocolate brown}}$$

8. Silver-mirror test (Tollens-test)

Diamine-silver in alkaline solution is a week oxidation agent that oxidize aldehydes to carboxylic acids. Accordingly, by heating of alkaline solution of diamine-silver with aldehydes (formaldehyde, reducing sugars, etc.) the appearance of silver-mirror on the test tube can be observed. It should be mentioned that the oxidation does not work with ketons.

$$2[Ag(NH_3)_2]^{+} + R\text{-}CHO + 2OH^{-} = 2\underline{Ag} + R\text{-}COOH + H_2O + 4NH_3$$

5.1.2. Reactions of Lead(II)-ion

Lead is a chemical element, a heavy metal with the symbol Pb. Pure lead is blue-white, characteristic properties of this element is high density, malleability, ductility, and high resistance to corrosion due to passivation. It has significant industrial uses: lead sheets are used as architectural metals in roofing material, is still used in statues and sculptures, it was often used to balance the wheels of cars. Pharmaceutically, lead and its copmounds are very toxic. Lead enters the body via inhalation, ingestion, or skin absorption. A small amount of lead (1%) is stored in bones. In the case of acute toxication (after absorption of 2-3 g lead salt) colocs are reported. In the case of chronic toxication the following symthoms were reported: pale skin colour, headache, lack of appetite, and vacillation.

The lead ion is colourless, generally has oxidation number +2 or +4. $Pb(CH_3COO)_2$ (0.05 M) solution can be used to study the reactions of lead (II).

1. Dissolving of lead metal

The lead metal, similar to silver metal, can be dissolved by heating with cc. nitric acid. During the reaction, the formation of the brownish nitrogen-dioxide can be observed.

$$3Pb + 2NO_3^{-} + 8H^{+} = 3Pb^{2+} + 2NO\uparrow + 4H_2O$$

$$2NO + O_2 = 2NO_2 \qquad \boxed{\text{brown}}$$

2. Group reaction

By adding hydrogen-chloride, lead-ion gives white precipitate. The solid can be observed just if the concentration of the lead-ion is high enough, therefore the reaction is not sensitive enough if the concentration of the lead-ion is too low. The precipitation can be dissolved by heating, so the chloride precipitation of lead(II) can be washed from the other chlorides of group Ia.

$$Pb^{2+} + 2Cl^- = \underline{PbCl_2} \qquad \boxed{\textbf{white}}$$

3. Reactions with halogenides

The lead-ion also gives precipitates with halogenides. Characteristic is its reaction with iodide that gives golden yellow precipitation. By adding excess of solid potassium-iodide the formation of tetraiodo-plumbate(II) ($[PbI_4]^{2-}$) can be observed.

$$Pb^{2+} + 2I^- = \underline{PbI_2} \qquad \boxed{\textbf{golden yellow}}$$

In the excess of ammonium-hydroxide the lead-halogenide precipitation is not dissolving, but the sodium-hydroxide offer enough concentration of the hydroxid-ion to form tetrahydroxo-plumbate(II) complex, and finally leading to dissolution of the halogenide precipitation.

$$PbCl_2 + 4OH^- = [Pb(OH)_4]^{2-} + 2Cl^-$$

4. Precipitation with hydrogen-sulphide

Even if the pH is acidic, lead-ion gives black lead-sulphide precipitation. As the first step, the redish-brown lead-sulphide-chloride precipitate that will be transformed to the black lead-sulphide. The solubility product constant of the precipitate is very low.

$$Pb^{2+} + H_2S = \underline{PbS} + 2H^+ \qquad \boxed{\textbf{black}}$$

The sulphide precipitation can be dissolved by using cc. nitric acid, while the mixture of brownish nitrogen-oxides is forming.

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

5. Reaction with sodium-hydroxide and ammonium-hydroxide

By adding dropwise sodium-hydroxide solution, white lead-hydroxide precipitates, that dissolves in the excess of the reagent as tetrahydroxo-plumbate(II).

$Pb^{2+} + 2OH^{-} = \underline{Pb(OH)_2}$ **white**

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

The hydroxide precipitation is also forming with ammonium-hydroxide that can not be dissolved in the excess of the reagent.

6. Reaction with chromate-ion

By adding chromate-ion, yellow lead-chromate precipitation is forming. The precipitation does not dissolve neither in diluted nitric-acid nor in ammonia. In sodium-hydroxide solution, the precipitation is dissolving parallel with the formation of the yellow chromate-ion.

$Pb^{2+} + CrO_4^{2-} = \underline{PbCrO_4}$ **yellow**

7. Precipitation with sulphate-ions

The addition of sulphate-ion (e.g. diluted sulphuric-acid) precipitate white lead-sulphate that can be dissolved in the excess of alkaline-hydroxides via formation of tetrahydroxo-plumbate(II).

$Pb^{2+} + SO_4^{2-} = \underline{PbSO_4}$ **white**

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

5.1.3. Reactions of Mercury(I)-ion

Mercury is a chemical element, with the symbol Hg. Mercury is heavy silvery-white, the only metallic element that is liquid at standard conditions for temperature and pressure. It is a poor conductor of heat, but a fair conductor of electricity. Mercury is used: in thermomethers, especially ones which are used to measure high temperatures; as gaseous mercury in fluorescent lamps. Mercury and its compounds for eaxample mercury (I)-chloride (chalomel) was used internally in medicine and in optometry. Another useful and important application of the mercury is as an amalgam in dentistry. Dental amalgam is formed by mixing liquid mercury with an alloy made of silver, tin, and copper solid particles. Mercury and its compounds are toxic. The water soluble mercury compounds are more toxic, because of their easier absorption, but the hydrophyl mercury compounds in the organism can get throught to the membrane causing serious impairment. In the organism, mercury reacts with the thiole (-

SH) group, hence the corresponding functions are blocked. Mercury and most of its compounds are extremely toxic; elemental mercury is volatile, by inhalation chronic poisoning were effected. Symptoms typically include headache, nerves, memory weakening, salivation. Solid sulfur is used in spill kits to absorb mercury.

Mercury (I)-nitrate (0.025 M) solution can be used to study the reactions of mercury (I) ion.

1. Dissolving of mercury metal

Mercury metal can be dissolved by heating with cc. nitric acid. During the reaction, the formation of the brownish nitrogen-dioxide can be observed.

$$3Hg + 2NO_3^- + 8H^+ = 3Hg^{2+} + 2NO\uparrow + 4H_2O$$

$$2NO + O_2 = 2NO_2 \qquad \boxed{\textbf{brown}}$$

2. Group reaction

By adding hydrogen-chloride, mercury(I)-ion gives white (calomel) precipitate. The solid does not dissolve by using the usual complex-forming (OH^-, NH_3) agents. When ammonia is added to the white precipitation, the colour turns black thanks to the disproportion of the mercury, and the mixture of white mercury(I)-amido-chloride, and black elemental mercury is forming. The disproportion is characteristic for mercury(I).

$$Hg_2^{2+} + 2Cl^- = \underline{Hg_2Cl_2} \qquad \boxed{\textbf{white}}$$

$$Hg_2Cl_2 + 2NH_3 = \underline{Hg} + \underline{HgNH_2Cl} + NH_4^+ + Cl^- \quad \boxed{\textbf{black}}$$

3. Reactions with halogenides

The mercury(I)-ion gives greyish-green precipitation with iodide. The reaction is not stoichiometric and two parallel reactions take place. First, the instable yellowish-green mercury(I)-iodide is precipitating, but the excess of iodide-ions inducing the disproportion of mercury(I)-ion. Accordingly, mercury(I)-iodide dissolves partially as mercury(II)-iodide, and parallel with this, elemental mercury is forming. The greyish-green colour is due to the absorbed elemental mercury on mercury(I)-iodide.

$$Hg_2^{2+} + 2I^- = \underline{Hg_2I_2} \qquad \boxed{\textbf{yellow-green}}$$

$$Hg_2I_2 + 2I^- = \underline{Hg} + [HgI_4]^{2-} \qquad \boxed{\textbf{greyish-green}}$$

4. Precipitation with hydrogen-sulphide

Even if the pH is acidic, mercury(I)-ion gives black precipitation. During the precipitation, disproportion take place, therefore the mixture of mercury(II)-sulphide and elemental mercury is forming.

$$Hg^{2+} + S^{2-} = \underline{HgS} + \underline{Hg} \qquad \boxed{\text{black}}$$

The mercury(II)-sulphide can be dissolved from the mixture by using sodium-sulphide, because the basic pH helps to the formation of dithio-mercurate(II) complex.

$HgS + S^{2-} = [HgS_2]^{2-}$

The mixture of mercury(II)-sulphide and mercury metal can also be separated by using cc. nitric acid, because mercury(II)-sulphide does not dissolve while mercury metal dissolves according to equation 1.

5. Reaction with sodium-hydroxide and ammonium-hydroxide

Sodium-hydroxide causes the disproportion of mercury(I)-ion, while yellow mercury(II)-oxide and black mercury metal are forming.

$$Hg_2^{2+} + 2OH^- = \underline{HgO} + \underline{Hg} + H_2O \quad \boxed{\text{black}}$$

With ammonia, in the presence of nitrate-ion, disproportion take place, and next to the formation of mercury metal, brown basic mercury(II)-amido-nitrate can be obtained.

$$4Hg_2^{2+} + NO^{3-} + NH_3 + 3OH^- = \underset{\boxed{\text{brown}}}{\underline{HgO.HgNH_2NO_3}} + 2\underline{Hg} + 2H_2O$$

The formed precipitate does not dissolve neither in NaOH, nor in NH_4OH.

6. Redox reactions

Mercury(I)-ion can be easily reduced with copper metal to elemental mercury. Technically, one drop of the solution of mercury(I)-salt is added on the clean copper plate, that, on the dropping point became grey. The grey spot can easily be removed, and will disappear on heating.

$$Hg_2^{2+} + Cu = 2\underline{Hg} + Cu^{2+} \qquad \boxed{\text{grey}}$$

The reduction can also be achieved by using hydrochloric acid solution of tin(II)-chloride (Bettendorf reagent).

$Hg_2Cl_2 + [SnCl_4]^{2-} = 2\underline{Hg} + [SnCl_6]^{2-}$ **grey**

5.1.4. Simple analysis of cation group Ia

All cations give white precipitate with dilute hydrochloric acid (HCl). Ammonia is added to the mixture; if the precipitate is dissolved, silver (Ag^+) is present; if it becomes black, mercury(I) (Hg_2^{2+}) is present; if the precipitate does not change, lead(II) (Pb^{2+}) is present.

5.2. Cation group Ib

5.2.1. Reactions of Mercury(II)-ion

Applications and physiological effects of the elemental mercury and its compounds were discussed at mercury(I) ion. $HgCl_2$ (0.05 M) solution can be used to study the reactions of mercury(II) ion.

1. Group reaction

Mercury(II) gives no precipitation with hydrogen-chloride, but its acidic solution gives black sulphide precipitation with hydrogen-sulphide. In the presence of chloride-ions different composition of mercury(II)-chloride-sulphide is forming, and its colour turns from yellow to black, depending on the ratios of mercury(II)-sulphide.

$$(HgS)_x(HgCl_2)_y$$

$$Hg^{2+} + S^{2-} = \underline{HgS} \qquad \boxed{\text{black}}$$

2. Reaction with sodium-hydroxide and ammonium-hydroxide

Sodium-hydroxide gives typical yellow mercury(II)-oxide that characteristic for noble metal (water elimination from the hydroxide). The precipitate can not be dissolved in the excess of the reagent, because mercury(II) does not form hydroxy-complex.

$$Hg^{2+} + 2OH^- = \underline{HgO} + H_2O \qquad \boxed{\text{yellow}}$$

By adding ammonia white mercury(II)-amido-chloride is forming, that is soluble in hydrochloric acid.

$$HgCl_2 + 2NH_3 = \underline{HgNH_2Cl} + NH_4^+ + Cl^- \qquad \boxed{\text{white}}$$

3. Reactions with halogenides

The mercury(II)-ion gives dawn red precipitation with iodide, that is completely different from the colour of mercury(I)-iodide. In the small excess of the reagent, the mercury(II)-iodide dissolves as tetraiodo-mercurate(II).

$$Hg^{2+} + 2I^- = \underline{HgI_2} \qquad \boxed{\text{dawn red}}$$

$$HgI_2 + 2I^- = [HgI_4]^{2-} \qquad \boxed{\text{pale yellow}}$$

The formed complex has a pale yellow colour and its basic solution is sensitive toward the ammonia (Nessler-reagent). Mercury(II)-iodide precipitation with solid sodium-bromide gives a mixed composition complex (diiodo-dibromo-mercurate(II), Nessler-Winkler-reagent), that is colourless so the identification of ammonia is easier than with Nessler-reagent.

$$HgI_2 + 2Br^- = [HgI_2Br_2]^{2-}$$

4. Redox reactions

Similar to mercury(I), mercury(II) can also be easily reduced with copper metal to elemental mercury. The process is also similar, one drop of the solution of mercury(II)-salt is added on the clean copper plate, that, on the dropping point became grey. The grey spot can easily be removed, and will disappear on heating.

$$Hg^{2+} + Cu = \underline{Hg} + Cu^{2+} \quad \boxed{\textbf{grey}}$$

With the acidic solution of tin(II)-chloride (Bettendorf reagent) mercury(II)-ion gives first mercury(I)-chloride precipitation, that in the excess of reagent become grey because elemental mercury is forming.

$$2HgCl_2 + [SnCl_4]^{2-} = \underline{Hg_2Cl_2} + [SnCl_6]^{2-} \quad \boxed{\textbf{white}}$$

$$Hg_2Cl_2 + [SnCl_4]^{2-} = 2\underline{Hg} + [SnCl_6]^{2-} \quad \boxed{\textbf{black}}$$

5. Thermal analysis

It is characteristic for mercury salts that after heating they are able to sublimate.

Mercury salt	Observations
Hg_2Cl_2	Melt at 277 °C. Boil at 304 °C and without changes crystallize at the wall of the vial
$HgCl_2$	Sublimate at 384 °C without melting and crystallize at the wall of the vial
$HgNH_2Cl$	Decomposes to mercury(II)-chloride, nitrogen and ammonia. From these, mercury(II)-chloride sublimate
HgO	Decomposes to elemental mercury and to oxygen
HgS	Decomposes to elemental mercury and to sulphur-dioxide

5.2.2. Reactions of Copper(II)-ion

Copper is a chemical element, with the symbol Cu. The clean metal copper is ruddy, and widely good thermal and electrical conductor. Thanks to this properties in electrotechnics and in the integrated circuits is applied. It is a soft, malleable metal, therefore it has several building engineering application. Besides of this copper is used as a constituent of various metal alloys. Also in low concentration metal copper and its salts have antibacterial and antifungal activities. Copper is not formed in the body and must be ingested from dietary sources every day. Some foods are especially rich in copper: nuts, seeds, chickpeas, liver and oysters, cereals, meat and fish. Copper is needed by animals and plants also, it plays an important part in normal growth and metabolism. Copper has been used in medicine, it helps to prevent inflammation in arthritis and similar diseases. There are some anti-ulcer and anti-inflammatory medicines containing copper, and it is used in radiology and for treating convulsions and epilepsy.

In aqueous solution, the copper(II) ion has a pale-blue colour, whereas a concentrated aqueous solution of copper(I) chloride is green. In its compounds the oxidation state of copper is +1 or

+2. Copper(II) sulphate ($CuSO_4$, Fehling I solution) can be used to study the reactions of copper(II).

1. Dissolving of copper metal

The copper metal can be dissolved by heating with cc. nitric acid. During the reaction, the formation of the brownish nitrogen-dioxide can be observed. Copper metal is also soluble in cc. sulphuric acid.

$$3Cu + 2NO_3^- + 8H^+ = 3Cu^{2+} + 2NO\uparrow + 4H_2O$$

$$2NO + O_2 = 2NO_2 \qquad \boxed{\text{brown}}$$

$$Cu + SO_4^{2-} + 4H^+ = Cu^{2+} + SO_2\uparrow + 2H_2O$$

2. Group reaction

Copper(II) gives no precipitation with hydrogen-chloride, but its acidic solution gives brownish-black sulphide precipitation with hydrogen-sulphide that dissolves in cc nitric acid.

$$Cu^{2+} + S^{2-} = \underline{CuS} \qquad \boxed{\text{brownish-black}}$$

$$3CuS + 2NO_3^- + 8H^+ = 3Cu^{2+} + 3\underline{S} + 2NO\uparrow + 4H_2O$$

3. Reaction with sodium-hydroxide and ammonium-hydroxide

By adding sodium-hydroxide solution, light-blue precipitation is forming that after heating transforms to the brown copper(II)-oxide *via* water elimination (noble metal character).

$$Cu^{2+} + 2OH^- = \underline{Cu(OH)_2} \qquad \boxed{\text{light-blue}}$$

$$\underline{Cu(OH)_2} = \underline{CuO} + H_2O \qquad \boxed{\text{brown}}$$

The hydroxide precipitation is also forming with ammonium-hydroxide that in the excess of the reagent dissolves as blue tetraamine-copper(II) complex.

$$Cu(OH)_2 + 4NH_3 = [Cu(NH_3)_4]^{2+} + 2OH^-$$

4. Reaction with potassium-iodide

Iodide-ion reduces copper(II) to copper(I)-iodide, while elemental iodine is forming. The brownish colour of the iodine can be disappeared by using thiosulphate, and in this case the white colour of copper(I)-iodide can be observed.

$$2Cu^{2+} + 4I^- + = \underline{CuI} + I_2 \qquad \boxed{\text{white}}$$

$$I_2 + 2S_2O_3^{2-} = 2I^- + S_4O_6^{2-}$$

In the high excess of iodide copper(I)-iodide is dissolving in form of diiodo-cuprate(I).

$$CuI + I^- = [CuI_2]^-$$

5. Reaction with potassium-cyanide

Caution! The reactions should be carried out in alkaline conditions in the presence of ammonia! By adding cyanide-ion to copper(II)-ion first, yellowish-white copper(II)-cyanide is forming. The precipitate after heating will be transformed to the white copper(I)-cyanide and parallel with this, dicyan gas is eliberating.

$$Cu^{2+} + 2CN^- = \underline{Cu(CN)_2} \qquad \boxed{\text{yellowish-white}}$$

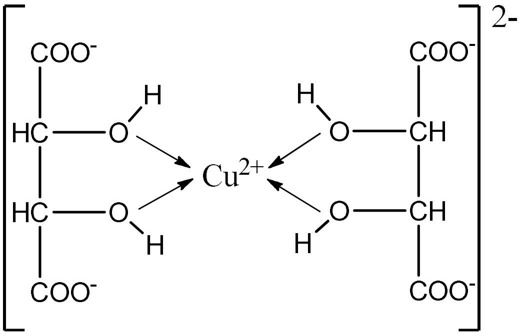
$$2Cu(CN)_2 = 2\underline{CuCN} + (CN)_2\uparrow \qquad \boxed{\text{white}}$$

If the reagent is in excess, copper(I)-cyanide is dissolving in the form of tetracyano-cuprate(I) complex.

$$CuCN + 3CN^- = [Cu(CN)_4]^{3-}$$

6. Fehling-reaction

The alkaline solution of copper(II) reduces aldehydes and reducing sugars to the corresponding carboxylic acids. In alkaline medium copper(II) can be kept in solution by mixing copper(II)-sulphate and basic potassium-sodium tartrate. Some drops of formaldehyde solution is added to the mixture, and the formation of red copper(I)-oxide will be observed. It should be mentioned, that sometimes copper-mirror can also be formed.



$$2Cu^{2+} + CH_2O + 5OH^- = \underline{Cu_2O} + HCOO^- + 3H_2O \qquad \boxed{\text{red}}$$

7. Reduction to elemental copper

Elemental copper is precipitating onto the surface of Fe and Zn (metals with more negative normal potential).

$$Cu^{2+} + Fe = \underline{Cu} + Fe^{2+}$$

The ammoniac solution of copper(II)-ion can be reduced to elemental copper by adding solid sodium-dithionite on heating.

$$2[Cu(NH_3)_4]^{2+} + S_2O_4^{2-} = 2Cu^+ + 2SO_2 + 4NH_3$$

$$2Cu^+ + S_2O_4^{2-} = 2\underline{Cu} + 2SO_2$$

8. Thermal analysis

Volatile copper-halogenides colour the colourless Bunsen-flame to green. By heating organic halogenocompounds in the presence of elemental copper, the forming copper-halogenides will also colour the colourless Bunsen-flame to green (Beilstein-test).

5.2.3. Reactions of Cadmium(II)-ion

Cadmium is a chemical element, with the symbol Cd. Cadmium compounds are used as red, orange and yellow pigments to color glass and to stabilize plastics. Application of cadmium is decreasing because it is toxic, nickel-cadmium batteries have been replaced with nickel-metal hydride and lithium-ion batteries. One of its few new uses are cadmium telluride solar panels. Several cadmium compounds have useful laboratory applications: cadmium sulfide (CdS) is used as a photoconductive surface, helium–cadmium lasers are common sources of blue-ultraviolet laser light. The water soluble cadmium compounds are absorbed rapidly and they are toxic, up to about 30 mg of cadmium is commonly inhaled throughout human childhood and adolescence. Cadmium potentially affecting mechanisms and risks of cancer, cardiovascular disease, and osteoporosis. Cadmium is an environmentally hazard element.
The oxidation state of cadmium in its compounds is +2. A $CdSO_4$ (0.05 M) solution can be used for studies.

1. Dissolving of cadmium metal

The cadmium metal, opposite to the other metals from group I, dissolves with hydrogen formation in the acids.

2. Group reaction

The characteristic yellow cadmium-sulphide precipitates only from acidic medium. The precipitate is dissolving in diluted acids, and during the reaction hydrogen-sulphide eliberating.

$$Cd^{2+} + S^{2-} = \underline{CdS} \quad \boxed{\text{yellow}}$$

$$CdS + 2H^{+} = Cd^{2+} + H_2S\uparrow$$

3. Reaction with sodium-hydroxide and ammonium-hydroxide

By adding sodium-hydroxide, white cadmium(II)-hydroxide is forming that in the excess of the reagent does not dissolve.

$$Cd^{2+} + 2OH^{-} = \underline{Cd(OH)_2} \quad \boxed{\text{white}}$$

The hydroxide precipitation is also forming with ammonium-hydroxide that in the excess of the reagent dissolves as tetraamine-cadmium(II) complex.

$$Cd(OH)_2 + 4NH_3 = [Cd(NH_3)_4]^{2+} + 2OH^{-}$$

Cadmium(II)-hydroxide precipitation is also dissolving by adding solid potassium-iodide. In this case tetraiodo-cadmiate(II) is forming.

$$Cd(OH)_2 + 4I^{-} = [CdI_4]^{2-} + 2OH^{-}$$

6. Reaction with potassium-cyanide

Caution! The reactions should be carried out in alkaline conditions in the presence of ammonia! By adding cyanide-ion to cadmium(II)-sulphate, white cadmium(II)-cyanide is forming. In the excess of the reagent, the precipitate dissolves as tetracyano-cadmiate(II).

$$Cd^{2+} + 2CN^{-} = \underline{Cd(CN)_2} \quad \boxed{\text{white}}$$

$$Cd(CN)_2 + 2CN^{-} \rightleftharpoons [Cd(CN)_4]^{2-}$$

The stability of the cyano-complex is relatively low, so by adding hydrogen-sulphide yellow cadmium(II)-sulphide precipitates. This latter reaction can be used to identify cadmium(II)-ion next to those ions that form stable complexes with cyanide (*e.g.* Cu^{2+}). The process is named as “masking” of the disturbing ion with cyanide-ion.

$$[Cd(CN)_4]^{2-} + S^{2-} = \underline{CdS} + 4CN^{-} \quad \boxed{\text{yellow}}$$

5.2.4. Reactions of Bismuth(III)-ion

Bismuth is a chemical element, with the symbol Bi. It is a brittle metal with a silvery white color. Bismuth has an important metallurgic application, many bismuth alloys have low melting points and are found in special applications such as solders. The most significant alloy is bismuth-telluride (Bi_2Te_3), which is a semiconductor and an excellent thermoelectric (Seebeck-effect) material. Compared to the other heavy metals, compounds of bismuth have unusually low toxicity. Some of the bismuth compounds, for example bismuth oxychloride (BiOCl) is used in cosmetics, as a pigment in paint for eye shadows, nail polishes and hair sprays. Bismuth subsalicylate is used in medicine as an antidiarrheal and it is also used to treat some gastrointestinal diseases.

