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NAMANGAN STATE UNIVERSITY

Department of organic chemistry

Training and metodology complex
of the subject

ANALYTICAL CHEMISTRY

Field of knowledge:	500000-Natural sciences, mathematics and statistics
Field of study:	530000-Physics and natural sciences
Undergraduate course of study:	60530100-Chemistry (daytime)

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CONTENT

1. Educational materials

1.1 Lectures.

Lecture No. 1

The subject of analytical chemistry, the scope of research, the purpose and objectives of the subject.

Plan

1. **Subject of analytical chemistry**
2. **Purpose, objectives and methods**
3. **History of the development of science**

Analytical chemistry is an important independent science. Analytical chemistry is the scientific basis of chemical analysis. The role of chemical analysis in the life of society is well known. Analysis is the main means of monitoring the state of the environment, production, and quality of products in the chemical, petrochemical, pharmaceutical, mining, and oil refining industries, as well as in metallurgy and geological surveys. Chemical analysis is necessary for the normal functioning of the agro-industrial complex (analysis of the composition of soils, fertilizers, feed, agricultural products), in biotechnology, medical diagnostics, and forensics. The objects of chemical analysis are almost everything that surrounds us.

Main purpose of analytical chemistry- to ensure, depending on the task at hand, accuracy, high sensitivity, rapidity and (or) selectivity of analysis. Methods are being developed that make it possible to analyze micro-objects (see Microchemical analysis), conduct local analysis (at a point, on a surface, etc.), analysis without destroying the sample (see Non-destructive analysis), at a distance from it (remote analysis), continuous analysis (for example, in a flow), and also establish in the form of what chemical compound and in what phase the component being determined exists in the sample (phase analysis). Important trends in the development of analytical chemistry are automation of analyses, especially in the control of technological processes, and mathematization, in particular the widespread use of computers.

Structure. Three major areas of analytical chemistry can be distinguished: general theoretical foundations; development of analysis methods; analytical chemistry of individual objects. Depending on the purpose of the analysis, a distinction is made between qualitative analysis and quantitative analysis. The task of the first is to detect and identify the components of the analyzed sample, the second is to determine their concentrations or masses. Depending on which components need to be detected or determined, there are isotopic analysis, elemental analysis, structural group analysis (including functional analysis), molecular analysis, and phase analysis. Based on the nature of the analyzed object, the analysis of inorganic and organic substances is distinguished.

In the theoretical foundations of analytical chemistry, metrology of chemical analysis, including statistical processing of results, occupies a significant place. The theory of analytical chemistry also includes the study of the selection and preparation of analytical samples. about drawing up an analysis scheme and choosing methods, principles and ways to automate analysis, the use of computers, as well as the foundations of national economies. use of chemical results. analysis. A feature of analytical chemistry is the study of not general, but individual, specific properties and characteristics of objects, which ensures the selectivity of many analytical methods. Thanks to close connections with the achievements of physics, mathematics, biology and various fields of technology (this especially concerns methods of analysis), analytical chemistry has been turned into a discipline at the intersection of sciences.

In analytical chemistry, there are methods of separation, determination (detection) and hybrid ones, combining methods of the first two groups. Determination methods are divided into chemical methods of analysis (gravimetric analysis, titrimetry), physicochemical methods of analysis (for example, electrochemical, photometric, kinetic), physical methods of analysis (spectral, nuclear physical and others) and biological methods of analysis. Sometimes determination methods are divided into chemical, based on chemical reactions, physical, based on physical phenomena, and biological, using the response of organisms to changes in the environment.

Analytical chemistry defines the general approach to the selection of analytical pathways and methods. Methods for comparing methods, conditions for their interchangeability and combination, principles and ways to automate analysis are being developed. For the practical use of analysis, it is necessary to develop ideas about its result as an indicator of product quality, the doctrine of express control of technological processes, and the creation of cost-effective methods. Of great importance for analysts working in various sectors of the national economy is the unification and standardization of methods. A theory is being developed to optimize the amount of information required to solve an analytical problem.

