Analytical chemistry

Lecture №1

Tools of analytical chemistry

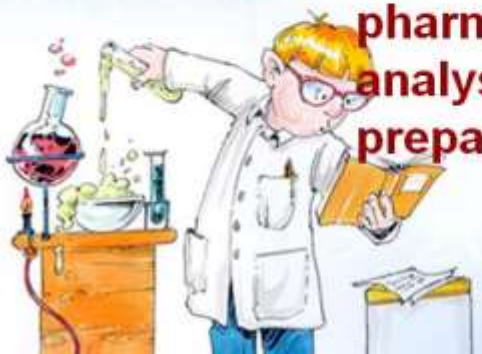
"Unless our knowledge is measured and expressed in numbers, it does not amount to much."

Lord Kelvin

ANALYTICAL CHEMISTRY - science about methods of examination of chemical composition of substances, materials and natural objects, ways and methods of support of reliability of analysis results.

• The science about methods and ways of chemical analysis. The main functions of analytical chemistry as a branch of knowledge: development of general subjects of chemical analysis, development of methods of analysis and solution of particular subjects (development of methods of medicines analysis, methods of chemical and toxicological analysis, etc.). Analytical chemistry gives significant consideration to development of ways and methods of ensuring the analysis results validity.

Analytical service - system of institutions, which carry out analysis of objects by methods used in analytical chemistry. Pharmaceutical analytical service ensures medicines quality control carried out in analytical laboratories of chemical and pharmaceutical plants, analytical laboratories (pharmacopoeial analysis) and in chemist's shop (quality control of medicines prepared in chemist's shop).



How Did Analytical Chemistry Originate?

The alchemists accumulated the chemical knowledge that formed the basis for quantitative analysis as we know it today.

Robert Boyle coined the term "analyst" in his book *The Sceptical Chymist in 1661*

Antoine Lavoisier used a precision balance for quantitative experiments on the conservation of mass. He is considered the "father of quantitative analysis."

How Did Analytical Chemistry Originate?

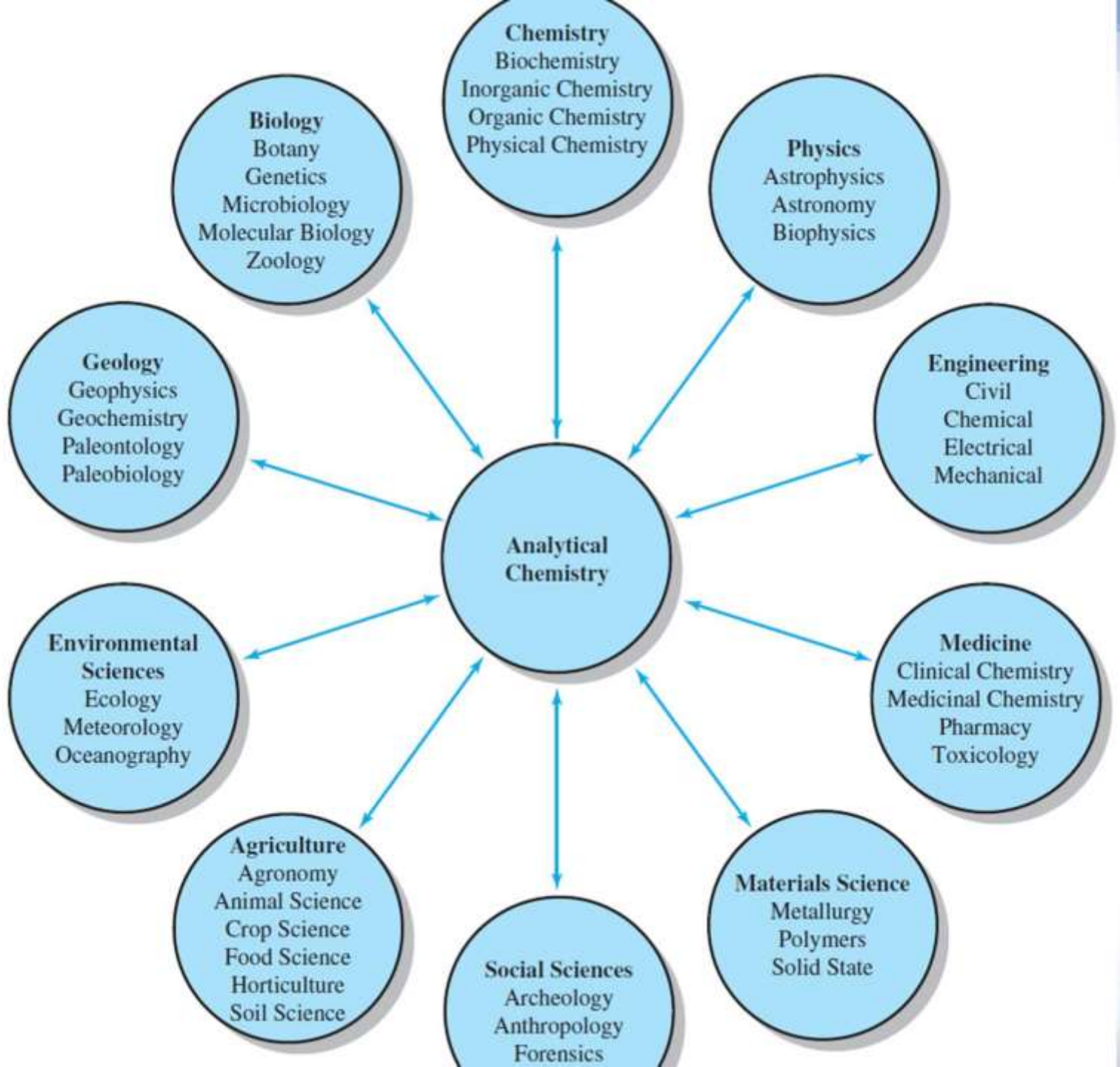
Gravimetry was developed in the seventeenth century, and ***titrimetry*** in the eighteenth and nineteenth centuries. The origin of titrimetry goes back to ***Geoffroy in 1729***; he evaluated the quality of vinegar by noting the quantity of solid K_2CO_3 that could be added before effervescence ceased. Gay-Lussac, in 1829, assayed silver by titration with relative accuracy and precision!