In its compounds, bismuth has the oxidation state +3 or +5. In water, the compounds hydrolyse, forming basic bismuth salts. The reactions can be studied on $Bi(NO_3)_3$ (0.05 M) solution.

1. Dissolving of bismuth metal

The bismuth metal can be dissolved by heating with cc. nitric acid. During the reaction, the formation of the brownish nitrogen-dioxide can be observed.

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

$$2NO + O_2 = 2NO_2 \qquad \boxed{\textbf{brown}}$$

2. Hydrolysis

Bismuth(III)-ion exists only in strong acidic conditions. In the presence of chloride-ions, even after dilution (adding diluted hydrochloric acid), white bismuthyl-chloride can be formed. This latter reaction (hydrolysis) can disturb the correct classification of bismuth(III)!

$$Bi^{3+} + Cl^- + H_2O \rightleftharpoons \underline{BiOCl} + 2H^+ \qquad \boxed{\textbf{white}}$$

3. Group reaction

Despite of the strong acidity of the solution, bismuth(III)-ion gives black sulphide precipitation with hydrogen-sulphide that dissolves in cc nitric acid.

$$2Bi^{3+} + 3S^{2-} = \underline{Bi_2S_3} \qquad \boxed{\textbf{black}}$$

$$\underline{Bi_2S_3} + 2NO_3^- + 8H^+ = 2Bi^{3+} + 3\underline{S} + 2NO\uparrow + 4H_2O$$

4. Reaction with potassium-iodide

Iodide-ion precipitates characteristic brownish-black bismuth(III)-iodide. In the excess of iodide, the precipitation can easily be dissolved as tetraiodo-bismuthate(III).

$$Bi^{3+} + 3I^- = \underline{BiI_3} \quad \boxed{\textbf{brownish-black}}$$

$$BiI_3 + I^- = [BiI_4]^- \quad \boxed{\textbf{orange solution}}$$

5. Reaction with sodium-hydroxide and ammonium-hydroxide

By adding sodium-hydroxide or ammonium-hydroxide, both of them precipitates white bismuth(III)-hydroxide that is not soluble in the excess of the reagents. It is characteristic for bismuth, that bismuth(III)-hydroxide after heating, will be transformed in a two-step reaction to bismuth(III)-oxide, while the white colour of the precipitation turns to yellow.

$$Bi^{3+} + 3OH^- = \underline{Bi(OH)_3} \quad \boxed{\textbf{white}}$$

$$Bi(OH)_3 = \underline{BiO(OH)} + H_2O \quad \boxed{\textbf{yellowish-white}}$$

$$2BiO(OH) = \underline{Bi_2O_3} + H_2O \quad \boxed{\textbf{yellow}}$$

6. Reduction to elemental bismuth

Alkaline solution of tetrahydroxo-stannate(II) reduces bismuth(III)-ion to elemental bismuth.

$$2Bi(OH)_3 + 3[Sn(OH)_4]^{2-} = 2\underline{Bi} + 3[Sn(OH)_6]^{2-} \quad \boxed{\textbf{black}}$$

Bismuth(III)-ion can be identified by a so-called induced reaction. The redox reaction between tetrahydroxo-plumbate(II) and tetrahydroxo-stannate(II) is very slow. At room temperature, even after one hour the separation of elemental lead cannot be observed. The bismuth(III)-ion catalysis the reaction and at the same time its reduction is also occurs.

$$[Pb(OH)_4]^{2-} + [Sn(OH)_4]^{2-} \xrightarrow{Bi^{3+}} \underline{Pb} + [Sn(OH)_6]^{2-} + 2OH^-$$

5.2.5. Simple analysis of cation group Ib

If HCl does not give a precipitate, H_2S is added. HgS, Bi_2S_3, CuS or CdS can be formed. CdS is yellow. If the precipitate is black, sodium hydroxide solution is added to a new test solution: a white precipitate indicates bismuth(III), a yellow precipitate mercury(II), and a blue one copper(II). The identity of the cations has to be proved through other characteristic reactions.

5.3. Cation group II

5.3.1. Reactions of Arsenite(III)-ion (AsO_3^{3-})

Arsenic is a chemical element with the symbol As. Arsenic is a metalloid. It has various allotropes: yellow, black, gray. Gallium arsenide is the second most common semiconductor after doped silicon. Due to the toxicity arsenic and its compounds are used in the production of pesticides, herbicides and insecticides. The most extensive industrial use of arsenic is in the wood preservative, chromated copper arsenate (also known as CCA or Tanalith) was used in this field, however reports health risk. Arsenic compounds were used in medicine: arsphenamine (syphilis and trypanosomiasis), arsenic trioxide (cancer). Due to the the non-demonstrability of the arsenic, it was used as a poison immemorially („Poison of the Kings, king of the poisons”). Since the invention of the Marsh probe (James Marsh, 1836), presence of the arsenic is easily demonstrable. Already 60 mg of arsenic trioxide in the organism causes death. The symptoms of the acute poison: puke, diarrhea, the skin feel cold. The hydrogen arsenide gas (H_3As) has hemolytic effect and it is very toxic.

In its compounds, arsenic has an oxidation state of -3, +3, +5. Arsenite (AsO_3^{3-}) and arsenate (AsO_4^{3-}) are colourless. The reactions can be studied on an aqueous solution of As_2O_3 (0.05 M).

1. Group reaction

Arsenite-ion in acidic medium gives yellow arsenic(III)-sulphide precipitation. In this case the stoichiometric amount of the acid is necessary.

$$2AsO_3^{3-} + 3S^{2-} + 12H^+ = \underline{As_2S_3} + 6H_2O \quad \boxed{\text{yellow}}$$

The precipitation is soluble in ammonium-sulphide, ammonium-hydroxide and in ammonium-carbonate, forming thioarsenite (AsS_3^{3-}) complex.

$$As_2S_3 + 3S^{2-} = 2AsS_3^{3-}$$

$$As_2S_3 + 6OH^- = AsO_3^{3-} + AsS_3^{3-} + 3H_2O$$

$$As_2S_3 + 3CO_3^{2-} = AsO_3^{3-} + AsS_3^{3-} + 3CO_2\uparrow$$

2. Precipitation with silver-nitrate

Arsenite-ion gives yellow silver-arsenite with silver-ion. The precipitate is soluble in diluted nitric acid and ammonia.

$$3Ag^{+} + AsO_3^{3-} = \underline{Ag_3AsO_3} \quad \boxed{\text{yellow}}$$

3. Reaction with elemental iodine

Arsenite reduces elemental iodine in frame of an equilibrium reaction, while iodide-ion and arsenate are forming. During the reaction, the brown colour of iodine will disappear. To increase the solubility of the reagent (iodine), the reagent is an aqua solution of potassium-iodide/iodine.

$$AsO_3^{3-} + I_2 + H_2O \rightleftharpoons AsO_4^{3-} + 2I^{-} + 2H^{+}$$

During the reaction acid is forming, that can be neutralized by using sodium-hydrogen-carbonate. By acidification, the reaction can be shifted to the formation of iodine.

4. Bettendorf-test

The solution of tin(II)-chloride in cc. hydrochloric acid (Bettendorf-reagent) reduces arsenic compounds to arsenic. The reagent is added in approx. 5 times excess to the examined sample, then it will be heated, and stand at room temperature. If the amount of arsenic was small, the formed brownish-grey precipitation will appeared only after 30 min. If the concentration is high enough, the formed black precipitation can be observed immediately.

$$2AsCl_3 + 3SnCl_2 = 2\underline{As} + 3SnCl_4 \quad \boxed{\text{brownish-grey or black}}$$

5. Marsh-test

The base of this reaction is that arsenic compounds can be reduced to arsene-hydrogen (AsH_3) with nascent hydrogen. The formed AsH_3 by heating decomposes to arsenic and hydrogen. Furthermore, burning of AsH_3, arsenic-trioxide as white smoke can be observed.

$$As_2O_3 + 6Zn + 12H^{+} = 2AsH_3\uparrow + 3H_2O + 6Zn^{2+}$$

$$2AsH_3 = 2As + 3H_2 \quad \boxed{\text{arsenic-mirror}}$$

$$2AsH_3 + 3O_2 = As_2O_3 + 3H_2O \quad \boxed{\text{white smoke}}$$

Technically, the test is carried out in a Marsh apparatus, in which hydrogen is evolved from metallic zinc with sulphuric acid. After drying in a $CaCl_2$-tube, the gas is conducted through a high-melting glass-tube in which there is constriction. When the gas has become free of air it is ignited and glass-tube before the constriction is heated with a flame: no brownish-black arsenic mirror is formed if the reagents are arsenic-free (blank-test).

Next, the test substance is placed in the gas-evolving tube. If an arsenic mirror is formed at the constriction during 20 min., the substance contains arsenic. In the presence of a significant amount of arsenic, the flame is extinguished with a porcelain plate, an arsenic mirror is formed on it. The reaction is highly sensitive. Antimony gives similar mirror, but arsenic is soluble in hypochlorite (NaOCl), whereas antimony is insoluble.

6. Gutzeit-test

It can be interpreted as a technically simplified Marsh-test. The test solution, metallic zinc and dilute sulphuric acid are placed in a test-tube with cotton-wool in the mouth of the tube, filter paper on it, $AgNO_3$ crystals on the paper. The crystals become yellow and then black when treated with a few drops of water. The reaction is highly sensitive.

$$AsH_3 + 6AgNO_3 = \underline{Ag_3As.3AgNO_3} + 3HNO_3 \quad \boxed{\text{yellow}}$$

$$Ag_3As.3AgNO_3 + 3H_2O = 6\underline{Ag} + H_3AsO_3 + 3HNO_3 \quad \boxed{\text{black}}$$

7. Thiele-test

In this reaction, hypophosphite ($H_2PO_2^-$) reduces arsenic compounds to elemental arsenic, while phosphite (phosphonic acid) is forming.

$$2AsO_3^{3-} + 3H_2PO_2^- + 9H^+ = 2\underline{As} + 3H_3PO_3 + 3H_2O \quad \boxed{\text{brown}}$$

5.3.2. Reactions of Arsenate(V)-ion (AsO_4^{3-})

Applications and physiological effects of the elemental arsenic and its compounds see at arsenite ion. The reactions can be studied on Na_2HAsO_4 solution (0.05 M).

1. Group reaction

Arsenate-ion only in strong acidic conditions and after heating gives yellow arsenic(III)-sulphide precipitation, that makes difficulties for classification of As(V)-ion. During the reaction, hydrogen-sulphide reduces arsenate to arsenite, while elemental sulphur is forming. Arsenic(V)-sulphide precipitates only with special conditions: e.g. strong acidic conditions and by using quick hydrogen-sulphide flow.

$$H_3AsO_4 + H_2S = H_3AsO_3 + \underline{S} + H_2O$$

$$2H_3AsO_4 + 3H_2S = \underline{As_2S_3} + 6H_2O \quad \boxed{\text{yellow}}$$

The solution of arsenic(III)-sulphide in alkaline medium gives the same reaction discussed in frame of arsenite.

2. Precipitation with silver-nitrate

Arsenate-ion gives chocolate-brown silver-arsenate with silver-ion. The precipitate is soluble in diluted nitric acid and ammonia.

$$AsO_4^{3-} + 3Ag^+ = \underline{Ag_3AsO_4} \quad \boxed{\text{chocolate-brown}}$$

3. Precipitation with magnesium-mixture

By applying magnesium-nitrate in ammonium-chloride buffer, white magnesium-ammonium-arsenate precipitates, that is not specific for arsenite. Phosphates can disturb the determination, and their presence can be checked by using silver-nitrate.

$$Mg^{2+} + NH_4^+ + AsO_4^{3-} = \underline{MgNH_4AsO_4} \quad \boxed{\text{white}}$$

4. Determination of arsenate in low concentration

See Marsh-, Gutzeit- and Thiele-test described for arsenite!

5.3.3. Reactions of Antimony(III)-ion

Antimony is a chemical element with the symbol Sb. Antimony is a breakable, lustrous gray metalloid, it is a bad electric and heat conductor. The largest applications for metallic antimony is as an alloy with lead. Alloys of lead with antimony have improved properties for solders, bullets, and plain bearings. It is used in semiconductor as a dopant in the preparation of diods, infrared detectors. Antimony trioxide has a flame retarding effect, it is used for the production of fireproof plastics, clothes, paint. Antimony(III) sulfide is used in the heads of safety matches. Antimony compounds have been already used in medicine and cosmetics since ancient times, often known by the Arabic name, kohl. They are used as antiprotozoan drugs, potassium antimonyl tartarate is used as an antischistosomal drug in developing countries. Compounds of antimony are toxic, especially antimony trioxide and antimony potassium tartarate. May cause respiratory irritation, cardiac arrhythmias, gastrointestinal symptoms. The hydrogen antimony gas (H_3Sb) is very toxic, like hydrogen arsenide (H_3As), causes hemolysis.

In its compounds, antimony exhibits an oxidation state of +3 or +5. In water antimony(III) compounds are readily hydrolysed. The reactions can be studied on $SbCl_3$ solution (0.15 M).

1. Hydrolysis

Antimony(III)-chloride can only be dissolved via complex-formation by using 1 M hydrochloric-acid. Antimony(III)-ion exists only in strong acidic conditions. In the presence of chloride-ions, even after dilution (adding diluted hydrochloric acid), white antimonyl-chloride can be formed. This latter reaction (hydrolysis) can disturb the correct classification of antimony(III)! The reaction is similar with that observed for bismuth(III), the difference is that antimonyl-chloride can be dissolved in tartaric acid.

$$[SbCl_4]^- + H_2O \rightleftharpoons \underline{SbOCl} + 2H^+ + 3Cl^- \quad \boxed{\textbf{white}}$$

2. Group reaction

Antimony(III)-ion in acidic conditions gives orange-red sulphide precipitation with hydrogen-sulphide.

$$2Sb^{3+} + 3S^{2-} = \underline{Sb_2S_3} \quad \boxed{\textbf{orange-red}}$$

The precipitate dissolves as thioantimonate (SbS_3^{3-}) by adding ammonium-sulphide. It is also soluble in excess of ammonium-hydroxide and in 20 % hydrochloric acid. The precipitate can not be dissolved with ammonium-carbonate, that together with its solubility with hydrochloric-acid, differs from arsene-sulphide.

$$Sb_2S_3 + 3S^{2-} = 2SbS_3^{3-}$$

$$Sb_2S_3 + 4OH^- = SbS_3^{3-} + [Sb(OH)_4]^-$$

$$Sb_2S_3 + 6H^+ + 8Cl^- = 2[SbCl_4]^- + 3H_2S$$

Antimony(III)-sulphide can also be dissolved in ammonium-polisulphide. In this case antimony(III) will be oxidized and thioantimonate is forming.

$$Sb_2S_3 + 3S^{2-} + 2S = 2SbS_4^{3-}$$

3. Reaction with sodium-hydroxide and ammonium-hydroxide

By adding sodium-hydroxide or ammonium-hydroxide, both of them precipitates white antimony(III)-acid, that in the excess of sodium-hydroxide dissolves. The precipitation does not dissolve even in the excess of cc ammonium-hydroxide.

$$Sb^{3+} + 3OH^- + H_2O = H[Sb(OH)_4] \quad \boxed{\text{white}}$$

$$H[Sb(OH)_4] + OH^- = [Sb(OH)_4]^- + H_2O$$

4. Redox reactions

In weak acidic conditions, by adding elemental zinc or iron, black elemental antimony is forming.

$$2Sb^{3+} + 3Fe = \underline{2Sb} + 3Fe^{2+} \quad \boxed{\text{black}}$$

By using zinc, in acidic medium nascent hydrogen is forming that forms antimony(III)-hydrogen (SbH_3). This can disturb the Marsh- and Gutzeit-test of arsenic compounds.

5.3.4. Reactions of Antimony(V)-ion

Applications and physiological effects of the elemental antimony and its compounds can be seen at antimony(III) ion. The reactions can be studied on potassium hexahydroxo antimonate(V) solution (0.05 M).

1. Group reaction

The solution of hexahydroxo-antimonate(V) is alkaline, and for the group reaction with hydrogen-sulphide acidic condition is needed. Antimony(V)-ion can only by dissolved by using cc hydrochloric acid, and during the acidification white antimonic acid precipitates, that in the excess of reagent dissolves via complex-formation. By using this hexachloro-antimonate(V)-ion, in acidic medium, hydrogen-sulphide gives orange-red antimony(V)-sulphide precipitation. The precipitate is not stable and transforms to antimony(III)-sulphide, while elemental sulphur is forming.

$$2SbCl_6^- + 5S^{2-} = \underline{Sb_2S_5} + 12Cl^- \quad \boxed{\text{orange-red}}$$

$$Sb_2S_5 = Sb_2S_3 + 2S$$

Further reactions of antimony(III)-sulphide can be found among the reactions of antimony(III). Antimony(V)-sulphide dissolves in cc. hydrochloric acid with elemental sulphur formation.

$$Sb_2S_5 + 6H^+ + 8Cl^- = 2[SbCl_4]^- + 3H_2S + 2\underline{S}$$

2. Reaction with potassium-iodide

In strong acidic conditions, antimony(V) oxidizes iodide-ion into iodine, that can be observed as brownish solution.

$$[SbCl_6]^- + 2I^- \rightleftharpoons I_2 + [SbCl_4]^- + 2Cl^- \quad \boxed{\textbf{brown solution}}$$

5.3.5. Reactions of Tin(II)-ion

Tin is a chemical element with the symbol Sn. It is a soft metal, with low melting point. Tin in combination with other elements forms a variety of useful alloys, for example with lead as a solder, with copper as an ingredient of the bronze. Tin-plated steel containers are used for food preservation. Tin(II) fluoride is added to some dental care products. The main application of tin compound is in the stabilization of PVC plastics. Tributyltin oxide is used as a wood preservative and fungicide. Organic tin compounds are more toxic than inorganic representatives.

In its compounds, tin has an oxidation state of +2 or +4. Tin(II) compounds are used as reductants, because of the ready oxidation to tin(IV). The reactions can be studied on tin(II) chloride solution (0.05 M) in hydrochloric acid, where the tin(II) is actually present as the tetrachlorostannate(II) complex ($SnCl_4^{2-}$).

1. Group reaction

Tin(II)-ion in acidic conditions gives brown tin(II)-sulphide precipitation with hydrogen-sulphide. The precipitation is not soluble in ammonium-sulphide, but ammonium-polisulphide dissolves it by oxidation via thiostannate ($[SnS_3]^{2-}$) formation. The acidification of thiostannate gives yellow tin(IV)-sulphide precipitate.

$$Sn^{2+} + S^{2-} = \underline{SnS} \quad \boxed{\textbf{brown}}$$

$$SnS + S_2^{2-} = [SnS_3]^{2-}$$

$$[SnS_3]^{2-} + 2H^+ = \underline{SnS_2} + H_2S \quad \boxed{\textbf{yellow}}$$

Tin(II)-sulphide is not soluble neither in ammonium-hydroxide nor in ammonium-carbonate, but it dissolves in 20 % hydrochloric acid, when hydrogen-sulphide is liberated.

$$SnS + 4HCl = [SnCl_4]^{2-} + H_2S\uparrow + 2H^+$$

2. Reaction with sodium-hydroxide and ammonium-hydroxide

By adding sodium-hydroxide or ammonium-hydroxide, both of them precipitates white tin(II)-hydroxide, that dissolves in the excess of sodium-hydroxide as tetrahydroxo-stannate(II) complex.

$$Sn^{2+} + 2OH^- = \underline{Sn(OH)_2} \quad \boxed{\textbf{white}}$$

$$\underline{Sn(OH)_2} + 2OH^- = [Sn(OH)_4]^{2-}$$

If the solution of tetrahydroxo-stannate(II) stays for longer time, or is heated, disproportion of tin(II) takes place, and hexahydroxo-stannate(IV) is forming and grey tin metal separates out from the solution.

$$2[Sn(OH)_4]^{2-} = \underline{Sn} + [Sn(OH)_6]^{2-} + 2OH^- \quad \boxed{\textbf{grey}}$$

3. Redox reactions

Tin(II)-ion is a strong reducing compound. In alkaline medium tetrahydroxo-stannate(II) reduces bismuth(III)-ion to bismuth metal (see reactions of bismuth(III)-ions), while in acidic conditions mercury-ions can be reduced to elemental mercury (see reactions of mercury-ions). Tin(II)-ion in acidic conditions cannot be reduced with iron metal (difference from antimony), but the reaction works with zinc metal.

$$[SnCl_4]^{2-} + Zn = \underline{Sn} + Zn^{2+} + 4Cl^-$$

4. Luminescence-test

A small amount of stannane (SnH_4) can be formed when tin compounds are treated with hydrogen. If concentrated hydrochloric acid and zinc filings are added to a solution of tin compound in a porcelain vessel and the mixture is stirred with a test-tube half filled with water, when the tube is held in a Bunsen flame a blue luminescence can be observed on its external surface. This colour is due to the decomposition of SnH_4. This is a characteristic and sensitive reaction; arsenic compounds interfere.

$$Sn^{2+} + 6'H' = SnH_4 + 2H^+$$

5.3.6. Reactions of Tin(IV)-ion

Applications and physiological effects of the elemental tin and its compounds see at tin(II) ion. The reactions can be carried out with ammonium hexachlorostannate(IV) solution (0.05 M). In water the $(NH_4)_2SnCl_6$ is hydrolysed. Hydrochloric acid is therefore used for dissolution when $SnCl_6^{2-}$ ions are present in the solution.