Analysis methods. Depending on the mass or volume of the analyzed sample, separation and determination methods are sometimes divided into macro-, micro- and ultra-micro methods.

Separation of mixtures is usually resorted to in cases where direct determination or detection methods do not provide the correct result due to the interfering influence of other components of the sample. Particularly important is the so-called relative concentration - the separation of small quantities of analyte components from significantly larger quantities of the main components of the sample. The separation of mixtures can be based on differences in the thermodynamic, or equilibrium, characteristics of the components (ion exchange constants, stability constants of complexes) or kinetic parameters. For separation, chromatography, extraction,

precipitation, distillation, as well as electrochemical methods, such as electro-precipitation, are mainly used.

Physico-chemical methods of analysis, are based on the dependence of the physical properties of a substance on its nature, and the analytical signal is a value of a physical property that is functionally related to the concentration or mass of the component being determined. Physicochemical methods of analysis may include chemical transformations of the compound being analyzed, sample dissolution, concentration of the analyzed component, masking of interfering substances, and others. Unlike "classical" chemical methods of analysis, where the analytical signal is the mass of a substance or its volume, physicochemical methods of analysis use radiation intensity, current strength, electrical conductivity, potential difference, etc. as an analytical signal.

Of great practical importance are methods based on the study of the emission and absorption of electromagnetic radiation in various regions of the spectrum. These include spectroscopy (for example, luminescent analysis, spectral analysis, nephelometry and turbidimetry, and others). Important physicochemical methods of analysis include electrochemical methods that use the measurement of the electrical properties of a substance.

Lecture No. 2

Metrological foundations of analytical chemistry

Plan

1. Metrological foundations of analytical chemistry
2. Calculation method.

Any method of chemical analysis has as its task the extraction of information about a substance using certain measuring instruments. Thus, the analysis technique is a complex, multi-stage measurement procedure. It is at the measurement stage (and subsequent processing and interpretation of the results) that the deep internal unity of the most diverse methods of analysis is clearly manifested, and the patterns of measurement of chemical quantities are of fundamental importance for all sections of analytical chemistry, essentially constituting its philosophical basis. A special branch of analytical chemistry, called chemical metrology, deals with the study of general issues related to the measurement, processing and interpretation of the results of chemical analysis.

Chemical quantities, methods of their expression and measurement. Analytical signal, calibration function

The basic chemical quantity is the quantity of a substance (n), and its basic unit of measurement is the mole. By definition, 1 mole is the amount of substance containing as many particles as there are atoms contained in 0.012 kg of isotopically pure simple substance 12C. It is approximately 6.02045.1023 particles. Thus, in meaning, the quantity of a substance is the

number of particles that make up the substance. This quantity should not be identified with mass, volume, or any other physical characteristics.

Along with the quantity of a substance, quantities derived from it are also widely used in chemistry. The most important of them is concentration (c), which is the amount of substance per unit volume V:

$$c = \frac{n}{V} \text{ . (1)}$$

The most commonly used unit for measuring concentration is mol/l (M). In what follows, we will denote all chemical quantities, both the amount of a substance itself and its derivatives, by the collective term “content.”

From the definition of the concept “amount of substance” it follows that direct, direct measurements of chemical quantities are impossible. Indeed, to directly measure the amount of any substance in a sample would mean counting all the particles of a certain type in it individually, which is technically impossible. However, there are many physical quantities that are completely accessible to direct measurements and are functionally related to the content of matter. For example, the mass (m) of any pure substance is proportional to its quantity:

m = Mn(2)

(proportionality coefficient - molar mass M). During titration, the amount of the analyte is related to the volume of the standard titrant solution VT concentration cT:

$$V_T = \frac{n}{c_T} \text{ . (3)}$$

In colored solutions there is a relationship between the concentration of the light-absorbing substance and the optical density A:

A=εlc(4)

(basic law of light absorption). And so on. Thus, almost any mechanical, optical or electrical quantity can, under certain conditions, be associated with the content of a substance and, therefore, be used to determine it. In general, such a physical quantity is called an analytical signal (y). The functional relationship between the analytical signal and the content (for example, concentration) can be represented as

y = f(c) . (5)

The function f connecting the content and the analytical signal is called the calibration function.

