

Qualitative analysis of important elements from the point view of biology and toxicology

Medical fields use a whole range of analytical methods in their specialized laboratories (clinical biochemistry, molecular biology, etc.).

By chemical analysis we mean a series of operations that are carried out with the analyzed (examined) material in order to find out:

1. its chemical composition – **qualitative analysis** , evidence of individual components
2. amount of individual components – **quantitative analysis**

Qualitative analysis almost always precedes quantitative analysis. An average sample is taken from the examined material, which is assessed by preliminary analysis in **the dry way** (appearance, color of the sample, behavior during pyroreaction – annealing in the flame, coloration of the flame, etc.) and in **the wet way** (evidence of chemical compounds in aqueous solutions).

Most inorganic compounds in aqueous solutions dissociate into **ions** – positively charged **cations** and negatively charged **anions**. For the evidence of individual ions (cations, possibly anions) in solutions, precipitation analytical reactions are most often used, which are actually a double exchange (conversion) of ions to form a slightly soluble product of the given ionic compound, which is excluded from the solution as a white precipitate. colored precipitate. The other ions remain mostly unchanged in the (mother) solution above the precipitate. However, slightly soluble ionic compounds are not absolutely insoluble in water, it is only a matter of quantitative differences in their solubilities, which can be considerable, see approximate solubilities of ionic compounds , or solubility products of ionic compounds. Tabulated solubility values of inorganic compounds are given in most chemical tables. Reactions in which colored, mostly soluble, less dissociated coordination compounds, complexes , are also used to a large extent to prove individual ions .

Various systematic procedures are then used to determine individual cations and anions in mixed samples, using reactions with group reagents that divide individual ions into analytical classes. Specific ions are determined by special targeted reactions after the previous gradual elimination of other cations and anions. The most well-known analytical qualitative procedure for the determination of cations is the sulfane (formerly hydrogen sulfide) procedure. However, these systematic procedures are laborious and tedious and are currently being replaced by looser and more purposeful combinations of group and selective reactions. The analysis adapts to the individual nature of the sample.



Toxicology

Group reagents

Very often used group reagents, which are used for the rapid **determination of cations**, are: hydrochloric acid HCl, sulfuric acid H_2SO_4 , saturated solution of hydrogen sulfide H_2S in an acidic environment, white ammonium sulfide $(\text{NH}_4)_2\text{S}$, alkaline hydroxides NaOH , KOH, ammonia NH_3 , NH_4OH , ammonium carbonate $(\text{NH}_4)_2\text{CO}_3$, alkaline iodide KI, hydrolytic reactions (reducing the acidity of the solution by diluting it with water, adding sodium acetate).

Group reagents for **detecting anions** are: barium salt solution $\text{Ba}(\text{NO}_3)_2$, silver salts AgNO_3 , oxidation reaction with MnO_4 or I_2 , reduction reaction with I^- .

Determination of cations

According to the hydrogen sulfide procedure, cations are divided into 5 analytical classes:

I. class

Ag^+ , Pb^{2+} , Hg_2^{2+} . The group reagent is HCl . The chlorides of these cations are insoluble in water, as are their sulfides, see tab. solubility products .

II.A class

Cu²⁺, Hg²⁺, Bi³⁺ . The group reagent is hydrogen sulfide **H₂S** from an acidic environment (a small concentration of S²⁻ is enough to precipitate the sulfides of these cations), see K_s . The chlorides of these cations are soluble in water. Sulfides are insoluble in dilute acids, in ammonium hydroxide NH₄OH and in yellow ammonium sulfide (NH₄)₂S_x .

II.B class

As³⁺ . Sulfides are soluble in yellow ammonium sulfide (NH₄)₂S_x .

III. class

Zn²⁺, Fe²⁺, Fe³⁺ . The group reagent is white ammonium sulfide, **(NH₄)₂S** (its complete dissociation guarantees a high concentration of S²⁻ necessary for the precipitation of sulfides of these cations, see K_s). Sulfides are already soluble in dilute acids, they are split into hydrogen sulfide and the corresponding metal hydroxide by hydrolysis.