1. Group reaction

Tin(IV)-ion in acidic conditions gives yellow tin(IV)-sulphide precipitation with hydrogen-sulphide. *(Note: for visible precipitation, use concentrated tin(IV) solution. Otherwise, only the solution will turn yellow.)* The precipitation is soluble in ammonium-sulphide as thiostannate ($[SnS_3]^{2-}$). The acidification of thiostannate gives yellow tin(IV)-sulphide precipitate that dissolves in 20 % hydrochloric acid, and during the reaction hydrogen-sulphide is liberated.

$$Sn^{4+} + 2S^{2-} = \underline{SnS_2} \quad \boxed{\text{yellow}}$$

$$\underline{SnS_2} + S^{2-} = [SnS_3]^{2-}$$

$$[SnS_3]^{2-} + 2H^+ = \underline{SnS_2} + H_2S$$

$$SnS_2 + 6Cl^- + 4H^+ = [SnCl_6]^{2-} + 2H_2S$$

2. Reaction with sodium-hydroxide and ammonium-hydroxide

By adding sodium-hydroxide or ammonium-hydroxide, both of them precipitates white tin(IV)-hydroxide, but only the excess of sodium-hydroxide is able to dissolve as hexahydroxo-stannate(IV) complex.

$$[SnCl_6]^{2-} + 4OH^- = \underline{Sn(OH)_4} + 6Cl^- \quad \boxed{\text{white}}$$

$$Sn(OH)_4 + 2OH^- = [Sn(OH)_6]^{2-}$$

3. Redox reactions

By using iron metal tin(IV)-ion can be reduced to tin(II)-ion, but elemental tin does not form (compare with the reactions of Sb(III)-ions and Sn(II)-ions). Zinc metal in acidic medium reduces tin(IV)-ion first to tin(II)-ion, then the elemental tin is also precipitate out from the solution.

$$[SnCl_6]^{2-} + Zn = [SnCl_4]^{2-} + 2Cl^- + Zn^{2+}$$

$$[SnCl_4]^{2-} + Zn = \underline{Sn} + Zn^{2+} + 4Cl^-$$

5.3.7. Simple analysis of cation group II

With a solution in hydrochloric acid, H_2S gives a precipitate. If its colour is yellow, arsenite, arsenate or tin(IV) is present. (Arsenates precipitates only at boiling!) The sulphides are soluble in ammonium sulphide. If the yellow precipitate is insoluble in 20% HCl, but soluble in ammonium carbonate, arsenite or arsenate is present. If the yellow sulphide precipitate can be dissolved in 20% HCl, but not in ammonium carbonate, tin(IV) is present. In the case of antimony(III) or antimony(V), the precipitate is orange. If the precipitate is brown, tin(II) sulphide was formed, which dissolves in ammonium polysulphide, and gives a yellow precipitate of SnS_2 with HCl. Proof: if the original solution is treated with mercury(II) chloride, white mercury(I) chloride is precipitated; then, in the case of a tin(II) excess, grey metallic mercury is formed.

5.4. Cation group III

5.4.1. Reactions of Cobalt(II)-ion

Cobalt is a chemical element with a symbol Co. Cobalt is a hard, ferromagnetic metal. Cobalt has been used in the production of high-performance alloys and rechargeable batteries. Cobalt-based alloys are corrosion- and wear-resistant, and they have a high temperature stability. Cobalt has also been used as a pigment to make smalt, a blue-colored glass. Cobalt pigments (cobalt blue, cobalt green, cobalt violet) are used as artist's pigments. In terms of radiotherapy and technologic Cobalt-60 isotope is useful as a gamma-ray source. Cobalt is an essential element for life. It is a central constituent of vitamin B12. Oral dose (20-50 mg) repairs the effect of the iron in anemia. However, chronic cobalt ingestion causes serious health problems: nausea, blood-pressure decrease.

In its compounds, cobalt has an oxidation number +2 or +3. Only the cobalt(II) compounds are stable; they are pink in aqueous solution, but the anhydrous salts are blue. The reactions can be studied on cobalt(II)-sulphate solution (0.05 M).

1. Group reaction

In alkaline or neutral medium ammonium-sulphide precipitates black cobalt(II)-sulphide. The precipitation cannot be formed in acidic medium. The sulphide precipitation is not soluble in diluted hydrochloric acid. This can be explained by the quick exchange between the first forming □-type crystal and almost insoluble □-type crystal form of the cobalt(II)-sulphide. In the presence of the air, cobalt(II)-sulphide will be transformed to cobalt(III)-sulphide. The colour of this latter crystal is also black.

$$Co^{2+} + S^{2-} = \underline{CoS} \quad \boxed{\text{black}}$$

$$4CoS + 2S^{2-} + O_2 + 2H_2O = 2\underline{Co_2S_3} + 4OH^- \quad \boxed{\text{black}}$$

Cobalt(II)-sulphide with oxidative reagents (hydrogen-peroxide/acetic acid; bromine/HCl; cc. nitric acid) dissolves by forming elementary sulphur.

$$3CoS + 2NO_3^- + 8H^+ = 3Co^{2+} + 3\underline{S} + 2NO\uparrow + 4H_2O$$

$$CoS + Br_2 = Co^{2+} + \underline{S} + 2Br^-$$

2. Reaction with sodium-hydroxide and ammonium-hydroxide

By adding sodium-hydroxide, first basic cobalt(II)-chloride is forming. that dissolves in the excess of the reagent by forming pink cobalt(II)-hydroxide. The hydroxide-precipitation both in the presence of the air and by using hydrogen-peroxide will be oxidized to the brownish cobalt(III)-hydroxide.

$$CoCl_2 + OH^- = \underline{Co(OH)Cl} + Cl^- \quad \boxed{\textbf{blue}}$$

$$Co(OH)Cl + OH^- = \underline{Co(OH)_2} + Cl^- \quad \boxed{\textbf{pink}}$$

$$2Co(OH)_2 + 1/2\ O_2 + H_2O = 2\underline{Co(OH)_3} \quad \boxed{\textbf{brown}}$$

Ammonium-hydroxide first precipitates blue basic cobalt(II)-chloride, that in the excess of the reagent dissolves as hexaamine-cobalt(II) complex. As the results of oxidation, the colour of the solution become brownish-red, thanks to the formation of hexaamine-cobalt(III) complex.

$$CoCl_2 + OH^- = \underline{Co(OH)Cl} + Cl^- \quad \boxed{\textbf{blue}}$$

$$Co(OH)Cl + 6NH_3 = [Co(NH_3)_6]^{2+} + OH^- + Cl^- \quad \boxed{\textbf{yellow solution}}$$

$$2[Co(NH_3)_6]^{2+} + 1/2\ O_2 + H_2O = 2[Co(NH_3)_6]^{3+} + 2OH^-$$
$$\boxed{\textbf{brownish-red solution}}$$

3. Reaction with potassium-cyanide

Caution! The reactions should be carried out in alkaline conditions in the presence of ammonia! By adding cyanide-ion, brownish-red cobalt(II)-cyanide is forming. In the excess of the reagent, the precipitate dissolves as brownish-yellow hexacyano-cobaltate(II) complex. The complex in this case is also able for oxidation by using hydrogen-peroxide, and the yellow hexacyano-cobaltate(III) is forming.

$$Co^{2+} + 2CN^- = \underline{Co(CN)_2} \quad \boxed{\textbf{red-brown}}$$

$$Co(CN)_2 + 4CN^- = [Co(CN)_6]^{4-} \quad \boxed{\textbf{brownish-yellow solution}}$$

$$2[Co(CN)_6]^{4-} + H_2O_2 = 2[Co(CN)_6]^{3-} + 2OH^- \quad \boxed{\textbf{yellow solution}}$$

4. Reaction with ammonium-thiocyanate

Cobalt(II)-ion with thiocyanate-ion gives pink precipitation, that by adding solid ammonium-thiocyanate and after extraction with organic solvents (diethyl-ether, benzyl-alcohol) dissolves with blue colour.

$$Co^{2+} + 2SCN^{-} = \underline{Co(SCN)_2} \quad \boxed{\text{pink}}$$

$$Co(SCN)_2 + 2NH_4SCN = H_2[Co(SCN)_4] + 2NH_3 \quad \boxed{\text{blue solution}}$$

5. Reaction with potassium-nitrite

In the presence of acetic acid, nitrite-ion oxidizes cobalt(II)-ion to cobalt(III), that will be stabilized by forming nitrito-complex (hexanitrito-cobaltate(III)). This latter complex in the presence of potassium-ion gives yellow precipitation.

$$Co^{2+} + NO_2^{-} + 2H^{+} = Co^{3+} + NO\uparrow + H_2O$$

$$Co^{3+} + 6NO_2^{-} + 3K^{+} = \underline{K_3[Co(NO_2)_6]} \quad \boxed{\text{yellow}}$$

6. Borax-test

The experiment will be achieved according to the process described earlier. In this case intensive blue coloured cobalt-borate is forming.

5.4.2. Reactions of Nickel(II)-ion

Nickel is a chemical element with the symbol Ni. It is white lustrous ferromagnetic metal. Nickel is widely used in many alloys with copper, aluminium, chromium, lead, silver, gold. Nickel foam or nickel mesh is used in gas diffusion electrodes for alkaline cells. Nickel and its alloys are often used as catalysts for hydrogenation reactions, for example Raney Nickel is widely used for hydrogenation of unsaturated oils to make margarine.

It is known that nickel plays an important role in the biology of some plants: eubacteria, archaebacteria or fungi. Urease, which is nickel-containing metalloenzyme, is considered a virulence factor in some organisms. Nickel compounds do not have therapeutic interests. The absorption of nickel salts is slowly and they are toxics. The main symptoms are stomachache, retching. In its compounds, nickel occurs as a coloured cation (often green) in an oxidation state of +2 or +3. The reactions can be studied on Nickel(II)-sulphate solution (0.05 M).

1. Group reaction

In alkaline or neutral medium ammonium-sulphide precipitates black nickel(II)-sulphide. The sulphide precipitation is not soluble in diluted hydrochloric acid. This can be explained by the quick exchange between the first forming □-type crystal and almost insoluble □-type crystal form of the nickel(II)-sulphide. In the presence of the air, nickel(II)-sulphide cannot be oxidized.

$$Ni^{2+} + S^{2-} = \underline{NiS} \quad \boxed{\textbf{black}}$$

Nickel(II)-sulphide can be dissolved by using cc. nitric acid, while elementary sulphur is forming.

$$3NiS + 2NO_3^- + 8H^+ = 3Ni^{2+} + 3\underline{S} + 2NO\uparrow + 4H_2O$$

2. Reaction with sodium-hydroxide and ammonium-hydroxide

By adding sodium-hydroxide green nickel(II)-hydroxide is forming, that does not dissolves in the excess of the reagent. The hydroxide-precipitation neither in the presence of the air nor by using hydrogen-peroxide cannot be oxidized (difference from cobalt(II)), but by using sodium-hypochlorite (NaOCl) black nickel(III)-hydroxide is forming.

$$Ni^{2+} + 2OH^- = \underline{Ni(OH)_2} \quad \boxed{\textbf{green}}$$

$$2Ni(OH)_2 + OCl^- + H_2O = 2\underline{Ni(OH)_3} + Cl^- \quad \boxed{\textbf{black}}$$

Ammonium-hydroxide first precipitates green nickel(II)-hydroxide, that in the excess of the reagent dissolves as hexaamine-nickel(II) complex.

$$Ni(OH)_2 + 6NH_3 = [Ni(NH_3)_6]^{2+} + 2OH^- \quad \boxed{\textbf{blue solution}}$$

3. Reaction with potassium-cyanide

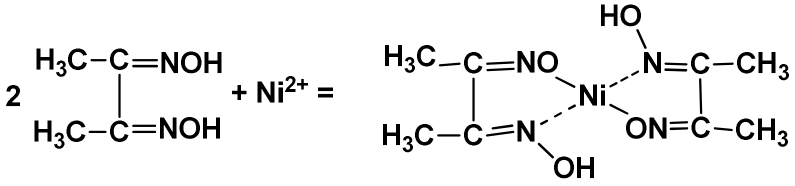
Caution! The reactions should be carried out in alkaline conditions in the presence of ammonia! By adding cyanide-ion, green nickel(II)-cyanide is forming. In the excess of the reagent, the precipitate dissolves as yellow tetracyano-nickelate(II) complex.

$$Ni^{2+} + 2CN^- = \underline{Ni(CN)_2} \quad \boxed{\textbf{green}}$$

$$Ni(CN)_2 + 2CN^- = [Ni(CN)_4]^{2-} \quad \boxed{\textbf{yellow solution}}$$

4. Precipitation with dimethyl-glioxime

In the presence of ammonia, alcoholic solution of glioxime, precipitates specific red bis(dimethylglioximato)-nickel(II) precipitation, that dissolves in strong acids. The chelate complex precipitates from the solution thanks to its neutrality and hydrophobic character.



5.4.3. Reactions of Iron(II)-ion

Iron is a chemical element with the symbol Fe, it is the most common element on Earth (35% weight of the Earth). Iron is the most widely used of all the metals, iron alloys (steel, inox, special steels) are most common industrial metals, because of their mechanical properties and their low cost. It can be found in many food: red meat, beans, fish, vegetables, black-eyed peas, lentils, poultry.

Iron is an essential element in the organism. The body of an adult human contains about 4-5 g of iron, mostly in hemoglobin and myoglobin. Iron deficiency is the most common nutritional deficiency in the world and it occurs anemia. In this case iron-complexes, such as iron-fumarate is added as a therapeutic use. Overdoses of iron is toxic, high level of free iron can get into the blood, which reacts with peroxides to produce highly reactive free radicals. Humans experience iron toxicity when the iron exceeds 20 milligrams for every kilogram of body mass; 60 milligrams per kilogram is considered a lethal dose.

In its compounds, iron exhibits an oxidation state of +2 or +3. Mainly in solution, iron(II) can be oxidized to iron(III); thus iron(II) is a reductant. The hydrated salts and aqueous solutions of iron(II) are green. The reactions can be studied on $FeSO_4$ solution (0.05 M).

1. Group reaction

In alkaline or neutral medium ammonium-sulphide precipitates black iron(II)-sulphide. The precipitation dissolves in week acids and hydrogen is liberated.

$$Fe^{2+} + S^{2-} = \underline{FeS}\ \boxed{\text{black}}$$

$$FeS + 2H^{+} = Fe^{2+} + H_2S\uparrow$$

2. Reaction with sodium-hydroxide and ammonium-hydroxide

By adding sodium-hydroxide and ammonium-hydroxide (excluding the oxygen from the air) white iron(II)-hydroxide precipitates. None of the excess of reagents are able to dissolve the precipitation. Leaving the precipitation in normal conditions its colour turns to greenish-white, and then to brown, that indicate the formation of iron(III)-hydroxide.

$$Fe^{2+} + 2OH^{-} = \underline{Fe(OH)_2} \quad \boxed{\textbf{white (greenish-white)}}$$

$$4Fe(OH)_2 + O_2 + 2H_2O = 4\underline{Fe(OH)_3} \quad \boxed{\textbf{brown}}$$

3. Precipitation with potassium-hexacyano-ferrate(III)

In the presence of hexacyano-ferrate(III)-ions, iron(II)-ion gives characteristic blue (Turnbull-blue) precipitation.

$$3Fe^{2+} + 2[Fe(CN)_6]^{3-} = \underline{Fe_3[Fe(CN)_6]_2} \quad \boxed{\textbf{blue}}$$

4. Redox reactions

Iron(II)-ion is a good reducing agent, therefore mild oxidants (bromine-water; hydrogen-peroxide) oxidize it to iron(III).

$$2Fe^{2+} + Br_2 = 2Fe^{3+} + 2Br^{-}$$

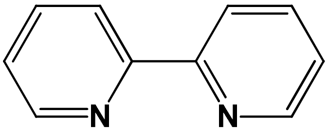
$$2Fe^{2+} + H_2O_2 + 2H^{+} = 2Fe^{3+} + 2H_2O$$

When permanganate-ion is added to the sulphuric acidic solution of iron(II)-ion, the violet colour of permanganate will disappear.

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

5. Complex-formation with α,α'-dipyridyl

In acidic medium, iron(II)-ion gives intensive red coloured complex with α,α'-dipyridyl. The reaction is characteristic and specific.



5.4.4. Reactions of Iron(III)-ion

Applications and physiological effects of the elemental iron and its compounds can be seen at iron(II) ion. Iron(III) compounds are more stable than those of iron(II) in aqueous solution they are pale-yellow; the solution is acidic because of hydrolysis. The reactions can be carried out with $FeCl_3$ solution (0.05 M).

1. Group reaction

Parallel reactions can be observed by reacting iron(III)-ion with ammonium-sulphide. In alkaline or neutral conditions sulphide-ion reduces iron(III)-ion to iron(II)-ion, this latter formed ion gives black iron(II)-sulphide. Otherwise, in the week alkaline conditions, the hydrolysis of iron(III)-ion can be observed and brownish-red iron(III)-hydroxide precipitates.

$$2Fe^{3+} + S^{2-} = 2Fe^{2+} + \underline{S}$$

$$Fe^{2+} + S^{2-} = \underline{FeS} \quad \boxed{\textbf{black}}$$

$$2Fe^{3+} + 3S^{2-} + 6H_2O = 2\underline{Fe(OH)_3} + 3H_2S$$

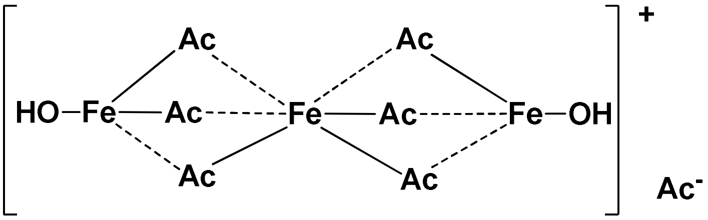
2. Reaction with sodium-hydroxide and ammonium-hydroxide

By adding sodium-hydroxide and ammonium-hydroxide gelatinous brownish-red white iron(III)-hydroxide precipitates, that is not soluble in the excess of reagents, but using mineral acids it can be dissolved.

$$Fe^{3+} + 3OH^{-} = \underline{Fe(OH)_3} \quad \boxed{\textbf{redish-brown}}$$

3. Precipitation with sodium-acetate

In the presence of acetate-ions, from neutral solution, iron(III)-ion forms brownish-red hexaacetato-dihydroxo-triferri-acetate.



hexaacetato-dihydroxo-triferri-acetate

4. Precipitation with potassium-hexacyano-ferrate(II)

In the presence of hexacyano-ferrate(II)-ions, iron(III)-ion gives characteristic blue (Preussen-blue) precipitation.

$$4Fe^{3+} + 3[Fe(CN)_6]^{4-} = \underline{Fe_4[Fe(CN)_6]_3} \quad \boxed{\text{blue}}$$

5. Reaction with potassium-iodide

Iron(III)-ion does not give precipitation with iodide-ion, and iron(III)-ion oxidizes it, and during the reaction, the formation of the brown iodine can be observed.

$$2Fe^{3+} + 2I^- = 2Fe^{2+} + I_2 \quad \boxed{\text{brown solution}}$$

5. Complex-formation with thiocyanate

By adding ammonium-thiocyanate to iron(III)-ion, various compositional iron(III)-thiocyanate complex is forming. Its colour is red, and with sodium-fluoride this colour will disappear while the more stable colourless iron(III)-fluoride complex is forming.

$$Fe^{3+} + n\,SCN^- = [Fe(SCN)_n]^{3-n} \quad \boxed{\text{red solution}}$$

$$[Fe(SCN)_n]^{3-n} + n\,F^- = [Fe(F)_n]^{3-n} + n\,SCN^-$$

5.4.5. Reactions of Manganese(II)-ion

Manganese is a chemical element with the symbol Mn. It is a transition metal with important industrial alloy use, especially in stainless steel. Manganese is used as a pigments of various colors, which depend on the oxidation state of the ions. Permanganate is a well known listerine, because it has a strong oxidative effect. Manganese compounds are less toxic than other metals, such as nickel end copper. Manganese is an essential human dietary element, it is present as a coenzyme in several biological processes, bone formation, free radical defense systems.

In its compounds, manganese exhibits an oxidation state of +2, +3, +4, +6 or +7. Mn(II) and Mn(III) occur as cations, while the anions mangante (MnO_4^{2-}) and permangante (MnO_4^-) contain manganese with oxidation numbers of +6 an +7. Mn(II) compounds are pink. Mn(III) is of no analytical importance. Among the Mn(IV) compounds, the brown water-insoluble MnO_2 is very common. Manganate is green, and permanganate is purple. Mn(IV), Mn(VI) and Mn(VII) compounds are reduced by H_2S, and in systematic analysis they are therefore found as Mn(II). The reactions can be studied on $MnSO_4$ solution (0.05 M).

1. Group reaction

In alkaline or neutral conditions sulphide-ion with manganese(II)-ion precipitates salmon-pink manganese(II)-sulphide. The precipitate dissolves in diluted mineral acids, while hydrogen-sulphide eliberating. The precipitation in the presence of the air, or by adding hydrogen-peroxide turns to brown, because of the formation of basic manganese(IV)-oxide.

$$Mn^{2+} + S^{2-} = \underline{MnS} \quad \boxed{\textbf{salmon-pink}}$$

$$MnS + 2H^+ = Mn^{2+} + H_2S\uparrow$$

$$MnS + O_2 + H_2O = \underline{MnO(OH)_2} + S \quad \boxed{\textbf{brown precipitate}}$$

2. Reaction with sodium-hydroxide and ammonium-hydroxide

By adding sodium-hydroxide and ammonium-hydroxide white manganese(II)-hydroxide precipitates, that can be oxidized easily in the air or by adding hydrogen-peroxide.

$$Mn^{2+} + 2OH^- = \underline{Mn(OH)_2} \quad \boxed{\textbf{white}}$$

$$2Mn(OH)_2 + O_2 = 2\underline{MnO(OH)_2} \quad \boxed{\textbf{brown precipitate}}$$

3. Oxidation to permanganate

By adding solid lead(IV)-oxide to the solution of manganese(II)-ion in cc sulphuric acid medium, after heating the appearance of permanganate-ion (violet colouration) can be observed.

$$2Mn^{2+} + 5PbO_2 + 4H^+ = 2MnO_4^- + 5Pb^{2+} + 2H_2O$$

The oxidation can also be achieved by using potassium-peroxodisulphate, in the presence of nitric acid. This reaction is catalysed by silver(I)-ions.

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

For the melting phase oxidations the five-time excess of the mixture (1:1) of sodium-hydroxide:potassium-nitrate is added to the solid manganese(II)-salt. The mixture will be melted then the cooled green coloured manganese-containing mixture will be dissolved in diluted acetic acid. The disproportion of manganese take place and next to the brown basic manganese(IV)-oxide, permanganate (with violet colour) is also forming.

$$MnSO_4 + 4NaOH + 2KNO_3 = Na_2MnO_4 + 2KNO_2 + Na_2SO_4 + 2H_2O$$

$$3MnO_4^{2-} + 4H^+ = 2MnO_4\text{-} + \underline{MnO(OH)_2} + H_2O$$

4. Oxidation with permanganate

Permanganate is a strong oxidizing agent, and it is oxidizing with 5 equivalents in acidic medium, while in alkaline medium with 3 equivalents. During the oxidation the disappearance of violet colour is characteristic.

$$2MnO_4^- + 5H_2S + 6H^+ = 2Mn^{2+} + 5\underline{S} + 8H_2O$$

$$2MnO_4^- + 5H_2O_2 + 6H^+ = 2Mn^{2+} + 5O_2\uparrow + 8H_2O$$

$$2MnO_4^- + 5(COO)_2^{2-} + 16H^+ = 2Mn^{2+} + 10CO_2\uparrow + 8H_2O$$

$$2MnO_4^- + 10I^- + 16H^+ = 2Mn^{2+} + 5I_2 + 8H_2O$$

$$2MnO_4^- + 3CH_3CH_2OH = 2MnO(OH)_2 + 2OH^- + 3CH_3CHO$$

5.4.6. Reactions of Chromium(III)-ion

Chromium is a chemical element with the symbol Cr. The elemental chromium is greyish white, lustrous transition metal. Particularly, it is used for the creation of metal alloys (85%), the remainder of chromium is used in the chemical, rafractory and foundry industries. Chromium is also the main additive in stainless steel, which provides anti-corrosive properties. Several chromium compounds (lead chromate, chromium oxides) are using as pigments. Chromium might play a role in the in the glucose metabolism. Chromium deficiency might cause disease. However chromium compounds are toxic, especially the chromates. By oral use puke, diarrhea, renal impaiment are caused. Frequent contact with chromates eczema, ulcerated sore are caused. Nevertheless chromates have carcinogen effects as well.