The general scheme for measuring the substance content is as follows.

1. Establishing the calibration function f.

2. Measurement of the analytical signal of the analyzed sample y.

3. Finding from the value y using the function f the content of the determined component c.

Thus, all measurements of chemical quantities are indirect, based on the use of a calibration function. In view of the key role of the calibration function in the process of chemical measurements, let us consider this concept in more detail.

Absolute and relative methods of analysis. Graduation. Comparison and reference samples

We emphasize that to carry out chemical analysis, it is necessary to know the exact form of the calibration function (i.e., for example, not only the general form of the algebraic equation describing it, but also the specific values of its parameters).

For some analysis methods, the exact form of the calibration function is known from theory. An example of such methods is gravimetry, in which the analytical signal is mass, and the calibration function is described by equation (2). Its only parameter is the molar mass of the substance M, established with high accuracy. Such methods, which do not require experimental determination of the calibration function, are called absolute. However, there are very few absolute methods of chemical analysis.

A much more common case is when, at best, the general (and often approximate) form of the calibration function is known from theory, and its parameters (in relation to given specific conditions of analysis) are either unknown in advance at all, or are known only approximately, with an accuracy that does not satisfy capabilities of the method and requirements for analysis results. In such cases, it is necessary to establish the calibration function experimentally, empirically, as a rule, immediately before carrying out the analysis, since it can greatly depend on its conditions. Such methods are called relative, and the procedure for experimentally constructing a calibration function is called calibration. Therefore, we can briefly say that absolute methods are methods that do not require calibration, and relative methods require it. And since relative methods make up the vast majority, calibration is the most important component of almost any analysis technique. How is it carried out?

Obviously, to carry out calibration, you first need a set of samples with a reliably established content of the component being determined. In general, such samples are called comparison samples (CS). Among OS, a class called standard samples (SS) should be highlighted. CO is a specially prepared material, the composition of which is reliably established and legally certified. The latter means that each RM has an official document (passport, certificate) issued by an authorized body (Gosstandart system, industry metrological service, etc.), which contains data on its composition (as a rule, the content of all macrocomponents and the most important microcomponents) . In many cases specified by law (primarily during the official certification of a new technique), the use of RM is mandatory.

The magnitudes of analytical signals (and, accordingly, the specific type of calibration function) can depend, and sometimes strongly, on the measurement conditions. Therefore, the most important requirement for the calibration process is to ensure the most accurate compliance of the calibration conditions and subsequent analysis of the sample. This means, in particular, that both calibration and the analysis itself should be performed on the same instrument, with the same values of instrumental parameters, and the time interval between calibration and analysis should be as short as possible. In addition, if the values of analytical signals are influenced by extraneous components of the sample (its matrix) or its physical state, then the OS used for calibration should correspond as closely as possible to the analyzed sample in terms of these parameters. Therefore, OS, and especially RM, very often imitate typical objects of analysis (there are, for example, RM from soils, food products, natural waters, ore concentrates, etc.). Special calibration techniques are also used to ensure maximum adequacy of its conditions to the conditions of analysis.

External standards method

The simplest and most common calibration method is the method of external standards. It is often also called the “regular” calibration method or the “calibration graph” method (the legality of using the latter term, however, is questionable, since with other, special calibration methods, the calibration function is also often presented in graphical form). In this method, a number of OS containing the determined component c1, c2, ... cn are taken, all the analytical procedures necessary according to the method are carried out with them and their analytical signals are measured (y1, y2, ... yn, respectively). Based on the obtained pairs of experimental values (ci, yi), the dependence of y on c is plotted and approximated by a suitable algebraic function or graphically (Fig. 1). In this case, they usually try to choose such analysis conditions so that this dependence is linear. Then the unknown sample is analyzed, its analytical signal yx is measured and, using the resulting calibration function, the corresponding value cx is found (also algebraically or graphically). For example, in the case of a linear calibration function described by the equation y = kc + b, the unknown content can be found as

$$c_x = \frac{y_x - b}{k} \quad . (6)$$

the quantity b, which represents the value of the analytical signal at zero concentration of the component being determined, is called the background value of the signal. It plays an important role in assessing the sensitivity of techniques (p. 33).