Textbooks of analytical chemistry began appearing in the 1800s. ***Karl Fresenius*** published *Anleitung zur Quantitaven Chemischen Analyse in Germany in* 1845. ***Wilhelm Ostwald*** published an influential text on the scientific fundamentals of analytical chemistry in 1894 entitled *Die wissenschaflichen Grundagen der analytischen Chemie, and this book introduced theoretical explanations of* analytical phenomena using equilibrium constants.

Karl Remigius Fresenius (1818–1897)

The twentieth century saw the evolution of instrumental techniques. Steven Popoff's second edition of *Quantitative Analysis in 1927 included* electroanalysis, conductimetric titrations, and colorimetric methods. Today, of course, analytical technology has progressed to include sophisticated and powerful computer-controlled instrumentation and the ability to perform highly complex analyses and measurements at extremely low concentrations.

Wilhelm Ostwald (1853–1932)


Chemistry
Biochemistry
Inorganic Chemistry
Organic Chemistry
Physical Chemistry
Biology
Botany
Genetics
Microbiology
Molecular Biology
Zoology
Physics
Astrophysics
Astronomy
Biophysics
Geology
Geophysics
Geochemistry
Paleontology
Paleobiology
Engineering
Civil
Chemical
Electrical
Mechanical
Analytical Chemistry
Environmental Sciences
Ecology
Meteorology
Oceanography
Medicine
Clinical Chemistry
Medicinal Chemistry
Pharmacy
Toxicology
Agriculture
Agronomy
Animal Science
Crop Science
Food Science
Horticulture
Soil Science
Social Sciences
Archeology
Anthropology
Forensics
Materials Science
Metallurgy
Polymers
Solid State

Applications of Analytical Chemistry

Analytical chemistry used in many fields:

• In medicine, analytical chemistry is the basis for clinical laboratory tests which help physicians diagnosis disease and chart progress in recovery.

• In industry, analytical chemistry provides the means of testing raw materials and for assuring the quality of finished products whose chemical composition is critical.