In its compounds, chromium has an oxidation state of +2, +3 or +6. Chromium(II) is of no analytical importance, because it can be oxidized to chromium(III), which is green. Chromium(VI) occurs in chromate (CrO_4^{2-}), which is yellow or orange. The reactions can be studied on $Cr_2(SO_4)_3$ solution (0.05 M).

1. Group reaction

Because sulphide-ion has a slightly alkaline character, the addition of ammonium-sulphide to chromium(III)-ions, the hydrolysis of it take place and green chromium(III)-hydroxide is forming.

$$Cr^{3+} + 3SH^{-} + 3H_2O = \underline{Cr(OH)_3} + 3H_2S \quad \boxed{\textbf{green}}$$

2. Reaction with sodium-hydroxide and ammonium-hydroxide

By adding sodium-hydroxide or ammonium-hydroxide, green chromium(III)-hydroxide precipitates. In the excess of sodium-hydroxide dissolves as greenish hexahydroxo-chromate(III) complex, while in the excess of ammonium-hydroxide, dissolves as violet hexamine-chromium(III) complex.

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

$$Cr(OH)_3 + 6NH_3 = [Cr(NH_3)_6]^{3+} + 3OH^{-} \quad \boxed{\textbf{violet solution}}$$

3. Oxidation to chromate

In alkaline medium, by adding hydrogen-peroxide, chromium(III)-hydroxide dissolves, and the appearance of yellow chromate can be observed.

$$2Cr(OH)_3 + 3H_2O_2 + 4OH^{-} = 2CrO_4^{2-} + 8H_2O \quad \boxed{\textbf{yellow solution}}$$

The reaction in acidic medium can be achieved by heating with solid ammonium-peroxodisulphate. Because of the acidic medium, in this case the characteristic orange colour of dichromate appear.

$$2Cr^{3+} + 3S_2O_8^{2-} + 7H_2O = Cr_2O_7^{2-} + 6SO_4^{2-} + 14H^{+} \quad \boxed{\textbf{orange solution}}$$

The reaction can also be achieved in melting phase. In this case the five-time excess of the mixture (1:1) of sodium-carbonate:potassium-nitrate is added to the solid chromium(III)-hydroxide. The mixture will be melted then the cooled yellow coloured mixture will be dissolved in water. The formed chromate-ion can be identified with lead-acetate.

$$Cr(SO_4)_3 + 3NaNO_3 + 5Na_2CO_3 = 2Na_2CrO_4 + 3NaNO_2 + 5CO_2 + 3Na_2SO_4$$

4. Chromate-dichromate equilibrium

In aqua phase chromate via water elimination can be transformed to dichromate while the oxidation number of chromium remains unchanged (+6). The equilibrium is depending on the pH. In acidic medium the orange dichromate, while in basic conditions yellow chromate is dominating.

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

5. Oxidation with dichromate

In sulphuric acid medium dichromate is a relatively strong oxidizing agent. It is oxidizing hydrogen-sulphide, ethanol, iron(II)-ions and hydrochloric acid (forming chlorine-gas). During the oxidation the dichromate is transformed to green chromium(III)-compounds.

$$Cr_2O_7^{2-} + 3H_2S + 8H^+ = 2Cr^{3+} + 3\underline{S} + 7H_2O$$

$$Cr_2O_7^{2-} + 3CH_3CH_2OH + 8H^+ = 2Cr^{3+} + 3CH_3CHO + 7H_2O$$

$$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ = 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

$$Cr_2O_7^{2-} + 6Cl^- + 14H^+ = 2Cr^{3+} + 3Cl_2\uparrow + 7H_2O$$

In the presence of sulphuric acid the reaction with hydrogen-peroxide take place in two steps. First, blue chromium-peroxide is forming, that in water via oxygen formation is decomposing. By extraction with diethyl-ether, the blue colour can be observed easily, because ether is coordinating to the chromium stabilizing the compound.

$$Cr_2O_7^{2-} + 4H_2O_2 + 2H^+ = 2CrO_5 + 5H_2O \qquad \boxed{\text{blue solution}}$$

5.4.7. Reactions of Aluminium(III)-ion

Aluminium is a chemical element with the symbol Al. Aluminium is the most widely used non-ferrous metal. The main use for aluminium metal is in the transportation (automobiles, railway cars, bicycles), packaging (cans, foil, frame), building and construction (windows, doors, roofing) electricity-related uses (conductor alloys, motors and generators), machinery and equipment (processing, pipes, tools). Aluminium has low density, it is non-toxic corrosion resistant, cheap and highly conductive metal. Aluminium salts can deposit in the brain. There is a research on correalation between Alzheimer's disease and aluminium levels. By external use water soluble aluminium compounds have protein precipitating and antiseptic effects.

In its compounds, aluminium occurs as a colourless cation in an oxidation state of +3. The reactions can be studied on aluminium-sulphate solution (0.05 M).

1. Group reaction

Because sulphide-ion has a slightly alkaline character, the addition of ammonium-sulphide to aluminium(III)-ions, the hydrolysis of it take place and gelatinous white aluminium(III)-hydroxide is forming. The precipitation can be dissolved by using acids. *Note: since ammonium-sulphide is often basic enough to dissolve* $Al(OH)_3$ *as tetrahydroxo-aluminate(III), add the reagent to aluminium(III)-ions dropwise.*

$$2Al^{3+} + 3S^{2-} + 6H_2O = \underline{2Al(OH)_3} + 3H_2S \quad \boxed{\text{white}}$$

2. Reaction with sodium-hydroxide and ammonium-hydroxide

By adding sodium-hydroxide, white gelatinous aluminium(III)-hydroxide is forming, that in the excess of the reagent dissolves as tetrahydroxo-aluminate(III). By adding solid ammonium-chloride the precipitation forms back, because with a slightly acidic reagents we decrease the concentration of hydroxyl-ion. Additionally, aluminium does not form amin-complex in the excess of the reagent. By heating, the reaction can furthermore shifted to the precipitate formation, because in this case the ammonia is removed from the system. This reaction identical and can be used to distinguish between zinc and aluminium.

$$Al^{3+} + 3OH^- = \underline{Al(OH)_3} \quad \boxed{\text{white}}$$

$$Al(OH)_3 + OH^- = [Al(OH)_4]^-$$

$$[Al(OH)_4]^- + NH_4^+ = \underline{Al(OH)_3} + NH_3 + H_2O \quad \boxed{\text{white}}$$

With ammonium-hydroxide also white aluminium(III)-hydroxide precipitates, that in the excess of the reagent does not dissolve.

3. Thenard-blue test

A slice of filtration paper is wetted with the solution of aluminium(III)-salt and dried. The process will be repeated with a solution of a cobalt-salt. After drying, the filtration paper will be annealed. The formation of the blue mixed oxide can be observed.

5.4.8. Reactions of Zinc(II)-ion

Zinc is a chemical element with the symbol Zn. The elemental application of zinc is in alloys and coatings. It is most commonly used as an anti-corrosion agent. Zinc is used as an anode material for batteries.

It is an essential mineral, zinc may be found in several active center of the enzymes (alcohol dehydrogenase), or plays the role as an activation ion (carbonic anhydrase). Insulin also contains zinc. A sufficient amount of zinc is needed for the development of the brain not only in embryo but also in early life. Zinc deficiency causes the following symptoms: loss of hair, diarrhea, losing weight, tasting, smelling and memory problems. Zinc has an antiseptic effect. Zinc-oxide is used in drying unguent. Zinc gluconate is used for the treatment of the common cold. Zinc chloride is one of the ingredients of the deodorants, zinc sulphate is component of the eye-drop.

In its compounds, zinc has an oxidation number of +2. Its reaction can be studied on $ZnSO_4$ solution (0.05 M).

1. Group reaction

By adding ammonium-sulphide to zinc(II)-ion, white zinc(II)-sulphide precipitation is forming. The precipitation is soluble in diluted mineral acids.

$$Zn^{2+} + H_2S = \underline{ZnS} + 2H^+ \quad \boxed{\text{white}}$$

$$ZnS + 2HCl = Zn^{2+} + 2Cl^- + H_2S$$

2. Reaction with sodium-hydroxide and ammonium-hydroxide

By adding sodium-hydroxide, white zinc(II)-hydroxide is forming, that in the excess of the reagent dissolves as tetrahydroxo-zincate(II).

$$Zn^{2+} + 2OH^- = \underline{Zn(OH)_2} \quad \boxed{\text{white}}$$

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

With ammonium-hydroxide also white zinc(II)-hydroxide precipitates, that dissolves in the excess of the reagent as tetraamine-zinc(II)-complex (differ comparing with aluminium(III)-hydroxide).

$$Zn(OH)_2 + 4NH_3 = [Zn(NH_3)_4]^{2+} + 2OH^-$$

Zinc(II)-hydroxide can also be dissolved by adding cyanide-ion. In this case tetracyano-zincate(II) is forming.

$$Zn(OH)_2 + 4CN^- = [Zn(CN)_4]^{2-} + 2OH^-$$

3. Precipitation with potassium-hexacyano-ferrate(II)

In the presence of hexacyano-ferrate(II)-ions, zinc(II)-ion gives white precipitation (differ comparing with aluminium(III)-ion!!).

$$2Zn^{2+} + [Fe(CN)_6]^{4-} = \underline{Zn_2[Fe(CN)_6]} \quad \boxed{\text{white}}$$

4. Rinmann-green test

A slice of filtration paper is wetted with the solution of zinc(II)-salt and dried. The process will be repeated with a solution of a cobalt-salt. After drying, the filtration paper will be annealed. The formation of the green mixed oxide can be observed.

5.4.9. Simple analysis of a cation group III

In ammonia-alkaline solution $(NH_4)_2S$ gives a precipitate.

(i) The precipitate is black in the cases of Co^{2+}, Ni^{2+}, Fe^{2+} and Fe^{3+}. In the case of cobalt(II) and nickel(II), the sulphides obtained with the group reagent $(NH_4)_2S$ are insoluble, but in the case of iron(II) and iron(III) are soluble in HCl. Cobalt(II) ion, in the reaction with NaOH a blue precipitate is formed, then in the excess of the reagent a pink solution is observed. The reaction with KNO_2 a yellow precipitate is formed. Nickel(II) ion in the reaction with NaOH a green precipitate is formed, which is insoluble in the excess of the reagent. With the alcoholic solution of dimethylglyoxime a deep-red complex is formed. Iron(II) ion with NaOH gives green-white precipitate, which quickly becomes brown through oxidation. In the case of iron(III) the reaction with NaOH a red-brown precipitate is observed.

(ii) The precipitate is not black in the cases of Cr^{3+}, Zn^{2+} Al^{3+} and Mn^{2+}.

–In the case of chromium(III) it is green. The reaction with NaOH a green precipitate is formed, which is soluble in the excess of the reagent.

–In the case of aluminium(III) it is white. The reaction with ammonia yields a white gelatinous precipitate which is insoluble in excess of the reagent. Thenard blue test also gives a positive reaction in the case of aluminium(III) ion.

–In the case of zinc(II) it is white. The reaction with ammonia a white precipitate is formed, which is soluble in NH_4OH. The Rinmann green test gives a positive reaction with zinc(II).

–In the case of manganese(II) it is salmon-pink. The reaction with NaOH a white precipitate is formed, which becomes brown in the air.

5.5. Cation group IV

5.5.1. Reactions of Calcium(II)-ion

Calcium is a chemical element with the symbol Ca. Calcium is a reactive, soft metal with low melting point. Calcium compounds are used in industry: in food and pharmaceuticals (calcium supplementation), in manufacture of soap, in paper industry as bleaches and as a component in cement. It is used as an alloying component in steelmaking and in making automotive batteries.

Calcium is an essential element, plays role in many biochemical process: it regulates the contraction of muscles, nerve conduction, clotting of blood. It is indispensable to the building of bone (hydroxyapatite, $Ca_5OH(PO_4)_3$) and of teeth (fluoroapatite, $Ca_5F(PO_4)_3$). The recommendable amount of calcium ingestion is necessary, about three-quarters of dietary calcium is from dairy products and grains, the rest from other foods (vegetables, protein-rich foods, sugar, oil). Calcium citrate, calcium lactate, but also calcium carbonate and calcium phosphates are also used as a nutritional supplement. Calcium has inflammation reducing effect.

The reactions can be studied on $CaCl_2$ solution (0.05 M).

1. Group reaction

In the presence of sulphide-ions, calcium(II)-ion gives no precipitation. Ammonium-carbonate precipitate white calcium(II)-carbonate, even in the presence of ammonia/ammonium-chloride puffer. The formation of the precipitate is not quantitative, because in this conditions hydrogen-carbonate is also present, that by heating can be removed from the system. The precipitate dissolves even by using carbonic acid.

$$Ca^{2+} + CO_3^{2-} = \underline{CaCO_3} \quad \boxed{\text{white}}$$

$$2HCO_3^- \rightleftharpoons H_2O + CO_2 + CO_3^{2-}$$

$$CaCO_3 + H_2O + CO_2 = Ca^{2+} + 2HCO_3^-$$

2. Precipitation with sulphate-ion

By adding reagent containing sulphate-ion (e.g. diluted sulphuric acid) white calcium(II)-sulphate is precipitating. The solubility ratio of the precipitate is relatively high, therefore its precipitates only from concentrated solution, that can be accelerate by adding ethanol.

$$Ca^{2+} + SO_4^{2-} = \underline{CaSO_4} \quad \boxed{\text{white}}$$

The precipitation is soluble in 20% hydrochloric acid, or by adding solid ammonium-sulphate. In this latter case disulphate-calciate is forming.

$$CaSO_4 + SO_4^{2-} = [Ca(SO_4)_2]^{2-}$$

3. Reaction with ammonium-oxalate

By adding ammonium-oxalate (even in acetic acid medium) white calcium(II)-oxalate precipitates. The reaction is sensitive and the formation of the white solid is quantitative. The precipitate cen be dissolve only with cc acids.

$$Ca^{2+} + C_2O_4^{2-} = \underline{Ca(COO)_2} \quad \boxed{\text{white}}$$

4. Precipitation with phosphates

Depending on the pH of the solution, white tertiary, or secondary calcium-phosphate precipitations are forming. The precipitation dissolves as primary phosphate in strong acids, or by adding acetic acid, but in this case heating is necessary.

$$Ca^{2+} + HPO_4^{2-} = \underline{CaHPO_4} \quad \boxed{\text{white}}$$

$$3Ca^{2+} + 2PO_4^{3-} = \underline{Ca_3(PO_4)_2} \quad \boxed{\text{white}}$$

$$CaHPO_4 + H^+ = Ca^{2+} + H_2PO_4^-$$

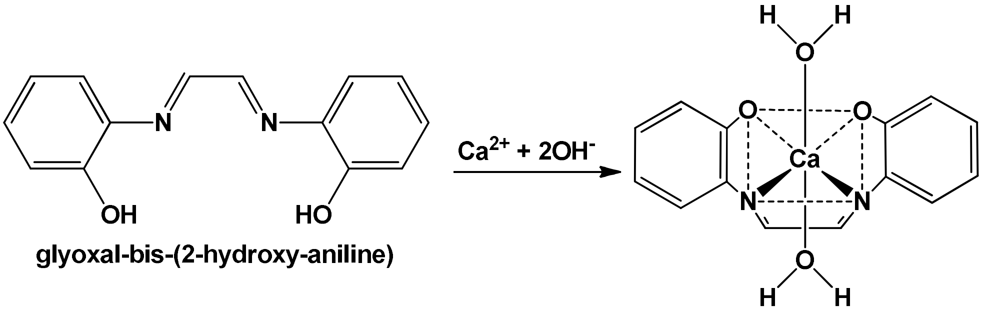
5. Reaction with potassium-hexacyano-ferrate(II)

By adding hexacyano-ferrate(II) in ammonia/ammonium-chloride puffer, after heating, white calcium(II)-ammonium-hexacyano-ferrate(II) precipitates. The precipitation is soluble in strong acids, and strontium(II)-ion or barium(II)-ion do not give this reaction.

$$Ca^{2+} + 2NH_4^+ + [Fe(CN)_6]^{4-} = \underline{Ca(NH_4)_2[Fe(CN)_6]} \quad \boxed{\text{white}}$$

6. Complex-formation with glyoxal-bis(2-hydroxyanil)

By adding 1% solution of glyoxal-bis(2-hydroxyanil), red chelate-complex is forming. This latter complex is soluble in chloroform. Ba^{2+} and Sr^{2+} also give colourful complexes, but these are not soluble in chloroform. By adding sodium-carbonate the selectivity of the reaction can be increased, because the disturbing strontium- and barium-ions give carbonate precipitations.



7. Flame colouration

Calcium(II)-ion, according to the method described in the chapter of methods, colour the colourless Bunsen flame to orange-red.

5.5.2. Reactions of Strontium(II)-ion

Strontium is a chemical element with a symbol Sr. It is a soft silver-white yellowish metal and it has high reactivity, similar to calcium. Strontium is absorbed by the body in a similar manner to calcium. Strontium aids bone growth and increases bone density. Strontium ranelate is used in the case of osteoporosis. The stable strontium isotopes are slightly toxic, but its presence in bones can cause bone cancer. In some cases these isotopes are used in radiotherapy.

The reactions can be studied on $Sr(NO_3)_2$ solution (0.05 M).

1. Group reaction

In the presence of sulphide-ions, strontium(II)-ion gives no precipitation. Ammonium-carbonate precipitate white calcium(II)-carbonate, even in the presence of ammonia/ammonium-chloride puffer. The precipitate dissolves even by using carbonic acid.

$$Sr^{2+} + CO_3^{2-} = \underline{SrCO_3} \quad \boxed{\text{white}}$$

2. Precipitation with sulphate-ion

By adding reagent containing sulphate-ion white strontium(II)-sulphate is precipitating. The solubility ratio of strontium(II)-sulphate is lower than this value for calcium(II)-sulphate, therefore by using saturated solution of calcium(II)-sulphate, the precipitation can be observed. In this case, strontium(II)-sulphate is forming slowly and the reaction can be accelerate by heating.

$$Sr^{2+} + SO_4^{2-} = \underline{SrSO_4} \quad \boxed{\text{white}}$$

3. Reaction with ammonium-oxalate

The white strontium(II)-oxalate precipitates only in slightly alkaline medium (difference from calcium(II)-oxalate). The precipitation dissolves in acetic acid only by heating.

$$Sr^{2+} + (COO)_2^{2-} = \underline{Sr(COO)_2} \quad \boxed{\text{white}}$$

4. Precipitation with phosphates

Depending on the pH of the solution, white tertiary, or secondary strontium-phosphate precipitations are forming. The precipitation dissolves as primary phosphate in strong acids, or by adding acetic acid, but in this case heating is necessary.

$$Sr^{2+} + HPO_4^{2-} = \underline{SrHPO_4} \quad \boxed{\text{white}}$$

$$SrHPO_4 + H^+ = Sr^{2+} + H_2PO_4^-$$

5. Reaction with potassium-chromate

By adding potassium-chromate (K_2CrO_4) strontium(II)-ion gives yellow strontium(II)-chromate precipitation in neutral conditions, that dissolves by adding acetic acid.

$$Sr^{2+} + CrO_4^{2-} = \underline{SrCrO_4} \quad \boxed{\text{yellow}}$$

6. Flame colouration

Strontium(II)-ion, according to the method described in the chapter of methods, colour the colourless Bunsen flame to Carmines-red.

5.5.3. Reactions of Barium(II)-ion

Barium is a chemical element with the symbol Ba. It is a silvery alkaline earth metal with high chemical reactivity like calcium and strontium. Barium compounds have several industrial applications: they are components of YBCO (high-temperature superconductors) and electroceramics; barium compounds are added to fireworks to impart the green colour;

barium sulphate is used as an additive to oil well drilling fluid. Furthermore in a pure form, barium is used as X-ray radiocontrast agent for imaging the human gastrointestinal tract.

Soluble barium compounds are poisonous, in low doses, barium act a muscle stimulant, and in higher doses affect the nervous system, causing cardiac irregularities, weakness, anxiety, paralysis. This toxicity may be caused by barium blocking potassium ion channels.

The reactions can be studied on $BaCl_2$ solution (0.05 M).

1. Group reaction

In the presence of sulphide-ions, barium(II)-ion gives no precipitation. Ammonium-carbonate precipitate white barium(II)-carbonate, even in the presence of ammonia/ammonium-chloride puffer. The precipitate dissolves even by using carbonic acid.

$$Ba^{2+} + CO_3^{2-} = \underline{BaCO_3} \quad \boxed{\text{white}}$$

$$BaCO_3 + H^+ = Ba^{2+} + HCO_3^-$$

2. Precipitation with sulphate-ion

By adding reagent containing sulphate-ion white barium(II)-sulphate is precipitating. The solubility ratio of barium(II)-sulphate is lower than for calcium(II)-sulphate and strontium(II)-sulphate, therefore by using saturated solution of calcium(II)-sulphate, the precipitation is forming. The precipitation is forming immediately comparing with strontium(II)-ion. The precipitate can only be dissolved by heating with cc sulphuric acid.

$$Ba^{2+} + SO_4^{2-} = \underline{BaSO_4} \quad \boxed{\text{white}}$$

Barium(II)-sulphate has one of the lowest solubility ratio in inorganic chemistry, therefore it can only be dissolved by using melt-phase solution. The sample is heated for 5-10 min. with the five-time excess of the mixture (1:1) of sodium-carbonate: potassium-carbonate. The melted mixture will be cooled down and by adding water sulphate-ion can be washed from the system and the formed barium(II)-carbonate will be dissolved by using hydrochloric acid.

$$BaSO_4 + Na_2CO_3 = BaCO_3 + Na_2SO_4$$

3. Reaction with ammonium-oxalate

The white barium(II)-oxalate precipitates only in slightly alkaline medium (difference from calcium(II)-oxalate). The precipitation dissolves in cold by adding acetic acid (difference from strontium(II)-oxalate).

$$Ba^{2+} + (COO)_2^{2-} = \underline{Ba(COO)_2} \quad \boxed{\text{white}}$$

4. Precipitation with phosphates

Depending on the pH of the solution, white tertiary, or secondary barium-phosphate precipitations are forming. The precipitation dissolves as primary phosphate in strong acids, or by adding acetic acid, but in this case heating is necessary.

$$Ba^{2+} + HPO_4^{2-} = \underline{BaHPO_4} \quad \boxed{\text{white}}$$

$$BaHPO_4 + H^+ = Ba^{2+} + H_2PO_4^-$$

5. Reaction with potassium-chromate or dichromate

By adding potassium-chromate or dichromate to barium(II)-ion, even in acetic acidic conditions, yellow barium(II)-chromate precipitation is forming (difference from strontium(II)-ion). During the reaction, acid is forming that shifts back the equilibrium. The precipitate forming process can be completed by adding sodium-acetate to the mixture. Barium(II)-chromate dissolves by adding strong acids.

$$2Ba^{2+} + Cr_2O_7^{2-} + H_2O = 2\underline{BaCrO_4} + H^+ \quad \boxed{\text{yellow}}$$

6. Flame colouration

Barium(II)-ion, according to the method described in the chapter of methods, colour the colourless Bunsen flame to pale-green.

5.5.4. Simple analysis of cation group IV

If no precipitation occurs with H_2S and $(NH_4)_2S$, ammonium carbonate is added to the test solution in the presence of NH_4Cl: a white precipitate is formed which is soluble in acids with the evolution of gas. Saturated $CaSO_4$ solution is added to a new test tube:

(i) even on boiling, the solution remains unchanged (clear): calcium

(ii) the solution is clear, but on boiling a white precipitate is formed: strontium

(iii) a white precipitate separates out immediately: barium is present.