Sometimes the method of external standards is further simplified by reducing the number of OS to two (method of limiting solutions) or even one (method of one standard). In the limiting solution method, the linear (in the selected concentration range) nature of the calibration function is postulated in advance (and, if possible, experimentally verified), and the OS is chosen so that c1<cx<c2. It is easy to verify by carrying out the appropriate mathematical transformations that in this case

$$c_x = c_1 + \frac{y_x - y_1}{y_2 - y_1}(c_2 - c_1) \quad . (7)$$

If c1 and c2 are close enough to cx, then the limiting solution method sometimes gives more accurate results than the "full" version of the external standard method.

In the method of one standard, they assume not just a linear, but a directly proportional form of the calibration function y = kx (without a free term, there is no background signal). In this case

$$c_x = \frac{y_x}{y_1} c_1 \quad . (8)$$

In any variant of the external standards method, the OS is prepared and used separately from the sample being analyzed (hence the name). Therefore, the composition and properties of OS do not always correspond quite accurately to those of the analyzed sample. In some cases, this can lead to significant errors in the results. In such situations, special calibration methods should be used

Lecture No. 3

Analysis errors

Any measurement process is influenced by many factors that distort measurement results. The difference between the measurement result and the true value of the measured value is called error. Due to the fact that any measurement result generally contains an error, the exact value of the measured quantity can never be established. However, it is possible to indicate a certain range of values within which the true value can lie with varying degrees of reliability. This range is called the uncertainty of the measurement result. Assessing the uncertainty of chemical analysis results is the most important task of chemical metrology.

Two different types of errors contribute to the total uncertainty of the measurement result. Let as a result of a single measurement of a certain quantity a value x* is obtained that differs from the true value x0 (Fig. 2, a). Let's repeat the measurement several more times. Possible options for the relative position of a series of measured values and the true value are shown in Fig. 2, b and 2, c. In the first case (Fig. 2, b), there is a shift in the entire data series (and its average) relative to the true value. The corresponding component of uncertainty is called systematic error. In the second case (Fig. 2, c) there is a scatter of data relative to the average value from the measurement results. This component of uncertainty is called random error. Of course, in a real case we always have both a systematic and a random component. So, in Fig. In Fig. 2, b, along with a significant shift in the data, we also see some scatter, and in Fig. 2, c - against the background of a large scatter, a slight shift of the average relative to the true one. The origin of systematic and random errors is associated with the different nature of factors affecting the measurement process. Factors of a constant nature or that change little from measurement to measurement cause systematic errors, quickly and

Two most important metrological concepts are closely related to the concepts of systematic and random errors - accuracy and reproducibility (or, in modern terminology, precision). Correctness is the quality of the measurement results (or the measurement procedure as a whole), which characterizes the smallness (close to zero) of the systematic error; reproducibility (precision) is the quality that characterizes the smallness of the random error. In other words, the correctness of the results is their unbiasedness, and reproducibility is their stability. A general concept that characterizes the smallness of any component of uncertainty, both systematic and random, is called accuracy. We will call the results accurate only if both the systematic and random errors for them are small. Thus, accuracy and reproducibility are two components of accuracy, therefore called accuracy characteristics.

In chemical metrology, it is traditional to evaluate accuracy characteristics separately. Let's consider the main ways to quantify the reproducibility and accuracy of chemical analysis results.