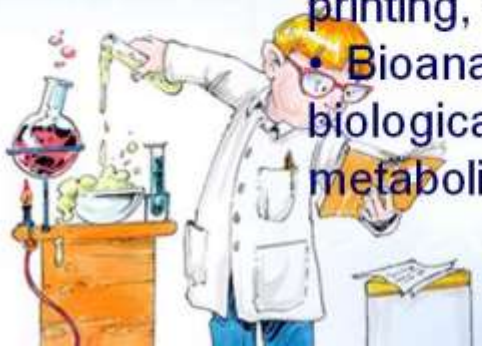
Many household products, fuels, paints, pharmaceuticals, etc. are analysed by the procedures developed by analytical chemists before being sold to the consumer.

• Enviermental quality is often evaluated by testing for suspected contaminants using the techniques of analytical chemistry.

• The nutritional value of food is determined by chemical analysis for major components such as protein and carbohydrates and trace components such as vitamins and minerals. Indeed, even the calories in a food are often calculated from the chemical analysis.

• Forensic analysis - analysis related to criminology; DNA finger printing, finger print detection; blood analysis.

• Bioanalytical chemistry and analysis - detection and/or analysis of biological components (i.e., proteins, DNA, RNA, carbohydrates, metabolites, etc.).



Applications of analytical chemistry in pharmacy sciences:

- Pharmaceutical chemistry.
- Pharmaceutical industry (quality control).
- Analytical toxicology is concerned with the detection, identification

And measurement of drugs and other foreign compounds (and their metabolites in
biological and related specimens.

- Natural products detection, isolation, and structural determination.

Analytical chemistry has an important place in system of training the specialists with pharmaceutical higher education, because it is the base for studying such special subjects as pharmaceutical chemistry, pharmacognosy, drug technology.