To prove the identity, the flame test is applied. The flame is coloured orange-red by calcium, red by strontium and pale-green by barium. In addition, the identities can be confirmed with the oxalate and hexacyanoferrate reactions (calcium), while strontium and barium can be demonstrated with the chromate and bichromate reactions.

5.6. Cation group V

5.6.1. Reactions of Magnesium(II)-ion

Magnesium is a chemical element with the symbol Mg. It is a shiny gray solid element; is present naturally only in combination with other elements, but the free element can be prepared artificially. Magnesium is used as a component in alloys (aluminum-magnesium).

Magnesium is very important element in the human body, is essential to all cells and many enzymes require magnesium ions to function. In addition magnesium ion interacts with ATP, DNA and RNA. An adult human body contains 22-26 g of magnesium (60% in the skeleton, 39% intracellular and 1% extracellular). Magnesium deficiency causes the following cases: cramp, anxiety disorder, glycohemia, hypertension, osteoporosis. There are many food, which are rich sources of magnesium: spices, nuts, cereals, cocoa, vegetables (spinach). In the case of magnesium deficiency several pharmaceutical products of magnesium and dietary supplements are available in the market, such as magnesium oxide, magnesium citrate, chloride, lactate and aspartate. Magnesium stearate is used in pharmaceutical technology to prevent tablets from sticking to the equipment while compressing the ingredient into tablet form. More amount of soluble magnesium salt causes diarrhea.

The colourless magnesium has only the oxidation state +2. Its reactions can be studied on $MgCl_2$ solution (0.05 M).

1. Reaction with sodium-hydroxide and ammonium-hydroxide

By adding sodium-hydroxide or ammonium-hydroxide, both of them precipitates white magnesium(II)-hydroxide, for its dissolution the slightly acidic character of the present ammonium-ion is enough.

$$Mg^{2+} + 2NH_4OH \rightleftharpoons \underline{Mg(OH)_2} + 2NH_4^+ \quad \boxed{\text{white}}$$

$$Mg(OH)_2 + 2NH_4Cl = Mg^{2+} + 2NH_3 + 2H_2O + 2Cl^-$$

Note: $(NH_4)_2S$ can be basic enough to produce white $Mg(OH)_2$ precipitate too.

2. Reaction with sodium-carbonate

By excluding ammonium-ion sodium-carbonate precipitates white, various composition basic magnesium(II)-carbonate.

$$4Mg^{2+} + 4CO_3^{2-} + H_2O = \underline{Mg(OH)_2} \cdot \underline{3MgCO_3} + CO_2 \quad \boxed{\text{white}}$$

Ammonium-chloride dissolves the precipitation, because by decreasing of the pH carbonate concentration decreases and parallel with this the concentration of hydrogen-carbonate will increase. Hydrogen-carbonate gives no precipitation with magnesium(II)-ion.

$$MgCO_3 + NH_4Cl = Mg^{2+} + HCO_3^- + NH_3 + Cl^-$$

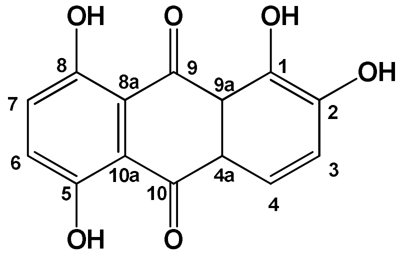
3. Reaction with secondary phosphate

By adding secondary phosphate-ion in the presence of ammonia/ammonium-chloride puffer, magnesium(II)-ion precipitates white magnesium(II)-ammonium-phosphate. Technically, ammonium-hydroxide is added to magnesium(II)-ion till opal formation can be observed. Then ammonium-chloride is added till the precipitate will be dissolved followed by adding of secondary phosphate. Many of the ions disturb this reaction, except ammonium-, sodium(I)-, and potassium(I)-ion.

$$Mg^{2+} + HPO_4^{2-} + NH_3 = \underline{MgNH_4PO_4}$$

4. Complex-formation with quinalizarine

Only few reactions of magnesium(II)-ion is known, and it has no flame colouration, therefore the complex-formation with quinalizarine is characteristic even if a lot of ions disturb the reaction.



1,2,5,8-tetrahydroxy-9,10-anthraquinone (quinalizarine)

Technically, the examined solution is added onto a watch-glass. Three drops of quinalizarin and sodium-hydroxide is added to the unknown, till the mixture become violet. If magnesium(II)-ion is present, blue precipitation can be observed.

5.6.2. Reactions of Lithium(I)-ion

Lithium is a chemical element with the symbol Li. It is a soft, silvery-white metal, which reacts vigorously with water while hydrogen is formed. Lithium compounds have several industrial application. Lithium oxide is used as a flux for processing silica in the preparation of ceramics and glass. Lithium is an important component of battery electrolytes and electrodes. Lithium hydroxide and lithium peroxide are used in the air purification.

Lithium has no known function is the human body, but it is an important trace element in some mammals (goat, rat). Lithium is used in the treatment of bipolar disorder. It could be a possible treatment for cluster headache. Lithium affects the action of the sodium channels. It is toxic only in big amount.

The reactions can be studied on LiCl solution (0.5 M).

1. Reaction with sodium-carbonate

By excluding ammonium-ion, sodium-carbonate precipitates white lithium(II)-carbonate. The precipitation can be dissolved by adding ammonium-chloride.

$$2Li^+ + CO_3^{2-} = \underline{Li_2CO_3} \quad \boxed{\textbf{white}}$$

$$Li_2CO_3 + NH_4^+ = 2Li^+ + HCO_3^- + NH_3$$

2. Reaction with secondary phosphate

By heating lithium(I)-ion and secondary phosphate-ion in alkaline medium (NaOH), white lithium(I)-phosphate precipitates.

$$3Li^+ + HPO_4^{2-} = \underline{Li_3PO_4} + H^+ \quad \boxed{\textbf{white}}$$

3. Flame colouration

Lithium(I)-ion, according to the method described in the chapter of methods, colour the colourless Bunsen flame to Carmines-red.

5.6.3. Reactions of Sodium(I)-ion

Sodium is a chemical element with the symbol Na. It is non stable in the air, sodium reacts vigorously with water while hydrogen is formed. Sodium is the sixth most abundant element in the Earth's crust.

Millions of tons of sodium chloride, hydroxide and carbonate are prepared annually. Sodium chloride is used ordinary in the kitchen as a salt (principal source of sodium in the diet), besides, it is used for anti-icing and de-icing as a preservative.

In human body, sodium is an essetial mineral that regulates blood volume, blood pressure, osmotic equilibrium and pH. Na^+ ion is an important electrolyte in neuron function and in osmoregulation between cells and the extracellular fluid. Sodium is the most frequent metallic ion in extracellular fluid. Low or high sodium levels in humans are known in medicine as hyponatremia and hypernatremia. These disease may be caused by genetic factors, diarrhea, ageing or prolonged vomiting.

Sodium has an oxidation number of +1. Sodium compounds are generally water-soluble, and only few reactions leading to a precipitate are known. The reactions can be studied on NaCl solution (1 M).

1. Reaction with potassium-hexahydroxo-antimonate(V)

In neutral or slightly alkaline medium sodium(I)-ion with potassium-hexahydroxo-antimonate(V) gives white precipitation. The reaction can be disturbed by many other ions.

$$Na^+ + [Sb(OH)_6]^- = \underline{Na[Sb(OH)_6]} \quad \boxed{\text{white}}$$

2. Reaction with zinc-uranyl-acetate

From the neutral or acetic acidic solution of sodium(I)-ion, zinc-uranyl acetate precipitates yellow sodium(I)-zinc-uranyl acetate. For the solid formation higher concentration is necessary, and a lots of ions disturb the identification.

$$2Na^+ + 3Zn(CH_3COO)_2 + 6UO_2(CH_3COO)_2 + 6H_2O = \underline{2NaZn(UO_2)_3(CH_3COO)_2 \cdot 6H_2O} + Zn^{2+}$$

$$\boxed{\text{yellow}}$$

3. Flame colouration

Sodium(I)-ion, according to the method described in the chapter of methods, colour the colourless Bunsen flame to intensive-yellow.

5.6.4. Reactions of Potassium(I)-ion

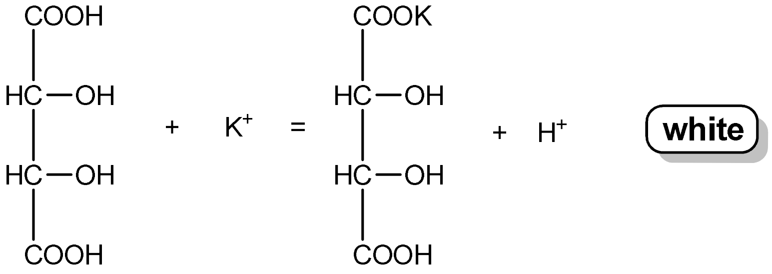
Potassium is a chemical element with the symbol K. It is a silvery-white metal, reacts vigorously with water while hydrogen is formed. Potasium compounds are used more often as a fertilizer, besides potassium is utilized in the preparation of glass and in the chemical industry.

Potassium is one of the most common element in the human body. K^+ is present in a wide variety of proteins and enzymes. Potassium, with sodium plays a key role in the action of nervous and muscle. Potassium deficiency causes myasthenia, dysrhythmia, decreased reflex response, and in more serious case paralysis. The physiological requirement for potassium is 5 g per day. Overdose potassium ingestion causes paralysis. Cardiac arrest is caused by intravenously dose.

In its salt, the colourless potassium exhibits an oxidation state of +1. Its reactions can be studied on KCl solution (0.1 M).

1. Reaction with tartaric acid

In the presence of sodium-acetate, potassium(I)-ion with the excess of tartaric acid gives white potassium-hydrogen-tartarate. Interesting to note that even tartaric acid is a dicarboxylic acid, with potassium only potassium-hydrogen-tartarate precipitates. If the tartaric acid is not in excess, potassium-tartarate is forming that is soluble in water. The role of sodium-acetate is that the reaction produces proton that can be puffered by using sodium-acetate. Ammonium-ion can disturb the determination and by heating it can be removed from the system.



$$\begin{array}{c} COOH \\ | \\ HC-OH \\ | \\ HC-OH \\ | \\ COOH \end{array} + K^+ = \begin{array}{c} COOK \\ | \\ HC-OH \\ | \\ HC-OH \\ | \\ COOH \end{array} + H^+ \quad \boxed{\text{white}}$$

$$CH_3COONa + H^+ \rightleftharpoons CH_3COOH + Na^+$$

2. Reaction with sodium-hexanitrito-cobaltate(III)

Hexanitrito-cobaltate(III)-complex can be prepared by mixing cobalt(III)-ion with nitrit-ion in the presence of acetic acid (see reactions of cobalt(II)-ion). This latter complex forms yellow precipitation with potassium(I)-ion.

$$3K^+ + [Co(NO_2)_6]^{3-} = \underline{K_3[Co(NO_2)_6]} \quad \boxed{\text{yellow}}$$

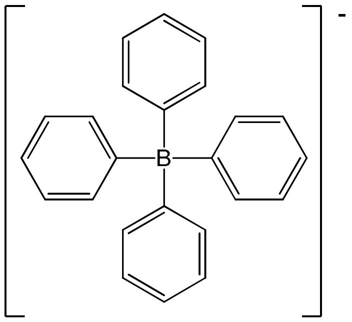
3. Reaction with perchloric acid

From the relatively high concentration of the potassium(I)-ion perchloric acid precipitates white potassium(I)-perchlorate. The solid formation can be accelerated by cooling, and ammonium-ions in high concentration also give positive reaction with perchloric acid.

$K^+ + ClO_4^- = \underline{KClO_4}$ $\boxed{\text{white}}$

4. Reaction with tetraphenyl-borate

Potassium(I)-ion with sodium(I)-tetraphenyl-borate gives white precipitation. The reaction is sensitive and by the aid of that the quantitative determination of potassium(I)-ion is also possible. The reason of the precipitation formation is the prefect fitting of potassium(I)-ion size on the crystal structure of tetraphenyl-borate ion. By the same reason ammonium-ion gives also positive probe with this latter reagent.



$NaB(Ph)_4 + K^+ = \underline{KB(Ph)_4} + Na^+$ $\boxed{\text{white}}$

5. Flame colouration

Potassium(I)-ion, according to the method described in the chapter of methods, colour the colourless Bunsen flame to pale violet.

5.6.5. Reactions of Ammonium(I)-ion

Ammonia is a colourless gas with a characteristic pungent smell with the formula NH_3. The main application of ammonia is in the production of fertilizers and explosives. Besides, it is presented as an additive in the cleaning supplies and baking powder. Ammonia is used as a refrigerant because of its high energy efficiency and low cost. Nevertheless contrary to the freon, ammonia does not have effect on the ozone.

Ammonia is a metabolic waste and important source of nitrogen for living system. Ammonium chloride is used as an expectorant. Ammonium aluminium sulfate is used in deodorant. High ammonia level is toxic, inhalation of the gas for a long time nervous system symptoms is effected. Ammonia is highly toxic to aquatic animals, and for this reason it is dangerous for the environment. It is a component of the tobacco smoke.

The solubilities of its salts are close to those of potassium. The reversible thermal decomposition of ammonium salts is characteristic and starts below 350 °C; when heated they are volatile without leaving a residue. The reactions can be studied on NH_4Cl solution (1 M).

1. Similarities with potassium(I)-ion

Ammonium-ion in higher concentration, gives all the reactions of potassium(I)-ion, except the flame colouration.

2. Reaction with sodium-hydroxide

By heating ammonium salts with sodium-hydroxide, ammonia is eliberating, that has characteristic smell. Ammonia has basic character, so it can be identified by using wet indicator paper.

$$NH_4^+ + OH^- \rightleftharpoons NH_4OH \rightleftharpoons NH_3\uparrow + H_2O$$

3. Identification with Nessler reagent

Ammonium-ion, even in low concentration can be identified by using Nessler reagent. The reagent is the alkaline solution of tetraiodo-mercurate(II), and ammonium-ion gives brownish-red basic mercury(II)-amido-iodide precipitation.

$$NH_3 + 2HgI_4^{2-} + 3OH^- = \underline{HgO}\cdot\underline{HgNH_2I} + 7I^- + 2H_2O \quad \boxed{\textbf{brownish-red}}$$

The reaction can also performed by using dibromo-diiodo-mercurate(II) (Nessler-Winkler reagent) that makes easier the identification (se reactions of mercury(II)-ion).

4. Thermal analysis of solid ammonium salts

Starting from the ammonium salts of volatile weak acids, the eliberating ammonia can be identified by its characteristic smell or by using wet indicator paper.

$$(NH_4)_2CO_3 \rightleftharpoons 2NH_3\uparrow + CO_2\uparrow + H_2O$$

The ammonium salts of volatile strong acids sublimates without melting that recrystallized by meeting with the cooler part of the vessel.

$$NH_4Cl \rightleftharpoons NH_3 + HCl$$

The salts of non volatile acids and ammonia, decomposes fist by loosing of ammonia followed by loosing of water. The liberated ammonia can be identified as described before.

$$(NH_4)_2SO_4 = NH_3\uparrow + NH_4HSO_4$$

$$2NH_4HSO_4 = (NH_4)_2S_2O_7 + H_2O$$

The ammonium salts of oxidizing acids (*e.g.* ammonium-nitrate) decomposes at 170 °C to dinitrogen-oxide and water. In higher temperature decomposes to nitrogen, oxygen and to water. Caution! The heating of ammonium-nitrate can cause explosion! Do the reaction with smaller amount!

$$NH_4NO_3 = N_2O + 2H_2O$$

$$2NH_4NO_3 = 2N_2\uparrow + O_2\uparrow + 4H_2O$$

5.6.6. Simple analysis of cation group V

If the test solution gives no precipitate with the group I-IV reagents, the following tests can be made:

(i) In the presence of NH_4OH and NH_4Cl, Na_2HPO_4 produces a white precipitate of $MgNH_4PO_4$: magnesium

(ii) On heating, the solid is volatile without leaving a residue: ammonium

(iii) The flame colour: intensive yellow: sodium
violet: potassium
deep-red: lithium

6. Groups of Anions

6.1. Anion group I

6.1.1. Reactions of Carbonate-ion

Carbonates are component of the limestone ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$). Carbonates are widely used in industry as a raw material for the cement, lime manufacture. Sodium carbonate (soda) and potassium carbonate (potash) have been used for cleaning and preservation. Carbon dioxide is the anhydride of the carbonate.

Carbonates are intermediates of the gas metabolism. Carbonates which are dissolved in the blood play important role in the regulation of the blood pH.

The alkali metal carbonates are readily soluble in water, and these solutions are alkaline as a consequence of hydrolysis. In water, other metal carbonates are insoluble. The reactions can be studied on Na_2CO_3 and $KHCO_3$ solutions (0.5 M).

1. Group reaction

Depending on the concentration by adding hydrogen-chloride to carbonates, liberation of CO_2 can be observed. White calcium-carbonate precipitates by introducing the formed gas into calcium-hydroxide solution. sulphite and thiosulphate ions disturb the reaction because both of them give precipitation with the formed sulphur-dioxide. These latter ions can be oxidized to sulphate-ion with potassium-permanganate.

$$CO_3^{2-} + H^+ = HCO_3^-$$

$$HCO_3^- + H^+ = H_2CO_3$$

$$H_2CO_3 = CO_2\uparrow + H_2O$$

$$Ca^{2+} + 2OH^- + CO_2 = \underline{CaCO_3} + H_2O \quad \boxed{\text{white}}$$

2. pH character

The aqua solution of sodium-carbonate is alkaline (pH > 10), by using phenolphthalein indicator it will turn to red. The aqua solution of sodium-hydrogencarbonate is only weekly alkaline (pH = 8-9), so the phenolphthalein indicator is light pink, that after heating, because of loosing one molecule of CO_2, become red.

$$2HCO_3^- \rightleftharpoons CO_3^{2-} + CO_2\uparrow + H_2O$$

3. Precipitation with magnesium-sulphate

In the presence magnesium-ion, white basic magnesium(II)-carbonate precipitates. Hydrogencarbonate at room temperature does not give precipitation, only after heating.

$$4CO_3^{2-} + 4Mg^{2+} + H_2O = \underline{Mg(OH)_2}\cdot\underline{3MgCO_3} + CO_2 \quad \boxed{\text{white}}$$

4. Carbonate as a general precipitating agent

Carbonate-ion with all of cations from group I-IV give precipitation.

5. Thermal analysis of solid carbonates

Hydrogen-carbonate salts after heating, decomposes thanks to losing CO_2 and water.

6.1.2. Reactions of Sulphite-ion

Sulphite ion is the conjugated base of bisulfite. It is widely used as a food preservative, because of its antifungal and antibacterial properties. Principally it is used for the preservation of wines, fresh vegetables and fruits and sea products. Allergic reactions to sulfites appear to be very rare in general population, but more common in hyperallergic individuals.

Sulfites are reductants. The reactions can be studied on Na_2SO_3 solution (0.05 M).

1. Group reaction

With strong acids (HCl), the unstable sulphurous acid (H_2SO_3) is forming, this decomposes to sulphur-dioxide, which escapes as gas. *(Usually without formation of visible bubbles.)* It can be detected by its sharp odour, or in the gas space with a potassium-iodate paper-strip, which becomes blue.

$$2SO_3^{2-} + 2H^+ \rightleftharpoons S_2O_5^{2-} + H_2O$$

$$SO_3^{2-} + 2H^+ \rightleftharpoons H_2SO_3 \rightleftharpoons H_2O + SO_2\uparrow \quad \boxed{\text{sharp odour}}$$

$$2IO_3^{2-} + 5SO_2 + 4H_2O = I_2 + 5SO_4^{2-} + 8H^+$$

$$\boxed{\text{blue colour with starch}}$$

Sulphur-dioxide subsequently reduces the iodine, and the blue colour disappears.

2. Reaction with barium-chloride

Even sulphite is from anion group I, with barium(II)-ion gives white precipitation, that dissolves in acids.

$$Ba^{2+} + SO_3^{2-} = \underline{BaSO_3} \quad \boxed{\text{white}}$$

$$BaSO_3 + 2H^+ \rightleftharpoons Ba^{2+} + SO_2\uparrow + H_2O$$

3. Reaction with silver-nitrate

In the excess of silver(I)-ions white silver-sulphite precipitates. It can be explained that first water soluble complex is forming. By heating disulphito-argentate(I) sulphite-ion reduces silver(I)-ion, and silver metal is forming.

$$SO_3^{2-} + 2Ag^+ = \underline{Ag_2SO_3} \quad \boxed{\text{white}}$$

$$Ag_2SO_3 + 3SO_3^{2-} = 2[Ag(SO_3)_2]^{3-}$$

$$2[Ag(SO_3)_2]^{3-} = 2\underline{Ag} + SO_4^{2-} + 2SO_3^{2-} + SO_2 \quad \boxed{\text{gray}}$$

4. Reaction with iodine

Iodine (mixture with potassium-iodide) oxidizes sulphite-ion to sulphate-ion, during that time, the brown colour of iodine disappear.

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

6.1.3. Reactions of Thiosulphate-ion

Thiosulphate occurs naturally and its produced by certain biochemical processes. In addition is produced also by the reaction of sulphite ion with elemental sulfur. Ammonium thiosulphate is widely used as a fixing salt in photography, to fix black and white negatives and prints after the developing stage. Sodium thiosulphate is used for cyanide poisoning, along with hydroxocobalamin. In the case of cyanide poisoning enzyme rhodanase catalyses the detoxification of cyanide by thiosulphate. Thiosulphate is non-toxic, but in larger amount causes diarrhea.

The reactions can be studied on $Na_2S_2O_3$ solution.

1. Group reaction

With strong acids (HCl), first thiosulphuric acid is forming, that decomposes to elemental sulphur, while sulphur-dioxide eliberating. It can be detected by its sharp odour, or in the gas space with a potassium-iodate paper-strip, which becomes blue. The formation of SO_2 can be accelerated by heating.

$$S_2O_3^{2-} + 2H^+ \rightleftharpoons H_2S_2O_3$$

$$H_2S_2O_3 = \underline{S} + SO_2\uparrow + H_2O \quad \boxed{\text{sharp odour, turbidity}}$$

2. Reaction with silver-nitrate

In the excess of silver(I)-ions white silver-thiosulphite precipitates. It can be explained that first water soluble complex is forming. After precipitation its colour turns to brown because of the disproportion of the silver(I)-thiosulphate.

$$S_2O_3^{2-} + 2Ag^{2+} = \underline{Ag_2S_2O_3} \quad \boxed{\text{white}}$$

$$Ag_2S_2O_3 + 3S_2O_3^{2-} = 2[Ag(S_2O_3)_2]^{3-}$$

$$Ag_2S_2O_3 + H_2O = \underline{Ag_2S} + SO_4^{2-} + 2H^+ \quad \boxed{\text{brownish-black}}$$

3. Reaction with iodine

Iodine (mixture with potassium-iodide) oxidizes sulphite-ion to tetrathionate-ion, during that time, the brown colour of iodine disappear.

$$2S_2O_3^{2-} + I_2 = 2I^- + S_4O_6^{2-}$$

4. Reaction with iron(III)-chloride

In the presence of iron(III)-ion, first thiosulphato-iron(III) complex (violet colour) is forming. that quickly transform to iron(II)-ion and to tetrathionate-ion.

$$Fe^{3+} + S_2O_3^{2-} = [Fe(S_2O_3)]^+ \quad \boxed{\text{violet solution}}$$

$$2[Fe(S_2O_3)]^+ = S_4O_6^{2-} + 2Fe^{2+}$$

5. Thermal analysis of the solid sample

Heating of sodium-thiosulphate, by losing of sulphur-dioxide it will burn with blue flame.