Random error: numerical characteristics of reproducibility

Reproducibility characterizes the degree of scattering of data relative to the average value. Therefore, to assess reproducibility it is necessary to first calculate the average $\bar{x}$ from a series of results of repeated (parallel) measurements x1, x2, ... xn:

$$\bar{x} = \frac{x_1 + x_2 + \ldots + x_n}{n} = \frac{\sum_{i=1}^{n} x_i}{n} \quad . (9)$$

Let us note that in the series being processed there should be no misses - individual values that differ sharply from the rest and, as a rule, obtained under conditions of a gross violation of the measurement procedure (analysis technique). Therefore, first of all (even before calculating the average), one should, using special statistical tests (p. 23) and, if possible, through a detailed study of the experimental conditions, check the series of data for errors and, if any are found, exclude them from consideration.

Dispersion is most often used as a measure of the spread of data relative to the mean.

$$V(x) = s^2(x) = \frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n - 1} \quad (10)$$

and its derivatives - (absolute) standard deviation

$$s(x) = \sqrt{V(x)} = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n - 1}} \quad (eleven)$$

and relative standard deviation

$$s_r(x) = \frac{s(x)}{\bar{x}} \quad . (12)$$

In its meaning, dispersion is the average value of the squared deviation of a measurement result from its average value. Despite the fact that the numerator of expression (10) contains n terms, the denominator is equal to n-1. The reason is that among the n terms of the numerator, only n-1 are independent (since, based on n-1 values of xi and the average $\bar{x}$ It is always possible to calculate the missing nth term). The denominator value in expression (10) is denoted by f (orv) and is called the number of degrees of freedom of the dispersion s2(x). It plays a very important role in the statistical testing of various hypotheses (p. 17).

In chemical analysis, to characterize reproducibility, it is usually not variance that is used, but absolute or, most often, relative standard deviation. This is explained by considerations of practical convenience. The dimensions of s(x) and x are the same, so the absolute standard deviation can be directly compared to the result of the analysis. The quantity sr(x) is dimensionless and therefore the most visual. Using relative standard deviations, you can compare the reproducibility of not only specific data, but also different methods and even methods in general.

Among all existing methods of chemical analysis, the best reproducibility (i.e., the smallest sr) is characteristic primarily of “classical” chemical methods of analysis - titrimetry and, especially, gravimetry. Under optimal conditions, typical sr values for them are of the order of n.10-3 (tenths of a percent). Among instrumental methods,

coulometry has the same (and in a number of methods even higher) reproducibility, especially in the direct version (up to n.10-4). Most other instrumental methods are characterized by sr values from 0.005 to 0.10. Methods with even lower reproducibility are classified as semi-quantitative. Despite their low accuracy, they often have other advantages: exceptional simplicity, rapidity, and cost-effectiveness (test methods). They can be very useful, for example, for quickly assessing the state of the environment.

We emphasize that any sr values given for techniques (especially methods) in general are only indicative and usually relate only to the optimal conditions for their implementation. Under other conditions, especially when the content of the component being determined is reduced (p. 32), these values can be significantly (an order of magnitude or more) higher.

Analysis conditions and reproducibility of results

As noted above, random errors are caused by the action of various (usually very many) factors, often of an unknown nature, changing rapidly and unpredictably over time. Therefore, strict control of experimental conditions plays a decisive role in improving the reproducibility of analytical results. Obviously, when performing a series of analyzes on the same sample in the same laboratory and on the same instrument, reproducibility will be higher than when working with the same sample in different laboratories on different instruments. Therefore, any numerical characteristics of reproducibility, generally speaking, make sense only when it is indicated to which analysis conditions they relate.

It is customary to distinguish three main types of such conditions, differing in the degree of severity of their control.

1. Work under the most strictly controlled conditions. This means performing a series of tests in the same laboratory, on the same equipment, by the same person and, importantly, within the shortest possible period of time (maximum within one day). Reproducibility calculated under such conditions is specially called convergence.