IV. class

Ca²⁺, Ba²⁺ . The group agent is ammonium carbonate **(NH₄)₂CO₃** . The sulfides of these cations are soluble in water, the carbonates form white precipitates that dissolve in dilute and strong acids, while carbon dioxide gas escapes.

V. class

Mg²⁺, Li⁺, Na⁺, K⁺, NH₄⁺ . There is no group reagent, each cation is tested with special reactions, and the colored **flame reactions** of some cations might be used.

Determination of anions

In a similar way to cations, anions are divided into three analytical classes according to their reactions with barium and silver salts, and then according to the reactions and behavior of the resulting compounds with other reagents. Some literature mentions the division of anions into 4 classes (SO₄²⁻, F⁻ form a separate class).

I. class

CO₃²⁻, PO₄³⁻, SO₃²⁻, CrO₄²⁻, SO₄²⁻, F⁻ . They are precipitated with both barium and silver nitrate .

II. class

Cl⁻, I⁻, CN⁻, S²⁻, HS⁻, NO₂⁻ . They are precipitated with silver nitrate .

III. class

NO₃⁻, ClO₄⁻, MnO₄⁻ . They do not precipitate with any group reagent.

Solubility product

We derive the **solubility product** from the relationship for equilibrium constants , which characterize the equilibrium of chemical reactions in heterogeneous systems. In precipitation reactions in aqueous solutions used in qualitative analysis, an equilibrium is established between unreacted ions in the solution above the precipitate and the solid phase of the precipitate. E.g. for the slightly soluble compound (precipitate) Ag₂CrO₄ , arising according to the chemical equation



applies to the steady state

$$K = \frac{[\text{Ag}^+]^2 \cdot [\text{CrO}_4^{2-}]}{[\text{Ag}_2\text{CrO}_4]} .$$

Since during precipitation the solution of the insoluble compound is saturated and the substance concentration of the insoluble compound is constant, the product of the equilibrium constant and the concentration of the insoluble compound will also be constant.

We get a relationship

$$K_s = K \cdot [\text{Ag}_2\text{CrO}_4] = [\text{Ag}^+]^2 \cdot [\text{CrO}_4^{2-}]$$

In general, therefore, the solubility product K_{sp} is given by the product of the equilibrium concentrations of ions in the solution above the precipitate, multiplied by the stoichiometric coefficients of the given chemical reaction. The solubility products of a number of substances are tabulated.

According to the solubility product, we can assess and calculate the solubility of substances under different conditions, it depends on temperature, pH and the presence of other foreign ions in the solution. This can be used in qualitative analysis, it can be influenced according to the need of the analytical procedures of the precipitation of poorly soluble compounds for the purpose of their better separations and evidence.

Complex compounds

Complex compounds , **coordination compounds** (complexes) can be molecules or ions that contain a central particle, atom or ion to which ligands are bound by a coordination covalent bond . Central particles are usually atoms or ions of transition elements with unoccupied valence orbitals that can accept free **electron pairs**, they are **electron acceptors** . The cores of the *d* and *f*-elements are the best, *the p* and *the s*-elements are the worst. **Ligands** (electron donors) can be anions, e.g. Cl^- – chloro, Br^- – bromo, CN^- – cyano, OH^- – hydroxo, or even neutral molecules that have an atom with a free electron pair, e.g. H_2O – aqua, NH_3 – ammine, NO – nitrosyl, CO – carbonyl. The maximum number of monovalent ligands around the central particle is called the coordination number of the compounds, it is most often the number 6, 4, 8, 2. Coordination compounds can contain a complex **cation**, **anion**, or **both**. The nomenclature of these compounds is discussed in ^[1].

Complex compounds are mostly water-soluble, less dissociated and, due to coordination bonds, differ from their original components in color and solubility. They are therefore widely used in analytical chemistry. Chemical equilibrium is established in solutions of complex compounds, e.g.