6.1.4. Reactions of Sulphide- and polysulphide-ion

Sulphides can be found in several minerals, as the major anion: argentite (silver sulphide), cinnebar (mercury sulphide), molybdenit (molybdenium sulphide), etc. Sulphide compounds are used in paper production (Na_2S), in photocells (CdS), in infra-red sensors (PbS). Molybdene sulphide is used as a calayst to remove sufur from fossil fuels.

Sulphide ion is a strong base ($pK_S>14$), thus its aqueous solution has alkaline pH. Only hydrogen-sulphide ion (HS^-) form can be found in aqueous solution, but then in lower pH as a hydrogen-sulphide can be detected. This complex acid-base equilibrium has a big influence for the reactivity of the sulphide ion. This property is used for the group reaction of the cations.

The water soluble sulphides are toxic, since hydrogen sulphide occurs naturally in the body, enzymes exist to detoxify it. Toxicity appears if the concentration of the hydrogen sulphide level is above 300-350 ppm, concentrations over 1000 ppm cause immediate collapse with loss of breathing. Nitrite compounds are added as an antidote. Exposure to lower concentrations can result in eye irritation. sore throat and cough, nausea, fluid in the lungs. Fortunately hydrogen sulphide has a characteristic foul odor of rotten eggs, which facilitates detection.

In sulphide ions, sulphure exhibits an oxidation state of -2, in polysulphide always have two sulphure with an oxidation state of -1. The reactions can be studied on $(NH_4)_2S$ and $(NH_4)_2S_x$ solutions.

1. Group reaction

With strong acids (HCl), in case of sulphide-ion hydrogen-sulphide, with characteristic odour is forming, and in case of polysulphide, formation of elemental sulphur can also be observed. Hydrogen-sulphide can also be identified by its reaction with lead-acetate test-paper, which becomes black.

$$S^{2-} + 2H^+ = H_2S\uparrow \qquad \boxed{\textbf{stinky gas (bad egg)}}$$

$$S_x^{2-} + 2H^+ = H_2S + \underline{(x-1)S} \qquad \mathbf{x = 2\text{-}6} \qquad \boxed{\textbf{odour and turbidity}}$$

2. Identification with sodium-nitroprusside

In alkaline medium, addition of nitroso-pentacyano-ferrate(II) (nitroprusside) forms with sulphide-ion violet-red colour complex. By adding acid, the solution become colourless.

$$[Fe(CN)_5NO]^{2-} + S^{2-} = [Fe(CN)_5NOS]^{4-} \qquad \boxed{\textbf{violet-red solution}}$$

3. Oxidation with permanganate

In acidic medium, sulphide-ion can be oxidize till the formation of elemental sulphur. During the reaction the violet colour of permanganate disappear while the appearance of sulphur can be observed.

$$2MnO_4^- + 5H_2S + 6H^+ = 2Mn^{2+} + 5\underline{S} + 8H_2O$$

4. Group reagent

Sulphide-ion, depending on the pH, gives precipitation with all of the cations from group I-III.

6.1.5. Reactions of Silicate-ion

Silicates are very often rock-forming in the Earth's crust. Silicon dioxide SiO_2 (silica, quartz) is the main component of the glass-making. The artificially prepared aluminium silicates are one of the main element of the catalyst of the oil industry. Other silicates are used in the laboratory as a separation technical element. There are some natural silicates, which are used in therapy, namely the white clay and the talcum ($Mg_3Si_4O_{10}(OH)_2$) as a component of the powders. As physiological aspect, silicates are indifferents, but inhaling the powder silicosis is caused.

The corresponding acid H_2SiO_3 is insoluble in water and forms isopolyacids. In aqueous solution, the colourless silicates exist as silica (SiO_2) and as condensed ions only in strongly alkaline medium. The reactions can be studied on Na_2SiO_3 solution.

1. Group reaction

Hydrogen-chloride precipitate white transparent, gelatinous silica, which is dissolved when boiled with sodium-hydroxide.

$$Na_2SiO_3 + 2H^+ = \underline{H_2SiO_3} + 2Na^+ \qquad \boxed{\textbf{jelly, transparent}}$$

$$H_2SiO_3 + 2Na^+ + 2OH^- = Na_2SiO_3 + 2H_2O$$

2. Formation of heteropolyacid

Silicate by acidification via condensation forms polyacid. If molibdenic acid, with similar property is present in the mixture, the solution turns yellow and heteropolyacid is forming.

$$3H_2MoO_4 = H_2(Mo_3O_{10}) + 2H_2O$$

$$H_2SiO_3 + H_2O = H_4SiO_4$$

$$H_4SiO_3 + 4H_2(Mo_3O_{10}) = H_4[Si(Mo_3O_{10})_4] + 4H_2O \qquad \boxed{\textbf{yellow solution}}$$

3. Tetrafluoride test

SiO_2 reacts with hydrogen-fluoride in the presence of dehydrating agents such as conc. sulfuric acid, yielding gaseous SiF_4.

$$2NaF + H_2SO_4 = H_2F_2 + Na_2SO_4$$

$$H_2SiO_3 + 2H_2F_2 \rightleftharpoons SiF_4\uparrow + 3H_2O$$

If a little quartz powder a few drops of cc. sulfuric acid and a little solid sodium-fluoride are heated in a platinum crucible on a water-bath, and a wet glass rod is held in the gas space above it, a white coating is formed in it; the SiF_4 is hydrolysed to silica.

The reaction can also be used for the identification of fluoride.

6.1.6. Reactions of Hypochlorite-ion

Hypochlorite is a strong oxidizing agent and a current listerin. The most common representative is the sodium hypochlorite, namely bleach. It is used for disinfecting and sterilizing, in swimming pool sanitation to control bacteria, viruses and algae and in many places where sterile conditions are required. The safety of bleaches depends on the compounds present, and their concentration.

On contact with the skin or eyes, it causes irritation, drying and burns. Bleach should never be mixed with vinegar or ammonia containing products as this will create highly toxic chlorine gas and can cause burns internally and externally.

In hypochlorite the chlorine exhibits an oxidation state of +1. Its reactions can be studied on freshly prepared NaClO.

1. Group reaction

Hydrogen-chloride liberates yellow-green chlorine, which turns iodine-starch test-paper blue: iodine is liberated:

$$\mathrm{ClO^- + Cl^- + 2H^+ = Cl_2\uparrow + H_2O}$$

greenish-yellow, sharp odour

$$\mathrm{Cl_2 + 2I^- = I_2 + 2Cl^-}$$

6.1.7. Simple analysis of anion group I.

Whereas the cation groups may be separated from each other, group reagents are not suitable for separation of the anions.

When solution of these anions are treated with strong acids (20% HCl), a gas or a bad smell of the sulphur dioxide (SO_2) is detected. In solution of carbonates, the indicator phenolphtalein turns red. Owing the hydrolysis, hydrogencarbonate solution are only weakly alkaline, and phenolphtalein becomes pale-pink but not red. On boiling, after partial removal of CO_2 becomes red. Reaction with KI/I_2 solution, the brown color of the reagent disappears in the case of sulphur containing compounds ($S_2O_3^{2-}$ and SO_3^{2-}) and the anions are differentiable from each other with the reagent of $BaCl_2$.

6.2. Anion group II

6.2.1. Reactions of Sulphate-ion

Sulphate occurs naturally mainly as a format of alkaline and alkaline earth metal sulphates. Sulphates are widely used in industry, gypsum ($CaSO_4$) is used to produce plaster; copper sulphate ($CuSO_4$) is used for galvanic cells as electrolyte; sodium sulphate is a detergent in shampoo formulation. Sulphate ion is non toxic, occurs also in organism. Sulphate ion is used as a counter at some cationic agent. In larger amount cause diarrhea.

In sulphate ion, the sulphur exhibits an oxidation state of +6. The reactions can be studied on sodium sulphate (Na_2SO_4) solution (0.05 M).

1. Group reaction

Reaction with Barium(II)-ion precipitates white barium(II)-sulphate. The solubility ratio of barium(II)-sulphate is low therefore it is insoluble in diluted acids. The precipitate can only be dissolved by heating with cc sulphuric acid.

$$SO_4^{2-} + Ba^{2+} = \underline{BaSO_4} \qquad \boxed{\text{white}}$$

2. Precipitation with lead(II)-acetate

In the presence of lead(II)-ion, sulphate precipitates white lead(II)-sulphate, that thanks to the complex forming ability of lead(II)-ion, can be dissolved by using sodium-hydroxide.

$$SO_4^{2-} + Pb^{2+} = \underline{PbSO_4} \qquad \boxed{\text{white}}$$

$$PbSO_4 + 4OH^- = Pb(OH)_4^{2-} + SO_4^{2-}$$

3. Hepar-reaction

When heated on charcoal, metal sulphates mixed with sodium-carbonate are reduced to sulphide, which can be identified on a wet silver plate: a black spot is formed (see reaction of sulphide).

$$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4$$

$$Na_2SO_4 + 4C = Na_2S + 4CO$$

$$2S^{2-} + 4Ag + O_2 + 2H_2O = 2\underline{Ag_2S} + 4OH^- \qquad \boxed{\text{brown}}$$

4. Thermal analysis of sulphate salts

Hydrogen-sulphate salts after heating, transform to disulphates. Alkali-sulphates do not decompose if the temperature is lower than 1000 °C.

6.2.2. Reactions of Phosphate-ion

Phosphates are occurring naturally in many minerals such as an calcium salt (phosphorite, $Ca_3(PO_4)_2$), as an apatite ($Ca_5X(PO_4)_3$, X = Cl, F, OH). They are a component in fertilizer, detergents.

Phosphates are most commonly found in the form of adenosine phosphates and in DNA and RNA. It can be released by the hydrolysis of ATP or ADP. Phosphates also can be found in biological systems in the bone and teeth. The phosphate nedds of one adult is 1-2 g. Phosphates are not toxic, in larger amount cause diarrhea.

Phosphates correspond to H_3PO_4 (ortho-), $H_4P_2O_7$ (pyro-) and HPO_3 (metaphosphoric acid). Orthophosphates can be primary ($H_2PO_4^-$), secondary (HPO_4^{2-}) or tertiary (PO_4^{3-}), but „phosphate” always means orthophosphate (the oxidation state of the P in all these anions is +5). Alkali metal phosphates are water soluble. As concern the alkaline earth phosphates, only the primary ones, but not the secondary and tertiary ones are soluble in water. The reactions can be studied on Na_3PO_4, Na_2HPO_4 and KH_2PO_4 solution (0.05 M).

1. Group reaction

Reaction with barium(II)-chloride, depending on the pH, white tertiary of secondary barium(II)-phosphate precipitates, that is soluble in weak acids.

$$2PO_4^{3-} + 3Ba^{2+} = \underline{Ba_3(PO_4)_2} \quad \boxed{\text{white}}$$

$$HPO_4^{2-} + Ba^{2+} = \underline{BaHPO_4} \quad \boxed{\text{white}}$$

$$Ba_3(PO_4)_2 + 4H^+ = 3Ba^{2+} + 2H_2PO_4^-$$

2. Reaction with silver-nitrate

In the presence of silver(I)-ion, in case of all phosphates, yellow tertiary silver(I)-phosphate precipitates. Silver(I)-phosphate is soluble in diluted nitric acid and in ammonia.

$$PO_4^{3-} + 3Ag^+ = \underline{Ag_3PO_4} \quad \boxed{\text{yellow}}$$

$$Ag_3PO_4 + 2H^+ = H_2PO_4^- + 3Ag^+$$

$$Ag_3PO_4 + 6NH_3 = 3[Ag(NH_3)_2]^+ + PO_4^{3-}$$

By this reaction the order of the phosphates can be determined. The solution of primary phosphates is weakly acidic, therefore the colour of methyl-red indicator is red. After adding silver-ion, tertiary silver-phosphate forms, while free acid is forming, so the colour of the indicator remains red (remain unchanged).

$$H_2PO_4^- + 3Ag^+ = \underline{Ag_3PO_4} + 2H^+ \qquad \boxed{\textbf{red} \rightarrow \textbf{red}}$$

The aqua solution of secondary phosphates is weakly alkaline, therefore the colour of the methyl-red indicator is yellow. By adding silver-ion and in the excess of silver-ion, tertiary silver-phosphate forms, while free acid is forming, so the colour of the indicator turns to red.

$$HPO_4^{2-} + 3Ag^+ = \underline{Ag_3PO_4} + H^+ \qquad \boxed{\textbf{yellow} \rightarrow \textbf{red}}$$

The aqua solution of tertiary phosphates is alkaline, therefore the colour of the methyl-red indicator is yellow. By adding silver-ion and in the excess of silver-ion, tertiary silver-phosphate forms, free acid in this case not forming, so the colour of the indicator remains yellow.

$$PO_4^{3-} + 3Ag^+ = \underline{Ag_3PO_4} \qquad \boxed{\textbf{yellow} \rightarrow \textbf{yellow}}$$

3. Precipitation with magnesium-mixture

By applying magnesium-nitrate in ammonium-chloride buffer, white magnesium-ammonium-phosphate precipitates. Arsenate can disturb the determination, and their presence can be checked by using silver-nitrate.

$$HPO_4^{2-} + Mg^{2+} + NH_3 = \underline{MgNH_4PO_4} \qquad \boxed{\textbf{white}}$$

4. Formation of heteropolyacid

Phosphates by acidification via condensation forms polyacid. If molibdenic acid, with similar property is present in the mixture, yellow heteropolyacid precipitates.

$$(NH_4)_2MoO_4 + 2H^+ = H_2MoO_4 + 2NH_4^+$$

$$3H_2MoO_4 = H_2Mo_3O_{10} + 2H_2O$$

$$HPO_4^{2-} + 12HMoO_4^{-} + 3NH_4^{+} + 11H^{+} = \underline{(NH_4)_3[P(Mo_3O_{10})_4]} + 12H_2O$$

$$\boxed{\text{yellow}}$$

6.2.3. Reactions of Borate-ion

Borates are the name of a numerous boron-oxigen compounds. Boric acid ($B(OH)_3$) and borax ($Na_2B_4O_7{*}10H_2O$) are the two more often occurrent borates. Borax is used for the prapartion of detergent, besides it is important raw material of the refractory borosilicate glass. Zinc borate is used as a flame retardant.

Boron is an essential plant nutrient, plays a strengthening role in the cell walls of all plants. Boron supplementation markedly reduced urinary calcium excretion and elevated the serum concentration of 17-beta-estradiol and testosterone. Boric acid and borax have antiseptic, antifungal and antiviral properties. Mild solution of boric acid is used as eye antiseptics. Boron compounds are relatively nontoxic to humans and animals.

Alkali metal borates are water-soluble and their solutions are alkaline. The reactions can be studied on $Na_2B_4O_7$ (borax) solution (0.05 M).

1. Group reaction

By adding barium(II)-chloride in the presence of ammonia, borate gives white precipitation. The precipitation forms only from concentrated solution of borate, and it can be dissolved even by adding ammonium-chloride.

$$2B(OH)_4^{-} + Ba^{2+} = \underline{Ba[B(OH)_4]_2} \quad \boxed{\text{white}}$$

2. pH character

Boric acid is a very weak acid, its aqua solution is neutral. It is not able to dissociate, but as Lewis-acid coordinates one molecule of water, that in the presence of a base can be dissociated. Boric acid in the alkaline medium is able to form polyanione, like the formation of tetraborate.

$$B(OH)_3 + H_2O \rightleftharpoons B(OH)_4^{-} + H^{+}$$

3. Reaction with silver-nitrate

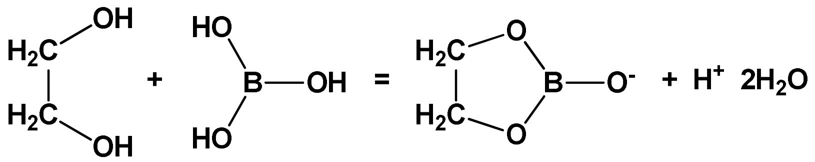
In the presence of silver-ion, white silver-borate is precipitating, that after heating decomposes, and because of the formation silver-oxide turns to brown. *Note: the $Ag[B(OH)_4]$ precipitate is sometimes greyish or even brownish.*

$$B(OH)_4^- + Ag^{+-} = \underline{Ag[B(OH)_4]} \quad \boxed{\text{white}}$$

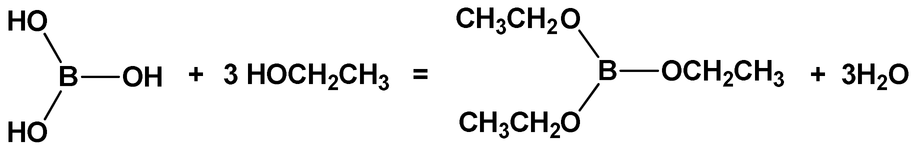
$$2Ag[B(OH)_4] = \underline{Ag_2O} + 2H_3BO_3 + H_2O \quad \boxed{\text{brown}}$$

4. Ester-formation with alcohols

Boric acid with vicinal polyols (ethylene-glycol or glycerine) forms stable complexes. These complexes are middle-strong acids, therefore by adding methyl-red indicator into the solution of boric acid, at the beginning it will be yellow, then by adding ethylene glycol the solution become acidic, so the colour of the indicator will turn to red.



When 1 ml of cc. sulfuric acid is added into the solid borate then some drops of ethanol is also added, the ethylester of boric acid is forming. The ester is volatile therefore burns with a green flame. The reaction is sensitive and is able to determine borates from mixtures.



5. Turmeric paper reaction

An acid borate solution gives a red stain on turmeric paper, which becomes pink on drying. If a drop of sodium-hydroxide is then added, the stain becomes blue-to-green.

With boric acid, the yellow colouring matter of the turmeric (curcumine) forms a red complex. Interfering substances: oxidants (e.g. nitrite and iron(III)), and iodine. In the absence of these, the reaction is sensitive and characteristic. Iron(III) turns turmeric red, but does not give the colour change with NaOH.

6.2.4. Reactions of Fluoride-ion

Fluoride is the simplest fluorine anion, it occurs on earth in several minerals (fluorite), but is present at low concentration in bodies of water in nature. The main uses of fluoride are in the production of cryolite (Na_3AlF_6), which is used in aluminium smelting. Sodium fluoride or sodium monofluorophosphate are used in fluoride therapy for preventing tooth decay. In the higher doses used to treat osteoporosis, sodium fluoride can cause pain in the legs, irritate the stomach, weight loss, constipation. 4 g of sodium fluoride causes fatal poisoning. Hydrogen fluoride is corrosive, especially toward glass.

The reactions of fluoride can be studied on NaF solution (0.05 M).

1. Group reaction

By adding barium(II)-chloride, fluoride forms white jelly-like precipitation that can be dissolved by heating with hydrochloric-acid. Calcium(II)-ion also forms white precipitation, but as an exception among halogens, fluoride-ion forms water-soluble compound with silver-ion.

$$Ba^{2+} + 2F^- = \underline{BaF_2} \quad \boxed{\textbf{white}}$$

$$Ca^{2+} + 2F^- = \underline{CaF_2} \quad \boxed{\textbf{white}}$$

$$BaF_2 + 2H^+ = Ba^{2+} + H_2F_2$$

2. Glass attack

On heating, cc sulfuric acid liberates H_2F_2 gas, which attacks glass.

$$2NaF + H_2SO_4 = Na_2SO_4 + H_2F_2$$

$$2H_2F_2 + SiO_2 = SiF_4 + 2H_2O$$

Place the solid substance to be examined in a platinum vessel and mix with cc sulfuric acid. Cover the vessel with a watch glass, a part of which has been waxed. When the vessel is heated, the unprotected parts of the glass are etched by the H_2F_2.

3. Decomposition of iron(III)-thiocyanate

Iron(III)-ion give blood-red solution with thiocyanate-ion. By adding fluoride-ion into this mixture, the red colour will disappear, because fluoride forms more stable complex with iron(III)-ion than thiocyanate-ion. *Note: phosphate and sulphate ions behave similarly.*

$$Fe(SCN)_3 + 3F^- = FeF_3 + 3SCN^-$$

6.2.5. Reactions of Bromate-ion

Currently no bromate-containing minerals are known, but it can occur when bromide ions containing water is purified by ozonation. Ozone reacts with bromide ions to produce bromate. Previously it was used as an additive in the food industry. Because of the potential carcinogenic effect, utilization is forbidden. Puke, diarrhea, collapse can be observed in the case of larger amounts of bromate.

The reactions can be studied on $KBrO_3$ solution (0.05 M).

1. Group reaction

By adding barium(II)-chloride white barium(II)-bromate precipitates that does not dissolve easily in acids. The precipitation forms only from concentrated solution of bromate.

$$2BrO_3^- + Ba^{2+} = \underline{Ba(BrO_3)_2} \quad \boxed{\text{white}}$$

2. Reaction with silver-nitrate

In the presence of silver-ion, white silver-bromate is precipitating, that cannot be dissolved by adding nitric acid, but in ammonia dissolves completely as diamin-silver complex.

$$BrO_3^- + Ag^+ = \underline{AgBrO_3} \quad \boxed{\text{white}}$$

$$AgBrO_3 + 2NH_3 = [Ag(NH_3)_2]^+ + BrO_3^-$$

3. Redox reactions

Bromate-ion is a relatively strong oxidation agent. In the presence of acidic medium (sulphuric acid) with 5 equivalents of bromide, brown bromine is forming (synproportion). The colour of bromine can be better seen by using chloroform.

$$BrO_3^- + 5Br^- + 6H^+ = 3Br_2 + 3H_2O \quad \boxed{\text{brown solution}}$$

In acidic medium, bromate also oxidize iodide-ion to elemental iodine, that has brownish colour in water, but using chloroform, it will have characteristic violet coloration.

$$BrO_3^- + 6I^- + 6H^+ = 3I_2 + Br^- + 6H_2O \quad \boxed{\text{violet solution}}$$

The heating of bromate-ion in hydrochloric-acid, elemental chlorine and bromochloride as an interhalogen with wine-yellow colouration are forming.

$$BrO_3^- + 5Cl^- + 6H^+ = BrCl + 2Cl_2 + 3H_2O \quad \boxed{\begin{array}{l}\text{"wine-yellow" solution,}\\ \text{greenish-yellow gas}\end{array}}$$

In acidic medium, by using zinc metal, bromate can be reduced to elemental bromine, that can be visualized by using chloroform.

$$BrO_3^- + 5Zn + 12H^+ = Br_2 + 6H_2O + 5Zn^{2+} \quad \boxed{\text{brown solution}}$$

4. Thermal analysis of bromate salts

By heating of bromate salts, perbromate (BrO_4^-) and bromide forms. The higher temperature causes the decomposition of perbromate to oxygen and bromide, so from the residue bromide can be tested.

6.2.6. Reactions of Iodate-ion

Iodate anions containing minerals are very rare, it is found in the caliche deposits of Chile. The most important iodate minerals are lautarite and brüggenite. In the case of ingestion of iodate iodide is formed and corrosive effect is observed.

Iodine can assume oxidation state +5 in the iodate ion. The reactions can be studied on KIO_3 solution (0.05 M).