The discipline of analytical chemistry consists of

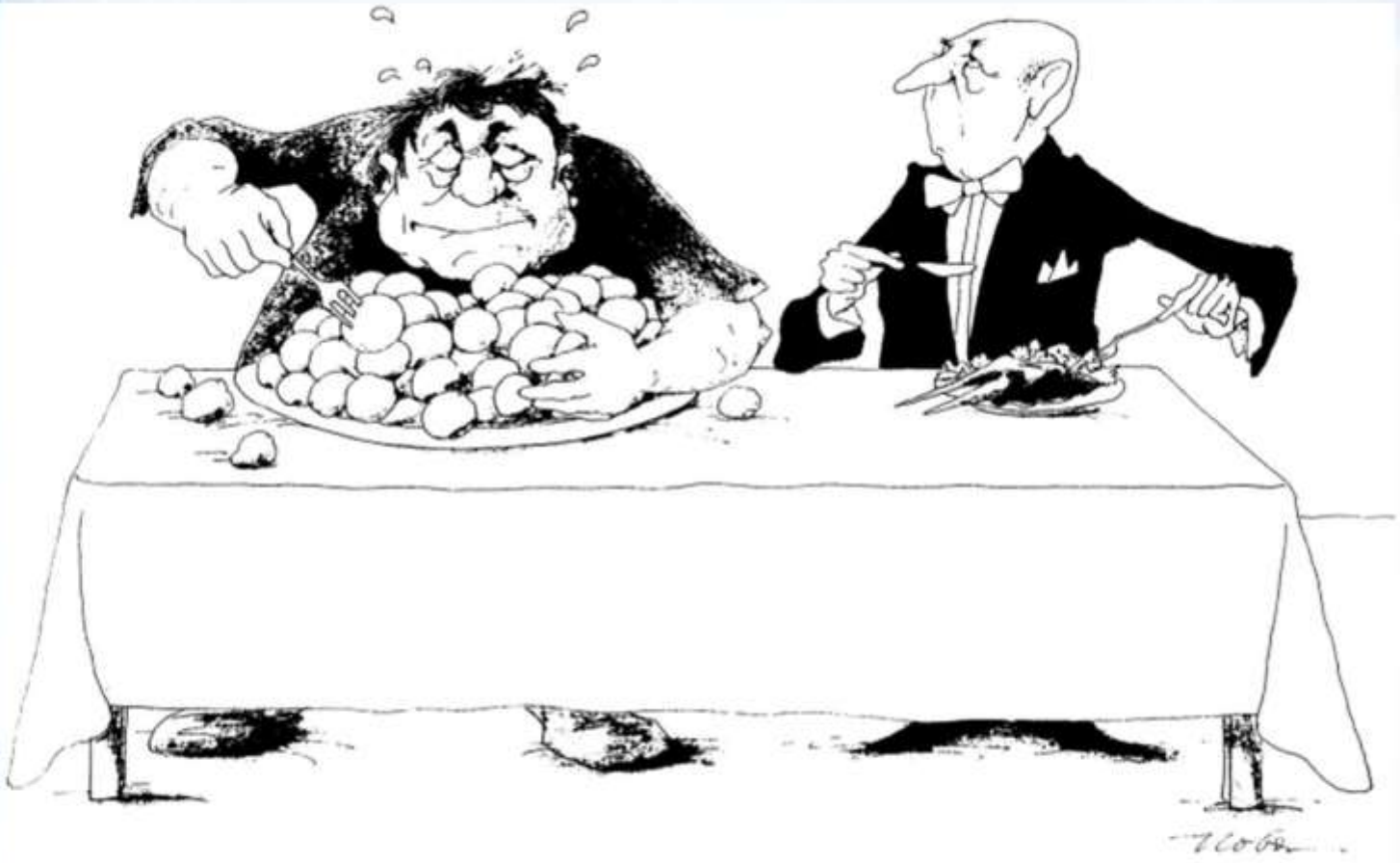
QUALITATIVE ANALYSIS

solves task about components contained in the object to be analysed; *the systematic and fractional analysis are distinguished*

identification detection

QUANTITATIVE ANALYSIS

solves task about quantitative content of all or some components, which are present in the object to be analysed



Quantitative analysis Qualitative analysis

Subjects of analytical chemistry :

- chemical elements and its compounds and processing of transformation of substances in run chemical reactions.
- chemical reaction as a source of information about chemical composition of substances using for qualitative and quantitative analysis.

Aims of analytical chemistry :

1. Establishing the chemical composition of analysed object (isotopic, elementary, ionic, molecular, phase) – qualitative analysis.
2. Determination of content (amount and concentration) some components in analysed objects – quantitative analysis.
3. Determination (establishing) of structure of chemical compound – nature and number of structural elements, its bonds one to another, disposition in space.
4. Detection of heterogeneity on surface or in volume of solids, distribution of elements in layers.
5. Research process in time: establishing character, mechanism and rate of molecular regrouping.
6. Developing of present analytical methods theory, working out the new methods of analysis.

Types of analysis:

1. *Elemental* — determination of sample elemental composition
2. *Substantial* — determination of presence form of the component to be analysed
3. *Functional* — determination of functional groups
4. *Molecular* — determination of chemical compounds (for example, analysis of gases mixture)
5. *Phase* — analysis of inclusions in non-homogeneous object (for example, in minerals)
6. *Isotopic* — determination of isotopes under analysis of artificial elements (for example, transuranium elements)

Classification of methods of analysis:

- ***Physical*** – determination of components of investigated substances without chemical reactions (destroying of sample) by its physical properties:

1. Spectral analysis – investigation of emission and absorption spectra.
2. Fluorescence analysis – investigation of luminescence, caused action of UV-radiation.
3. Roentgen-structural analysis – using X-ray.
4. Mass-spectra analysis.
5. Densimetry – measurement of density

- ***Physical-chemical*** – based on measurement of physical parameters (properties) of substances in run of chemical reaction. This method divides on

1. Electrochemical – measurement of electrical parameters of electrochemical reactions.
2. Optical – investigation the influence of various electromagnetic radiation on substance.
3. Thermal (heating) – investigation the changes the properties of substance by heat (undergo) action.

Classification of methods of analysis:

- **Chemical methods of analysis** – methods based on chemical interaction of atoms, molecules and ions. These methods are employed to detect characterize chemical properties of element or ion. Methods of chemical analysis can be divided according the type of chemical reaction, rate of chemical reaction and advisability (gravimetry, titrimetry, gas analysis, kinetic methods of analysis).

based on chemical reactions.