In this case it applies

$$K_k = \frac{[\text{Cu}(\text{NH}_3)_4]^{2+}}{[\text{Cu}^{2+}] \cdot [\text{NH}_3]^4}$$

K_k is **the stability constant** of the complex; the larger the value of K_k , the more stable the complex and vice versa.

Complex compounds also include **chelate complexes (chelates)**. In these complexes, the ligand is usually an organic compound that can simultaneously occupy several coordination sites around the central atom and contains several free electron pairs. A chelating agent is an organic substance that provides at least two **free electron pairs** to form a dative bond. Some of these reagents are used in analytical chemistry in titration determinations and otherwise, e.g. chelating agent EDTA (ethylenediaminetetraacetic acid and its salts), biuret and other. A number of chelating agents are used in **medicine** for acute poisoning by the cations of some divalent and trivalent metals, to bind them and remove them from the body. **Physiologically significant** are also the chelate structures of many enzymes , as well as eg hemoglobin , chlorophyll and other biological pigments .

Examples of some inorganic compounds important in medicine and toxicology

□

Ag	silver	colloidal silver, bactericidal effects, disinfection of wells, Sagen, amalgams
Al(OH) ₃	aluminum hydroxide	antacid
As ₂ O ₃	arsenic oxide	highly toxic
BaSO ₄	barium sulfate	use in radiology, intestibar
CaCl ₂	calcium chloride	it is given in case of calcium deficiency
CaSO ₄	calcium sulfate	gypsum
CO	carbon monoxide	toxic gas, gas poisoning
CO ₂	carbon dioxide	blood buffering system, carbonated drinks
Fel ₂	ferrous iodide	dsadsagiven in case of iron deficiency
HCO ₃ ⁻	bicarbonate anion	blood buffering system
H ₃ BO ₃	boric acid	pine water, disinfectant, component of eye drops
H ₂ O ₂	hydrogen peroxide	disinfectant solution
HCl	hydrochloric acid	contained in gastric juices
Hg	Quicksilver	stomatology, amalgamy
Hg ₂ Cl ₂	mercuric chloride	calomel, measuring electrodes in pH measurement
HgCl ₂	mercuric chloride	highly toxic
KCl	potassium chloride	given in case of potassium deficiency
KCN	potassium cyanide	highly toxic, cyankali
KI	potassium iodide	iodization of drinking water and table salt
KMnO ₄	potassium manganate	strong oxidizing agent, disinfectants
KNO ₂	potassium nitrite	antidote for cyanide poisoning
Li ₂ CO ₃	lithium carbonate	psychoactive drug (mood stabilizer)
Mg(OH) ₂	magnesium hydroxide	antacid
MgSO ₄	magnesium sulfate	laxative effects, laxatives
Na ₂ HPO ₄	sodium hydrogen phosphate	blood and urine buffering system
NaCl	sodium chloride	saline
NaClO	sodium hypochlorite	disinfectant, Savo
Na ₂ CO ₃	sodium carbonate	water softener (soda), acidity regulator in food
NaF	sodium fluoride	water fluoridation, toothpaste, toxic in higher doses
Na ₂ PO ₃ F	sodium phosphate-fluoride	toothpastes
NaH ₂ PO ₄	sodium dihydrogen phosphate	blood and urine buffering system
NaHCO ₃	sodium hydrogencarbonate	blood buffering system, antacid, baking powders
NH ₄ Cl	ammonium chloride	in the preparation Salnatrex with a salt-free diet, salmiak - dry cells
NH ₄ HCO ₃	ammonium bicarbonate	baking powders
(NH ₄) ₂ SO ₄	ammonium sulfate	it is used to desalt proteins
Pb ₃ O ₄ (2PbO+PbO ₂)	lead oxide	toxic, rust, primer paint
SO ₂	sulfur dioxide	toxic gas, air pollution
TiO ₂	titanium dioxide	titanium white
ZnO	zinc oxide	component of some ointments

Links

References

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