1. Group reaction

By adding barium(II)-chloride white barium(II)-iodate precipitates that does not dissolve easily in acids. The precipitation forms only from concentrated solution of iodate.

$$2IO_3^- + Ba^{2+} = \underline{Ba(IO_3)_2} \quad \boxed{\text{white}}$$

2. Reaction with silver-nitrate

In the presence of silver-ion, white silver-iodate is precipitating, that can not be dissolved by adding acids, but in ammonia dissolves completely as diamin-silver complex.

$$IO_3^- + Ag^+ = \underline{AgIO_3} \quad \boxed{\text{white}}$$

$$\underline{AgIO_3} + 2NH_3 = [Ag(NH_3)_2]^+ + IO_3^-$$

3. Redox reactions

Iodate-ion is weaker oxidation agent than bromate-ion. In the presence of acidic medium (sulphuric acid) with 5 equivalents of iodide, brown iodine is forming that can be visualized by using chloroform. In this case the colour of the chloroform will be violet.

$$IO_3^- + 5I^- + 6H^+ = 3I_2 + 3H_2O$$ voilet solution in chloroform

In acidic medium, by using zinc metal, iodate can also be reduced to elemental iodine, and its violet colour can be seen perfectly by using chloroform.

$$2IO_3^- + 5Zn + 12H^+ = I_2 + 5Zn^{2+} + 6H_2O$$ voilet solution in chloroform

6.2.7. Simple analysis of anion group II.

With strong acids the anions from group II (with the exception of bromate and iodate, from which chlorine is evoled with conc. HCl) are unchanged, but in neutral solution barium chloride gives a precipitate. The formed barium precipitate only in the case of sulphate is not soluble in weak acids. Silver nitrate gives different colour of silver precipitates in the case of phosphates, borate, bromate and iodate. Bromate and iodate are differentiable from each other with redox reactions. Difference from other halide ions, fluoride do not give a precipitate with $AgNO_3$, but with $Fe(SCN)_3$ the red colour of the reagent becomes colourless.

6.3. Anion group III

6.3.1. Reactions of Chloride-ion

The application of naturally occurring chloride compounds are very extensive. Sodium chloride is used for the preparation of chlorine, and detergents, in papermaking, it is an important compound in food industry. Sea water contains 1,94% chloride. The serum chloride (concentration of chloride in the blood) is regulated by the kidneys. Chloride ion is a structural component of some proteins. It plays a key role in maintaining cell homeostasis and transmitting action potential in neurons. Chloride appears as hydrochloric acid form in the stomach and it is responsible for the regulation of pH, which is necessary for the digestion. Chloride is nontoxic, but ingestion of sodium-chloride in larger amount can cause cardiovascular disease.

Its reactions can be studied on NaCl solution (0.1 M).

1. Group reaction

Silver-nitrate with chloride-ion gives white silver-chloride precipitation, that dissolves by adding ammonia, thiosulphate, or cyanide. It cannot be dissolved in nitric acid.

$$Cl^- + Ag^+ = \underline{AgCl} \quad \boxed{\text{white}}$$

2. Chromyl chloride reaction

When powdered potassium dichromate is heated with a mixture of solid chloride and cc sulphuric acid, a brown vapour of chromyl chloride, CrO_2Cl_2, is forming. If the vapour is trapped in NaOH solution, yellow chromate is obtained (difference from bromide, which also gives a brown vapour, but this becomes colourless in NaOH).

With this reaction, chloride can be identified in the presence of bromide and iodide.

$$4Cl^- + Cr_2O_7^{2-} + 6H^+ = 2CrO_2Cl_2\uparrow + 3H_2O \quad \boxed{\text{redish-brown gas}}$$

$$CrO_2Cl_2 + 4OH^- = 2Cl^- + CrO_4^{2-} + 2H_2O \quad \boxed{\text{yellow solution}}$$

$$6Br^- + Cr_2O_7^{2-} + 14H^+ = 3Br_2\uparrow + 2Cr^{3+} + 7H_2O$$

$$6I^- + Cr_2O_7^{2-} + 14H^+ = 3I_2\uparrow + 2Cr^{3+} + 7H_2O$$

$$I_2 + 2OH^- = IO^- + I^- + H_2O$$

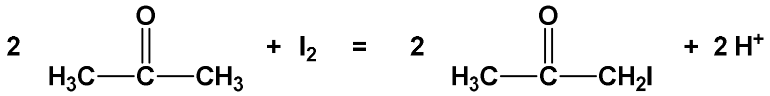
$$Br_2 + 2OH^- = BrO^- + Br^- + H_2O$$

3. Berg reaction

In sulphuric acid solution, bromide and iodide are oxidized by permanganate; at the same time, in dilute solution chloride remains intact. After decomposition of excess permanganate with hydrogen-peroxide, acetone is added. Bromine and iodine form bromo- and iodoacetone. Since the bromine and iodine in these compounds are covalent bonded, they do not react with silver-ion; however, chloride can be identified as silver-chloride. With this reaction, chloride can be identified in the presence of bromide and iodide.

$$10I^- + 2MnO_4^- 16H^+ = 5I_2 + 2Mn^{2+} + 8H_2O$$

$$10Br^- + 2MnO_4^- 16H^+ = 5Br_2 + 2Mn^{2+} + 8H_2O$$



$$2\ H_3C{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3 + I_2 = 2\ H_3C{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_2I + 2H^+$$

4. Oxidation with permanganate

If chloride salt is heated with potassium-permanganate in sulphuric acid, chlorine is liberated. Its oxidizing character can be demonstrated with redox indicator such as starch-iodine paper, which turns blue and then becomes colourless if an excess of chlorine is present.

$$2MnO_4^- + 10Cl^- + 16H^+ = 2Mn^{2+} + 5Cl_2\uparrow + 8H_2O$$

greenish-yellow gas

6.3.2. Reactions of Bromide-ion

Sea water contains 0,2% bromide of all dissolved salts. The most common bromide mineral is bromargyryte. Bromide compounds, such as potassium bromide and lithium bromide are used as a sedative and headache remedies. Bromide salts are used in veterinary medicine because of they antiepileptic properties. Bromide ion concentration in the cerebrospinal fluid are about 30 % of those in blood and strongly influenced by the body's chloride intake and metabolism. It is known that during the War I, British soldiers were given bromide in the tea to curb their sexual urges. Bromide toxicity can cause skin eruption, bromism, a syndrome with multiple neurological symptoms.

The reactions can be studied on KBr solution (0.05 M).

1. Group reaction

Silver-nitrate with bromide-ion gives yellowish-white silver-bromide precipitation, that dissolves hardly by adding ammonia, but easily in thiosulphate, or cyanide. It cannot be dissolved in nitric acid.

$$Br^- + Ag^+ = \underline{AgBr} \quad \boxed{\textbf{white}}$$

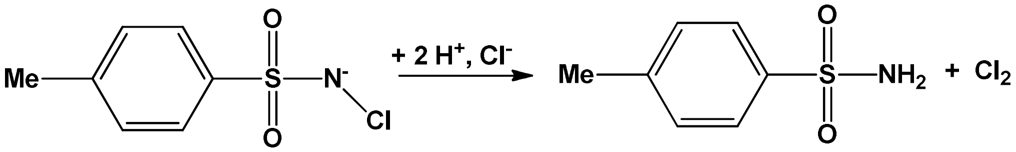
2. Oxidation of bromide to bromine

In acidic solution, chlorine-water oxidizes bromide to bromine, which yields brown solution in chloroform. When an excess of chlorine, the colouration does not disappear but is only weakened, because bromochlorine is formed (difference from iodide, which is oxidized to colourless iodate).

$$2Br^- + Cl_2 = Br_2 + 2Cl^- \quad \boxed{\textbf{brown solution}}$$

$$Br_2 + Cl_2 = 2\ BrCl \quad \boxed{\textbf{wine-yellow solution}}$$

Chlorine-water can easily be disproportioned, therefore it needs to be fresh prepared. A more convenient chlorine source is sodium-*p*-tolylbenzosulphonchloroamide (chloramine-T), that in acidic medium *in situ* liberates chlorine, while sulphonamide is forming.

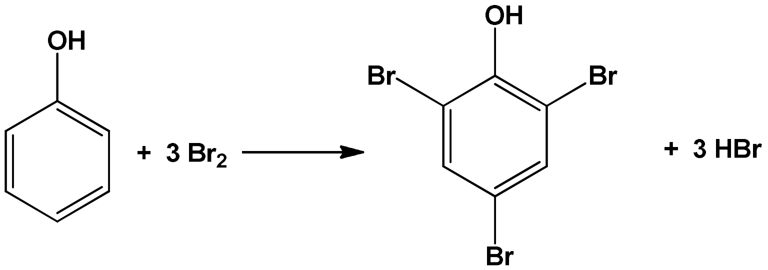


In sulphuric acid solution, potassium-permanganate oxidizes bromide to bromine (brown solution in chloroform), or the oxidation can also be achieved by using lead(IV)-oxide in acidic medium.

$$2Br^- + PbO_2 + 4H^+ = Br_2 + Pb^{2+} + 2H_2O$$

3. Reaction of phenol with bromine

Elemental bromine reacts with phenol that leads to the formation of tribromophenol as white precipitation.



2,4,6-tribromophenol

6.3.3. Reactions of Iodide-ion

Iodide minerals are rare, iodargyrite is the most common iodide mineral. Silver iodide is used in traditional photographic film and it also used for cloud seeding to induce rain. Iodide is important from physiological aspect, it plays role in the regulation of metablism. Iodide deficiency causes struma. The cooking salt is iodized, in order to prevent the disease. Radioactive iodine (^{131}I), which is a non-toxic radiocontrast material, is used to treat thyroid cancer. Besides, iodide is used as an expectorant. Extreme iodide ingestion causes hyperthyroidism. Tincture of iodine and Lugol's solution are used in therapy as disinfectant. Elemental iodine is toxic and excess of iodine can be more cytotoxic.

The reactions can be studied on KI solution (0.05M).

1. Group reaction

Silver-nitrate with iodide-ion gives yellow silver-iodide precipitation, that does not dissolve in ammonia, hardly in thiosulphate, and easily in cyanide. It cannot be dissolved in nitric acid.

$$I^- + Ag^+ = \underline{AgI} \quad \boxed{\text{yellow}}$$

2. Precipitation with cation group I

Iodide-ion precipitates cations from group I. with characteristic colour (see reactions of cation group I.).

3. Oxidation of iodide to iodine

In acidic solution, chlorine-water oxidizes iodide to iodine, which yields violet solution in chloroform. When an excess of chlorine, the colouration will disappear, because iodine will be oxidized to colourless iodate. Chlorine-water can easily be disproportioned, therefore it needs to be fresh prepared. A more convenient chlorine source is sodium-benzosulphonchloroamide (chlorogene), that in acidic medium *in situ* liberates chlorine, while sulphonamide is forming.

$$2I^- + Cl_2 = I_2 + 2Cl^- \quad \boxed{\text{violet in chloroform}}$$

$$I_2 + 5Cl_2 + 6H_2O = 2IO_3^- + 10Cl^- + 12H^+ \quad \boxed{\text{colourless}}$$

Iodide-ion can easily be oxidized, so in acidic medium reacts with many oxidation agents (e.g. potassium-permanganate, potassium-dichromate or hydrogen-peroxide).

$$2MnO_4^- + 10I^- + 16H^+ = 5I_2 + 2Mn^{2+} + 8H_2O$$

$$6I^- + Cr_2O_7^{2-} + 14H^+ = 3I_2 + 2Cr^{3+} + 7H_2O$$

$$2I^- + H_2O_2 + 2H^+ = I_2 + 2H_2O$$

Iron(III)-ion does not give precipitation with iodide, while it oxidize iodide to iodine. The reaction works also with iodate-ion and with bromate-ion.

$$2I^- + 2Fe^{3+} = I_2 + 2Fe^{2+}$$

6.3.4. Reactions of Cyanide-ion

Cyanides are synthetised in human body, are produced by certain bacteria, fungi and algae and are found in several plants. They also occur in fruit stones (bitter almonds, apricots, apples, peaches). In plants, cyanides are bound to sugar molecules in the form of cyanogenic glycosides and defend the plant against herbivores. Cyanides are very toxic. Cyanide anion is an inhibitor of the enzyme cytochrome c oxidase, the binding of the cyanide to this enzyme prevents transport of electrons from cytochrome c to oxygen, hence the electron transport chain is disrupted, and the cell can no longer aerobically produce ATP for energy. Hydrogen cyanide is the most hazardous compound, which has an odor of bitter almonds and kills by inhalation. Hydrogen cyanide is formed by adding acid to the solution of cyanide salt. Alkaline solutions of cyanide are safer. Oral ingestion of cyanide (200 mg) causes death within minutes. Sodium nitroprusside is used in clinical chemistry to measure urine ketone bodies as a follow-up to diabetic patients. Artificial vitamin B_{12} contains cyanide ligand (from cobalt cyanide) as an artifact of the purification process. Cobalt cyanide was used during World War I by Japanese physicians for the treatment of tuberculosis and leprosy.

The reactions can be studied on KCN solution (0.05 M).

1. Group reaction

Silver-nitrate with cyanide-ion gives white silver-cyanide precipitation only if the amount of silver-ion is in excess. If the silver-ion concentration is not high enough, water-soluble dicyano-argentate complex is forming. Silver-cyanide is soluble in ammonia, and in thiosulphate, but not in acids.

$$CN^- + Ag^+ = \underline{AgCN} \quad \boxed{\text{white}}$$

$$AgCN + CN^- = [Ag(CN)_2]^-$$

$$[Ag(CN)_2]^- + Ag^+ = 2\underline{AgCN} \quad \boxed{\text{white}}$$

2. Preussen-blue reaction

Iron(II)-sulphate is added to an alkaline solution of a cyanide, which is then boiled. After cooling and acidification with hydrochloric acid, a blue precipitate is forming.

The iron(III) is formed in the alkaline solution by oxidation. This is a characteristic and sensitive reaction.

$$Fe^{2+} + 6CN^- = [Fe(CN)_6]^{4-}$$

$$4Fe^{2+} + O_2 + 2H_2O = 4Fe^{3+} + 4OH^-$$

$$3[Fe(CN)_6]^{4-} + 4Fe^{3+} = \underline{Fe_4[Fe(CN)_6]_3} \quad \boxed{\text{Preussen-blue}}$$

3. Reaction with halides

With iodine or bromine, hydrogen-cyanides forms colourless iodocyanide or bromocyanide (the brown colour of the iodine or bromine disappear). The reactions are performed in alkaline medium (pH=9).

$$I_2 + HCN = ICN + H^+ + I^-$$

4. Elimination of cyanide

There are more possibilities to eliminate cyanide as a poisonous compound. Cyanide forms stable complexes with heavy metals. Unfortunately heavy metals even in this form pollute the environment. A more convenient method is the oxidation of cyanide. If cyanide is reacted with sodium-hypochlorite in the presence of cc sodium-hydroxide, through cyanate (OCN^-) intermediate, elemental nitrogen and carbonate-ion are forming. To set the alkaline medium is very important, because in lower pH, the poisonous chlorocyanide is forming. The remained cyanide-ion can be identified with the Preussen-blue reaction.

$$CN^- + OCl^- = OCN^- + Cl^-$$

$$2OCN^- + 3OCl^- + 2OH^- = N_2 + 2CO_3^{2-} + 3Cl^- + 2OH^-$$

In laboratory conditions, cyanide can be eliminated by using potassium-permanganate. To the solution of cyanide solid permanganate and base are added. In the reaction brown basic manganese-oxide is forming.

$$2MnO_4^- + 3CN^- + 3H_2O = 2MnO(OH)_2 + 3OCN^- + 2OH^-$$

6.3.5. Reactions of Thiocyanate-ion

Thiocyanate occur is small amount in spittle, blood and in urine. It is known to be an important part in the biosynthesis of hypothiocyanite by a lactoperoxidase. Thiocyanates decrease iodide transport into the thyroid follicular cell, hence foodstuffs containing thiocyanate are the best avoided by iodide deficient hypothyroid patients. Ingestion of thiocyanate of larger amount can cause retching and headache, 15-20 g from thiocyanate is already deadly.

The reactions can be studied on NH_4SCN solution (1 M).

1. Group reaction

The excess of silver-ion gives white precipitation with thiocyanate-ion. Before this, water-soluble dithiocyanato-argentate complex is forming. Silver-thiocyanate is soluble in ammonia, and in thiosulphate, but not in acids.

$$SCN^- + Ag^+ = \underline{AgSCN} \quad \boxed{\textbf{white}}$$

$$AgSCN + SCN^- = [Ag(SCN)_2]^-$$

2. Complex formation with iron(III)-ion

Iron(III)-chloride gives a deep-red colouration (see reaction of iron(III)) and the colourless fluoride complex is formed from the iron(III)-thiocyanate complex with fluorides. This is a highly sensitive reaction.

$$Fe^{3+} + nSCN^- = 2[Fe(SCN)_n]^{3-n} \quad \boxed{\textbf{deep-red solution}}$$

6.3.6. Simple analysis of anion group III

The anions are not changed by the former group reagents, but in nitric acid solution give a precipitate with $AgNO_3$. Bromide and iodide are simply differentiable from each other with the oxidation reactions. Identification of thiocyanate ion is achievable with $FeCl_3$ reagent.

6.4. Anion group IV

6.4.1. Reactions of Nitrite-ion

Nitrite can be found as a decomposition product of the organic materials and it is formed from ammonia trough bacterial oxidation. Nitrite appears in water, because of the incorrect fertilizing. Sodium nitrite is used in the food production industry for curing meat, because it prevents bacterial growth, gives the product a desirable pink-red color (fresh), such as with corned beef.

The therapic interest of nitrite is important. The nitrite compounds are efficient vasodilators, because they can transform to nitrogen monoxide in the human body. Nitrite is very dangerous especially for babies, but also for adult, it can cause poison in a dose of 1-2 g.

A corresponding acid is the unstable nitrous acid, in which the nitrogen has oxidation number +3. It can therefore act either as a reducing or as an oxidizing agent. The reactions can be studied on $NaNO_2$ solution (0.05 M).

1. Decomposition of nitrous acid

By adding diluted hydrochloric acid to nitrite-ion containing salt, after heating, the formed nitrous acid decomposes via dinitrogen-trioxide to nitrogen-oxides that can be identified with the blue colour of the starch-iodine paper. The positive reaction can also be observed based on the brown colour of nitrogen-dioxide.

$$2NO_2^- + 2H^+ \rightleftharpoons N_2O_3 + H_2O$$

$$N_2O_3 \rightleftharpoons NO_2\uparrow + NO\uparrow$$

$$2NO + O_2 = 2NO_2$$

$$2I^- + 2NO_2^- + 4H^+ = I_2 + 2NO + 2H_2O$$

The intermediate of the reaction is dinitrogen-trioxide that via disproportion decomposes quickly to nitrogen-monoxide and to nitrogen-dioxide. If the mixture is cooled down, and some drops of cc hydrogen-chloride is added, the blue colour of dinitrogen-trioxide can be observed.

2. Reduction of nitrite to ammonia

The identification of nitrite-ion via ammonia is also possible. For the reduction zinc (dust) can be used, that will be added to the alkaline solution of nitrite. When the mixture is heated the smell of ammonia can be observed, or it can be identified with litmus paper. The reduction to ammonia can also be achieved in acidic medium. The formed ammonium-ion can be identified with Nessler reagent.

$$NO_2^- + 3Zn + 5OH^- + 5H_2O = NH_3\uparrow + 3[Zn(OH)_4]^{2-}$$

$$NO_2^- + 3Zn + 8H^+ = NH_4^+ + 3Zn^{2+} + 2H_2O$$

3. Detection as nitroso-iron(II) complex

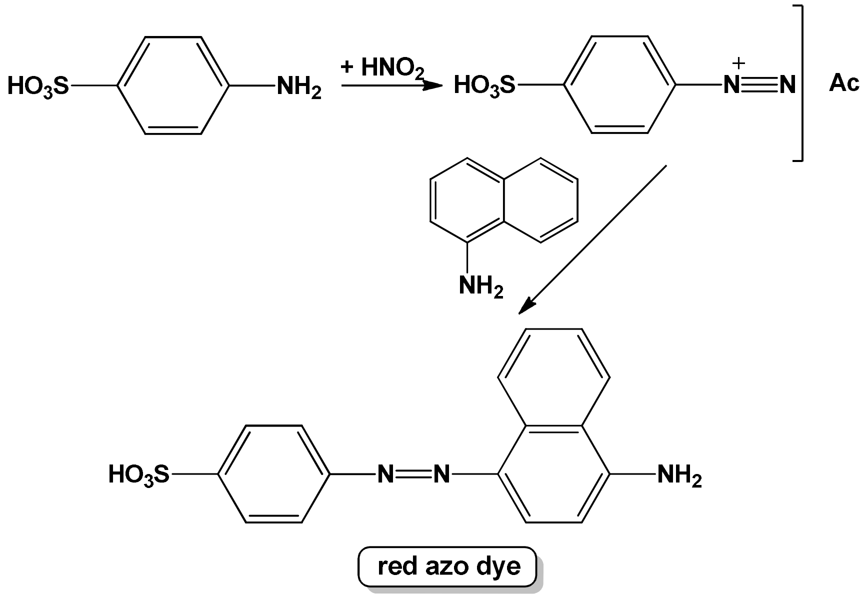
Nitrite gives the brown-ring test with iron(II)-sulphate in acetic acid solution. As the results of the reaction brown nitroso-iron(III) complex is forming. The necessary nitrogen-monoxide for the reaction is forming by the reaction of iron(II)-ion with nitrite-ion. The reaction can be disturbed by iodide, cyanide and thiocyanate-ions.

$$NO_2^- + Fe^{2+} + 2H^+ = NO + Fe^{3+} + H_2O$$

$$[Fe(H_2O)_6]^{2+} + NO = [Fe(H_2O)_5NO]^{2+} + H_2O \quad \boxed{\textbf{brown colouration}}$$

4. Griess-Ilosvay reaction

The presence of nitrite-ion can be detected by using azodyes. In this reaction, sulphanylic acid with nitrite forms diazonium derivatives, that reacts further with □-naphthylamine to form red azodye. To the solution of nitrite, acetic acidic solution of sulphanilic acid (Griess-Ilosvay A reagent) is added. The solution become yellow, and then acetic acid solution of □-naphthylamine (Griess-Ilosvay B reagent) is added to the previous mixture. If nitrite was present the colour of the solution will turn to red. *Note: Griess-Ilosvay B reagent usually has a pale red colour. Do not confuse this with the much stronger red colour of the azodye.*



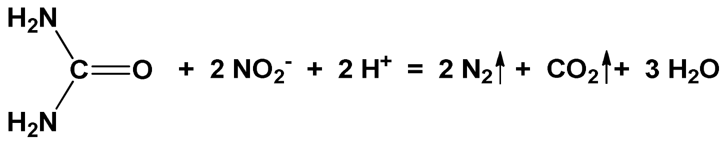
5. Oxidation of nitrite-ion with permanganate

In the presence of sulphuric acid, nitrite-ion reduces potassium-permanganate to manganese(II), while it will be oxidized to nitrate.

$$2MnO_4^- + 5NO_2^- + 6H^+ = 2Mn^{2+} + 5NO_3^- + 3H_2O$$

6. Elimination of nitrite-ion

The poisonous nitrite-ion can be eliminated by reductive methods. By heating nitrite in acidic medium with carbamide, nitrogen and carbon-dioxide are forming. One portion of nitrite-ion will be transformed (disproportion) to nitrogen-monoxide and to nitrate. In carbamide the oxidation number of nitrogen is -3, so synproportion is occurring.



$$(H_2N)_2C{=}O + 2\,NO_2^- + 2\,H^+ = 2\,N_2\uparrow + CO_2\uparrow + 3\,H_2O$$

$$3NO_2^- + 2H^+ = NO_3^- + 2NO + H_2O$$

Nitrite-ion in acidic medium reacts quickly with sodium-azide, during the reaction dinitrogen-oxide and nitrogen are forming.

$$N_3^- + NO_2^- + 2H^+ = N_2 + N_2O + H_2O$$

6.4.2. Reactions of Nitrate-ion

Nitrate salts are found naturally on earth in large deposits, the major source is sodium nitrate, but also can be found in fertilizers. Nitrate is used as an oxidizing agent, sodium nitrate is used to remove air bubbles from molten glass and ceramics. Nitrate as oxidizing agent is the main component of the gunpowder.