- **Biological** – use of life organism as analytical indicators

Classification of analytical methods in accordance with mass and volume of analytic sample

Method name	Mass of sample, g	Volume of sample, ml
Gramm-method/macroanalysis	1-10	10-100
Sentigramm-method/semi-microanalysis	0,05-0,5	1-10
Milligramm-method/microanalysis	$0,01\text{-}10^{-6}$	$0,1\text{-}10^{-4}$
Microgramm-method/ultramicroanalysis	$10^{-6}\text{-}10^{-9}$	$10^{-4}\text{-}10^{-6}$
Nanogramm-method/submicroanalysis	$10^{-9}\text{-}10^{-12}$	$10^{-7}\text{-}10^{-10}$
Picogramm-method	10^{-12}	10^{-10}

Steps in an analysis

Define the problem → Select a method → Obtain a representative sample → Prepare the sample for analysis → Perform the measurements → Calculate the results and report

Chemical methods of identification of inorganic substances.

Methods of Qualitative analysis

For identification (detection) and determination of substances the chemical reactions runs in solution or by "dry" way.

"Dry" way testing (without dissolving of sample) can be make by:
1) pyrochemical methods:
– flame test (colouring of gas torch flame),
– making a glass (alloys with Na_2CO_3, K_2CO_3, $Na_2B_4O_7$, $Na(NH_4)_2PO_4$),
– tempering;
2) crush (rub) sample to powder with analytical reagent;
3) microcrystalloscopic analysis – produce (receive) the specific crystals with analytical reagent and watching its with microscope (forms of crystals);
4) analysis in drops on filter paper – reaction between analysed substance and analytical reagent run on filter paper with some drops (1-2) of solutions – arise a coloured spots.

Requirements (demands) to analytical reactions:
1) reaction must run quickly, in practice – immediately;
2) reaction must accompanied with accordance (special) analytical effect;
3) reaction must be irreversible – run in one way (in one side);
4) reaction must have high specificity and have high sensitivity.

Analitical signal

Analitical signal - the average value of measuring results, which is connected with the content of the component to be determined (for example, in titrimetric analysis it is the difference between titrant volumes before and aft er titration). In qualitative analysis analytical signal is the change of external appearance or aggregate state of the substance as a result of chemical reaction.

Analytical signal	Example
Formation of the characteristic precipitate	$Ag^+ + Cl^- \leftrightarrow AgCl\downarrow$ white
Change of the solution color	$Cu^{2+} + 4\ NH_3 \leftrightarrow [Cu(NH_3)_4]^{2+}$ (a blue solution)
The gas liberation	$NH_4Cl + NaOH \rightarrow NH_3\uparrow + NaCl + H_2O$
The heat liberation	$HCN + NaOH \rightarrow NaCN + H_2O$

Analytical reaction

Group reaction

Use for selection from complex mixes some substances. Substances with definite properties are united in special analytical groups.

Group reagent - the reagent formed typical reaction products (precipitate, gas, coloured products) with a certain group of inorganic ions or with a certain class of organic compounds

individual reaction

analytical reactions that have the individual substance nature. These reactions distinguish to selectivity.

Selective reactions **give identical or alike analytical effects with small (little) number of ions (2-5).**

Extreme form of selectivity is specificity.

Specific reaction **gives an analytical effect only with one individual substance.**

For examples: – iodine with starch – complex compound blue (navy) colour; Alkalis at heating with ammonium salts evolve an ammonia:

$$NH_4Cl + NaOH \rightarrow NH_3\uparrow + NaCl + H_2O$$

Conditions of the analytical reactions

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

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

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

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

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

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

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

The most important characteristics of all methods of qualitative analysis are **specificity and sensitivity**.

Sensitivity is defined as the smallest quantity of an element that can be detected by a given method. Sensitivity of modern methods is expressed in magnitudes of the order of 1 mg (one millionth part of a gram).

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

C (Cmin) – minimal concentration, g/ml – the lowest concentration at which ion can be detected in a solution of sample;

V (Vmin) – volume, ml – a minimum volume of solution needed to determine this ion;

m – openear (detection) minimal – the least amount of substance, which present in the analysed solution and can be detected with the reagent. It is calculated in μg.

1 μg = 0,000001 g;

Fractional analysis

In fractional analysis the substance composition is determined by the specific reactions or the conditions, which allow to dispose the influence of another substances or ions (for example, with the help of ions masking) are created

Systematic analysis

In systematic analysis at first the complex mixture of ions is separated with the help of the group reagents into some separate groups, and then in the range of each groups the individual ions are detected by the characteristic reactions in the certain sequence.

The analysis of complex (complicated) mixes makes to next modes (ways):

I. Divide the mix on components (submixes) du to separation the detected substances and the preventing substances on various parts of mix (in various submixes) – systematic path (way) of analysis.

The ***systematic analysis*** - is full analysis of researched objects, which made du to separation of mix on groups (analytical groups) in definite (strong) sequence in accordance to various analytical properties of components. These separation makes until in one submix (phase) stay components, which simple detect (identify) with selective reagent.

II. Separate and detect one component in the researched mix (without divide) with the help of (by means of) specific reactions (reagents) – fractional path (way) of analysis.

The **fractional analysis** - the all mix divide on identical (the same) parts. And in each part detect only one individual component.

The method of cations analytical classification

The method of classification	The base of the method
The hydrosulphuric method of analysis	The different solubility of cations sulphides
The ammoniac-phosphatic method of analysis	The different solubility of cations phosphates in water and ammonia solution
The acid-base method of analysis	The different relation of cations to acids (HCl, H_2SO_4) and bases (NaOH, $NH_3 \times H_2O$)

Cations divide to analytical groups in according with solubility of salts, formed by its.

CLASSIFICATION OF CATIONS BY THE ACID-BASE METHOD

Group	Cations	Group reagent
1	Na^+, K^+, NH_4^+, Li^+	absent
2	Ag^+, Pb^{2+}, Hg_2^{2+}	HCl
3	Ba^{2+}, Sr^{2+}, Ca^{2+}	H_2SO_4
4	Al^{3+}, Zn^{2+}, Cr^{3+}, Sn(II), Sn (IV), As(III), As (V)	NaOH
5	Fe^{2+}, Fe^{3+}, Mg^{2+}, Mn^{2+}, Bi^{3+}, Sb (III), Sb (V)	NaOH
6	Co^{2+}, Ni^{2+}, Cd^{2+}, Cu^{2+}, Hg^{2+}	NH_3 solution

Classification of anions which is based on formation of insoluble salts of Barium and Silver

Group	Anions	Group reagent
I	SO_4^{2-} SO_3^{2-} $S_2O_3^{2-}$ $C_2O_4^{2-}$ CO_3^{2-} $B_4O_7^{2-}$ (BO_2^-), PO_4^{3-} AsO_4^{3-}, AsO_3^{3-}, F^-	Solution $BaCl_2$ in the neutral or less basic medium
II [1]	Cl^-, Br^-, I^-, BrO_3^-, CN^- SCN^-, S^{2-}	Solution $AgNO_3$ in diluted (2 mol/L)nitric acid
III [4]	NO_3^-, NO_2^-, CH_3COO^-	Haven't

Classification of anions which is based on their oxidation-reduction properties

Group	Anions	Group reagent
I Oxidizers	BrO_3^-, AsO_4^{3-}, $NO_3^-NO_2^-$	Solution of KI in sulfuric acidic medium
II Reducers	S^{2-}, SO_3^{2-}, $S_2O_3^{2-}$ AsO_3^{3-}	Solution of I_2 in KI
	S^{2-} SO_3^{2-} $S_2O_3^{2-}$ AsO_3^{3-} ,NO_2^- $C_2O_4^{2-}$ CL - BR - I- CN - SCN -	Solution of $KMnO_4$ in sulf uric acidic medium
III The indifferent	SO_4^{2-}, CO_3^{2-}, $B_4O_7^{2-}$ (BO_2^-), PO_4^{3-}, CH_3COO^-	Haven't

Majority of anions detect by fractional method, that's why the group reagents use only for separation of anions groups, that exclude necessity to search in solution the anions of given group in case of negative reaction with group reagents.