Internally, nitrate has diuretic and purgative effect, but some amount of nitrate transforms to nitrite in enteron, hence it has the same physiological effect as nitrite. Nitric acid is corrosive, stains human skin yellow due to its reaction with keratin.

The nitrate ion contains nitrogen in its highest oxidation state of +5. The reactions can be studied on KNO_3 solution (0.05 M).

1. Reduction of nitrate to ammonia

Similar to nitrite, nitrate-ion in the presence of zinc (dust) or in acidic or in alkaline conditions, via nitrite-formation, can be reduced to ammonia.

$$NO_3^- + 4Zn + 7OH^- + 6H_2O = NH_3 + 4[Zn(OH)_4]^{2-}$$

$$NO_3^- + 4Zn + 10H^+ = NH_4^+ + 4Zn^{2+} + 3H_2O$$

2. Detection as nitroso-iron(II) complex

The reaction similar with that for nitrite-ion, the difference is that nitrate-ion only in the presence of cc. sulphuric acid can be reduced by iron(II)-ion. Accordingly, nitrate can be distinguished from nitrite.

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

$$[Fe(H_2O)_6]^{2+} + NO = \underline{[Fe(H_2O)_5NO]^{2+}}$$

3. Griess-Ilosvay reaction

The red azodyes also forms in case of nitrate, if after adding of the reagents, zinc (dust) is also added into the mixture. In this case nitrate will be *in situ* reduced to nitrite. *Note: some red colour can be formed even before addition of Zn.*

6.4.3. Reactions of Chlorate-ion

Chlorate is an instable oxidizing agent. Mixtures of chlorate salts with organic and other oxidizable compounds will immediately deflagrate. For this reason, chlorates were widely used in pyrotechnics, but in our days the more stable perchlorates are used instead of chlorates.

Chlorates are toxic, though they form generally harmless chlorides on reduction.

The corresponding acid is $HClO_3$, in which the oxidation state of chlorine is +5. The reactions can be studied on $KClO_3$ solution (0.05 M).

1. Reaction with potassium-iodide

In cc hydrochloric acid solution, chlorate-ion oxidize iodide-ion to iodine. Its colour is violet by using chloroform.

$$ClO_3^- + 6I^- + 6H^+ = 3I_2 + Cl^- + 3H_2O$$

violet in chloroform

2. Reduction to chloride-ion

By adding zinc (dust) into the nitric acidic solution of chlorate-ion, chloride is forming. This can be identified by using silver-nitrate.

$$ClO_3^- + 3Zn + 6H^+ = Cl^- + 3Zn^{2+} + 3H_2O$$

Chlorate-ion in acidic medium can also be reduced to chloride with sodium-nitrite and with sodium-sulphite.

$$ClO_3^- + 3NO_2^- = Cl^- + 3NO_3^-$$

$$ClO_3^- + 3SO_3^{2-} = Cl^- + 3SO_4^{2-}$$

3. Reactions with concentrated acids

By adding cc sulphuric acid, the disproportion of chlorate-ion take place, and the formation of orange-red chloro-dioxide (ClO_2) and perchlorate-ion can be observed. By using this reaction, the presence of chlorate-ion in chloride-ion can be identified. By using cc hydrochloric acid, this latter reaction is just a side-reaction, the main product is chlorine gas that forms via synproportion, and can be identified by using starch-iodide paper. If the reaction is performed from solid chlorate salt, caution of explosion can be, therefore the reaction should be done under the hood, starting from clean and small amount of reagents.

$$3ClO_3^- + 2H^+ = 2ClO_2 + ClO_4^- + H_2O \qquad \boxed{\text{orange-red}}$$

$$ClO_3^- + 5Cl^- + 6H^+ = 3Cl_2 + 3H_2O \qquad \boxed{\text{greenish-yellow gas}}$$

4. Thermal analysis

If a small amount of clean sodium-chlorate in a test tube is heated, it will be decomposed to oxygen, chloride and perchlorate. Further heating will cause the decomposition of perchlorate to oxygen and chloride. The formed chloride can be identified after dissolving with silver-nitrate.

6.4.4. Reactions of Perchlorate-ion

Perchlorates were found first in terrestrial nitrate deposits in Chile. The natural perchlorate is globally deposited on Earth as a contaminant. In contrast with chlorate, perchlorate compounds do not oxidize organic compounds until the mixture is heated. This property is useful in pyrotechnics. Perchlorates reduces hormone production in the thyroid gland.

Perchloric acid is the strongest acid known. The chlorine in it has the oxidation state +7. The reactions can be studied on $NaClO_4$ solution (0.2 M).

1. Low reactivity

Very important difference from chlorate, that perchlorate neither by using iodine, nor by zinc (dust) can not be reduced to chloride.

2. Precipitation with potassium(I)-ion

By treating perchlorate-ion with potassium-chloride, white potassium-perchlorate precipitates. The precipitate forms only by using high concentrated reagents.

$$K^+ + ClO_4^- = KClO_4 \qquad \boxed{\text{white}}$$

6.4.5. Reactions of Acetate-ion

Acetate anion is the conjugate base of acetic acid, which is an organic carboxylic acid. Acetic acid is used in chemical industry not only as a chemical reagent also as a solvent. Glacial acetic acid is an excellent polar protic solvent. Acetic acid is used worldwide as a vinegar, as an acidity regulator and as a condiment. Acetic acid has been used to treat cancer, it is antiseptic against streptococci, pseudomonas, enterococci and others.

The reactions can be studied on sodium acetate solution (0.5 M).

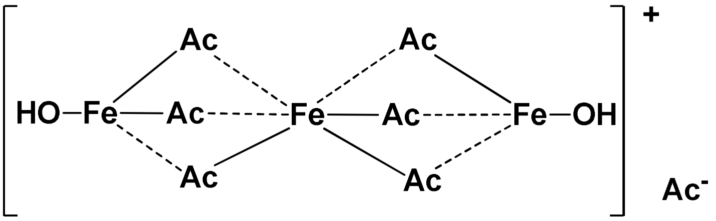
1. Reaction with strong acids

Acetic acid is a weak volatile acid. Acetate-ion can be protonated with mineral acids, then characteristic smell of acetic acid can be observed. Starting from solid sample, it will be homogenized with acidic salt (e.g. $KHSO_4$) and then some drops of water will be added.

$$H^+ + CH_3COONa = CH_3COOH\uparrow + Na^+ \quad \boxed{\text{characteristic smell}}$$

2. Reaction with iron(III)-ion

In the presence of iron(III)-ions, from neutral solution, acetate-ion forms brownish-red hexaacetato-dihydroxo-triferri-acetate.



hexaacetato-dihydroxo-triferri-acetate

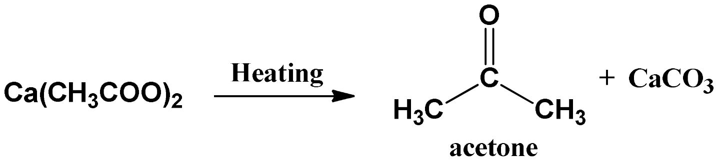
3. Reactions with silver-nitrate

When the neutralized (with nitric acid) solution of sodium-acetate is treated with silver-nitrate, white silver-acetate precipitates. The solubility of the precipitation is 1%.

$$Ag^+ + CH_3COO^- = \underline{CH_3COOAg} \quad \boxed{\text{white}}$$

4. Reaction with calcium-oxide

When solid sodium-acetate is homogenized with calcium-oxide, after heating, the characteristic smell of acetone can be observed.



6.4.6. Simple analysis of anion group IV

These anions have no common reagent, the ions can be identified only with special reagents.

(i) Griess-Ilosvay reaction can be used for the identification and differentiation of nitrite and nitrate.

(ii) From acetate, $KHSO_4$ liberates acetic acid, which can be detected when the solid mixture (acetate+$KHSO_4$) is stumped through its odor, which resembles that of vinegar.

7. References and recommended literature

[1] Dr. Stájer Géza: *Qualitative Inorganic Analysis*, university curriculum, Szeged, 1988
[2] Dr. Simon Lajos: *Kvalitatív kémiai analízis*, university curriculum, Szeged, 1992
[3] Dr. Martinek Tamás: *Kvalitatív kémiai analízis*, JATEPress, Szeged, 2007
[4] Burger Kálmán: *Az analitikai kémia alapjai: kémiai és műszeres elemzés*, Semmelweis Kiadó, Budapest, 1999
[5] Barcza Lajos, Buvári Ágnes: *A minőségi kémiai analízis alapjai (4th revised edition)*, Medicina Kiadó, Budapest, 1997
[6] George Svehla: *Vogel's Qualitative Inorganic Analysis, 7th ed.*, Longman, Edinburgh, 1997

8. Annexes

Acidity constants of common acids and important acids

Acid$_1$		**Base$_1$**		**Acid$_2$**		**Base$_2$**	**pK_a**
$HClO_4$	+	H_2O	$\rightleftharpoons$	H_3O^+	+	ClO_4^-	-10
H_2SO_4	+	H_2O	$\rightleftharpoons$	H_3O^+	+	HSO_4^-	-3.00
HSO_4^-	+	H_2O	$\rightleftharpoons$	H_3O^+	+	SO_4^{2-}	1,98
HI	+	H_2O	$\rightleftharpoons$	H_3O^+	+	I^-	-10
HBr	+	H_2O	$\rightleftharpoons$	H_3O^+	+	Br^-	-9
HCl	+	H_2O	$\rightleftharpoons$	H_3O^+	+	Cl^-	-6.00
HF	+	H_2O	$\rightleftharpoons$	H_3O^+	+	F^-	3.17
HNO_3	+	H_2O	$\rightleftharpoons$	H_3O^+	+	NO_3^-	-1.32
HNO_2	+	H_2O	$\rightleftharpoons$	H_3O^+	+	NO_2^-	3.34
H_2SO_3	+	H_2O	$\rightleftharpoons$	H_3O^+	+	HSO_3^-	1.78
HSO_3^-	+	H_2O	$\rightleftharpoons$	H_3O^+	+	SO_3^{2-}	7.20
H_3PO_4	+	H_2O	$\rightleftharpoons$	H_3O^+	+	$H_2PO_4^-$	2.14
$H_2PO_4^-$	+	H_2O	$\rightleftharpoons$	H_3O^+	+	HPO_4^{2-}	7.20
HPO_4^{2-}	+	H_2O	$\rightleftharpoons$	H_3O^+	+	PO_4^{3-}	12.34
H_2CO_3	+	H_2O	$\rightleftharpoons$	H_3O^+	+	HCO_3^-	6.36
HCO_3^-	+	H_2O	$\rightleftharpoons$	H_3O^+	+	CO_3^{2-}	10.33
$[Al(H_2O)_6]^{3+}$	+	H_2O	$\rightleftharpoons$	H_3O^+	+	$[Al(H_2O)_5(OH)]^{3+}$	-5
H_3O^+	+	H_2O	$\rightleftharpoons$	H_3O^+	+	H_2O	0
H_2O	+	H_2O	$\rightleftharpoons$	H_3O^+	+	HO^-	13.99
H_2S	+	H_2O	$\rightleftharpoons$	H_3O^+	+	HS^-	7.03
HS^-	+	H_2O	$\rightleftharpoons$	H_3O^+	+	S^{2-}	13.4
H_2O_2	+	H_2O	$\rightleftharpoons$	H_3O^+	+	HOO^-	11.67
HOCl	+	H_2O	$\rightleftharpoons$	H_3O^+	+	OCl^-	7.17
HOBr	+	H_2O	$\rightleftharpoons$	H_3O^+	+	OBr^-	8.65
NH_4^+	+	H_2O	$\rightleftharpoons$	H_3O^+	+	NH_3	9.2
HCN	+	H_2O	$\rightleftharpoons$	H_3O^+	+	CN^-	9.48
CH_3COOH	+	H_2O	$\rightleftharpoons$	H_3O^+	+	CH_3COO^-	4.76
$(COOH)_2$	+	H_2O	$\rightleftharpoons$	H_3O^+	+	$HOOC\text{-}COO^-$	1.37
$HOOC\text{-}COO^-$	+	H_2O	$\rightleftharpoons$	H_3O^+	+	$(COO)_2^{2-}$	3.81
$B(OH)_3$	+	H_2O	$\rightleftharpoons$	H_3O^+	+	$B(OH)_4^-$	9.14

Cumulative constants of some complex ion formations

Complex ion	**β**
$[Ag(CN)_2]^-$	5.6×10^{18}
$[Ag(NH_3)_2]^+$	1.7×10^{7}
$[Ag(S_2O_3)_2]^{3-}$	2.9×10^{13}
$[Cd(NH_3)_4]^{2+}$	1.0×10^{7}
$[Cu(CN)_4]^{3-}$	1.0×10^{16}
$[Cu(NH_3)_4]^{2+}$	4.8×10^{12}
$[Fe(CN)_6]^{4-}$	1.0×10^{35}
$[Fe(CN)_6]^{3-}$	9.1×10^{41}
$[Ni(CN)_4]^{2-}$	1.0×10^{31}
$[Ni(NH_3)_6]^{2+}$	5.6×10^{8}
$[Zn(NH_3)_4]^{2+}$	2.9×10^{9}
$[Zn(OH)_4]^{2-}$	2.8×10^{15}

Standard redox potentials of elements in increasing order

Reduced form		**Oxidized form**	**E_0 (V)**
Li	⇌	$Li^+ + e^-$	-3.02
K	⇌	$K^+ + e^-$	-2.93
Ba	⇌	$Ba^{2+} + 2\ e^-$	-2.90
Sr	⇌	$Sr^{2+} + 2\ e^-$	-2.89
Ca	⇌	$Ca^{2+} + 2\ e^-$	-2.87
Na	⇌	$Na^+ + e^-$	-2.71
Mg	⇌	$Mg^{2+} + 2\ e^-$	-2.34
Al	⇌	$Al^{3+} + 3\ e^-$	-1.67
Mn	⇌	$Mn^{2+} + 2\ e^-$	-1.05
Zn	⇌	$Zn^{2+} + 2\ e^-$	-0.76
Fe	⇌	$Fe^{2+} + 2\ e^-$	-0.44
Cd	⇌	$Cd^{2+} + 2\ e^-$	-0.40
Co	⇌	$Co^{2+} + 2\ e^-$	-0.28
Ni	⇌	$Ni^{2+} + 2\ e^-$	-0.25
Sn	⇌	$Sn^{2+} + 2\ e^-$	-0.14
Pb	⇌	$Pb^{2+} + 2\ e^-$	-0.13
½ H_2	⇌	$H^+ + e^-$	0
Sb	⇌	$SbO^+ + 3\ e^-$	0.21
Bi	⇌	$Bi^{3+} + 3\ e^-$	0.23

As + 3 H_2O	$\rightleftharpoons$	$As(OH)_3 + 3\ e^- + 3\ H^+$	0.24
Cu	$\rightleftharpoons$	$Cu^{2+} + 2\ e^-$	0.35
Ag	$\rightleftharpoons$	$Ag^+ + e^-$	0.80
2 Hg	$\rightleftharpoons$	$Hg_2^{2+} + 2\ e^-$	0.80
Hg	$\rightleftharpoons$	$Hg^{2+} + 2\ e^-$	0.85

Other standard redox potentials

Reduced form		**Oxidized form**		**E_0 (V)**
$2\ SO_4^{2-}$	$\rightleftharpoons$	$S_2O_8^{2-} + 2\ e^-$		2.06
Co^{2+}	$\rightleftharpoons$	$Co^{3+} + e^-$		1.84
$2\ H_2O$	$\rightleftharpoons$	$H_2O_2 + 2\ H^+ + 2\ e^-$		1.78
$Mn^{2+} + 4\ H_2O$	$\rightleftharpoons$	$MnO_4^{2-} + 8\ H^+ + 4\ e^-$		1.78
$\frac{1}{2}\ Cl_2 + H_2O$	$\rightleftharpoons$	$HOCl + H^+ + e^-$		1.59
$Mn^{2+} + 4\ H_2O$	$\rightleftharpoons$	$MnO_4^- + 8\ H^+ + 5\ e^-$		1.52
$\frac{1}{2}\ Br_2 + H_2O$	$\rightleftharpoons$	$HOBr + H^+ + e^-$		1.59
$\frac{1}{2}\ Br_2 + 3\ H_2O$	$\rightleftharpoons$	$BrO_3^- + 6\ H^+ + 5\ e^-$		1.52
$\frac{1}{2}\ Cl_2 + 3\ H_2O$	$\rightleftharpoons$	$ClO_3^- + 6\ H^+ + 5\ e^-$		1.47
$2\ Cr^{3+} + 7\ H_2O$	$\rightleftharpoons$	$Cr_2O_7^{2-} + 14\ H^+ + 6\ e^-$		1.36
$\frac{1}{2}\ I_2 + H_2O$	$\rightleftharpoons$	$HOI + H^+ + e^-$		1.45
$Pb^{2+} + 2\ H_2O$	$\rightleftharpoons$	$PbO_2 + 4\ H^+ + 2\ e^-$		1.46
Cl^-	$\rightleftharpoons$	$\frac{1}{2}\ Cl_2 + e^-$		1.36
$Mn^{2+} + 2\ H_2O$	$\rightleftharpoons$	$MnO_2 + 4\ H^+ + 2\ e^-$		1.28
$2\ H_2O$	$\rightleftharpoons$	$O_2 + 4\ H^+ + 4\ e^-$		1.23[a]
$\frac{1}{2}\ I_2 + 3\ H_2O$	$\rightleftharpoons$	$IO_3^- + 6\ H^+ + 5\ e^-$		1.20
Br^-	$\rightleftharpoons$	$\frac{1}{2}\ Br_2 + e^-$		1.07
$NO + H_2O$	$\rightleftharpoons$	$HNO_2 + H^+ + e^-$		0.99
$NO + 2\ H_2O$	$\rightleftharpoons$	$NO_3^- + 4\ H^+ + 3\ e^-$		0.96
$HNO_2 + H_2O$	$\rightleftharpoons$	$NO_3^- + 3\ H^+ + 2\ e^-$		0.94
Hg_2^{2+}	$\rightleftharpoons$	$2\ Hg^{2+} + 2\ e^-$		0.91
$Cl^- + 2\ OH^-$	$\rightleftharpoons$	$ClO^- + H_2O + 2\ e^-$		0.89
Fe^{2+}	$\rightleftharpoons$	$Fe^{3+} + e^-$		0.77
$Br^- + 2\ OH^-$	$\rightleftharpoons$	$BrO^- + H_2O + 2\ e^-$		0.76
Sb^{3+}	$\rightleftharpoons$	$Sb^{5+} + 2\ e^-$		0.75[a]
$[Fe(CN)_6]^{4-}$	$\rightleftharpoons$	$[Fe(CN)_6]^{3-} + e^-$		0.69[c]
H_2O_2	$\rightleftharpoons$	$O_2 + 2\ H^+ + 2\ e^-$		0.68
$2\ SbO^+ + 3\ H_2O$	$\rightleftharpoons$	$Sb_2O_5 + 6\ H^+ + 4\ e^-$		0.64

$Cl^- + 6\,OH^-$	⇌	$ClO_3^- + 3\,H_2O + 6\,e^-$		0.62
$Br^- + 6\,OH^-$	⇌	$BrO_3^- + 3\,H_2O + 6\,e^-$		0.61
$MnO_2 + 4\,OH^-$	⇌	$MnO_4^{2-} + 2\,H_2O + 2\,e^-$		0.58
$MnO_2 + 4\,OH^-$	⇌	$MnO_4^- + 2\,H_2O + 3\,e^-$		0.57
$H_3AsO_3 + H_2O$	⇌	$H_3AsO_4 + 2\,H^+ + 2\,e^-$		0.56
MnO_4^{2-}	⇌	$MnO_4^- + e^-$		0.54
$I^- + 2\,OH^-$	⇌	$IO^- + H_2O + 2\,e^-$		0.49
$[Fe(CN)_6]^{4-}$	⇌	$[Fe(CN)_6]^{3-} + e^-$		0.69[b]
$4\,OH^-$	⇌	$O_2 + 2\,H_2O + 4\,e^-$		0.40
$I^- + 6\,OH^-$	⇌	$IO_3^- + 3\,H_2O + 6\,e^-$		0.26
$2\,S_2O_3^{2-}$	⇌	$S_4O_6^{2-} + 2\,e^-$		0.17
Sn^{2+}	⇌	$Sn^{4+} + 2\,e^-$		0.15
$Cr(OH)_3 + 5\,OH^-$	⇌	$CrO_4^{2-} + 4\,H_2O + 3\,e^-$		0.12
$NO_2^- + 2\,OH^-$	⇌	$NO_3^- + H_2O + 2\,e^-$		0.01
$Mn(OH)_2 + 2\,OH^-$	⇌	$MnO_2 + 2\,H_2O + 2\,e^-$		-0.05
AsH_3	⇌	$As + 3\,H^+ + 3\,e^-$		-0.24
$NO + 2\,OH^-$	⇌	$NO_2^- + H_2O + e^-$		-0.46
$HS^- + OH^-$	⇌	$S + H_2O + 2\,e^-$		-0.48
$(COOH)_2$	⇌	$2\,CO_2 + 2\,H^+ + 2\,e^-$		-0.47
$2\,S^{2-}$	⇌	$S_2^{2-} + 2\,e^-$		-0.51
SbH_3	⇌	$Sb + 3\,H^+ + 3\,e^-$		-0.51
$SO_3^{2-} + 2\,OH^-$	⇌	$SO_4^{2-} + H_2O + 2\,e^-$		-0.90
$[Sn(OH)_4]^{2-} + 2\,OH^-$	⇌	$[Sn(OH)_6]^{2-} + 2\,e^-$		-0.96
$S_2O_4^{2-} + 4\,OH^-$	⇌	$2\,SO_3^{2-} + 2\,H_2O + 2\,e^-$		-1.12
$Zn + 4\,OH^-$	⇌	$[Zn(OH)_4]^{2-} + 2\,e^-$		-1.22
$Al + 4\,OH^-$	⇌	$[Al(OH)_4]^- + 3\,e^-$		-2.35

[a] in 3.5 M HCl

[b] in 0.01 M NaOH

[c] in 0.5 M H_2SO_4

Solubility products (pK_{sp}) of some precipitates

Precipitate	**pK_{sp}**		**Precipitate**	**pK_{sp}**
Ag_2S	49		Bi_2S_3	32.6
HgS	52		As_2S_3	28.6
PbS	28		SnS	28
CuS	44		SnS_2	26
CdS	27		As_2S_5	39.7
α-CoS	21.3		FeS	18.4
β-CoS	26.7		MnS	15
α-NiS	20.5		ZnS	24
β-NiS	26		AgSCN	12
AgF	-2.3*		$AgClO_3$	$0.6^{\#}$
AgCl	9.96		$AgBrO_3$	4.3
AgBr	12.4		$AgIO_3$	7.7
AgI	16		Ag_2CO_3	11.3
Ag_2O	7.7		Ag_2SO_4	$4.5^{\#}$
AgCN	11.4		$PbCO_3$	13.5
$PbCl_2$	4.7		$PbSO_4$	7.8
PbI_2	8.1		$PbCrO_4$	13.8
$Pb(OH)_2$	15.6		$^{\#}AgClO_3$ and Ag_2SO_4 are not really precipitates.	
*AgF is not a precipitate.				