2. Performing a series of analyzes in the same laboratory, on the same equipment, but possibly by different operators and on different days. In this case, reproducibility is called intralaboratory (in modern terminology, intermediate precision). Intralaboratory reproducibility is lower than repeatability (corresponding sr value is higher).

3. Performing a series of analyzes in different laboratories, on different equipment, by different people and at different times. In other words, this is varying the conditions for performing the technique within the widest possible range. The corresponding reproducibility is called interlaboratory (in modern terminology, simply reproducibility). If the technique is intended to be used everywhere, then it is obvious that it is interlaboratory reproducibility (and not intralaboratory, and certainly not convergence!) that is the real characteristic of the possible scatter of analysis results. Therefore, for all officially recommended or prescribed (certified, standardized) methods, an interlaboratory study is required - testing the method in different laboratories and assessing its interlaboratory reproducibility.

Due to the great practical importance of interlaboratory reproducibility, in modern regulatory documents this type of reproducibility is simply called reproducibility (without any additional definition). As for the term “reproducibility” in the broad sense of the word (i.e., the characteristics of the random error of results regardless of the conditions under which they were obtained), in order to avoid confusion, it is now recommended in this case to use the synonym “precision” mentioned above. However, the term “reproducibility” in its generalized meaning is deeply rooted in scientific usage, and from the context it is usually clear what kind of reproducibility we are talking about – reproducibility “in general” or specifically interlaboratory. Therefore, in this manual we will continue to use the term “reproducibility” in the broad sense of the word (as we have done so far).

Random error: interval estimation

The contribution of random error to the overall uncertainty of the measurement result can be assessed using methods of probability theory and mathematical statistics.

Due to the presence of a random error, the same value x acquires a new, unpredictable value with each subsequent measurement. Such values are called random. Random variables are not only individual measurement results xi, but also average $\overline{x}$ (as well as the variances s2(x) and all their derivatives). That's why $\overline{x}$ can only serve as an approximate estimate of the measurement result. At the same time, using the quantities $\overline{x}$ and s2(x), it is possible to estimate the range of values in which the result may lie with a given probability P. This probability P is called the confidence probability, and the corresponding interval of values is the confidence interval.

Rigorous calculation of the boundaries of the confidence interval of a random variable is possible only under the assumption that this value obeys some known distribution law. The distribution law of a random variable is one of the fundamental concepts of probability theory. It characterizes the relative proportion (frequency, probability of occurrence) of certain values of a random variable when it is reproduced multiple times. The mathematical expression of the distribution law of a random variable is its distribution function (probability density function) p(x). For example, the distribution function shown in Fig. 3 means that for the corresponding random variable x, values near x=10 are most common, and larger and smaller values occur less frequently the further they are from 10.

It is no coincidence that the bell-shaped, symmetrical distribution function is given as an example. It is this type of it that is most characteristic of the results of chemical analysis. In most cases, the distribution law of chemical analysis results can be satisfactorily approximated by the so-called normal (or Gaussian) distribution function

Errors in quantitative analysis.

By their nature, analysis errors are divided into systematic, random and misses.

1. Systematic - errors that are the same in sign and affect the result in the direction of its increase or decrease.

a) Methodological errors are errors that depend on the characteristics of the method used (incomplete reaction, partial dissolution of the precipitate, indicator property).

b) Operational – insufficient washing of the filter cake, errors

instrumentation or reagents, imbalance of scales.

c) Individual – errors of laboratory technicians (ability to accurately determine

coloring during titration, psychological errors).

G)Instrumental or reactive (these errors are associated with the insufficient accuracy of the instruments used, errors of the laboratory assistant).

2. Random - they are inevitable under any definition. They can be significantly reduced by increasing the number of parallel determinations.
3. Misses are gross errors that are caused by incorrect calculation of weights, watering part of the solution, or spillage of sediment.

Sensitivity, accuracy and accuracy of analysis.

Sensitivity– minimum detectable concentration of a substance.

Right– closeness of the obtained result to the true one.
Accuracy- characteristic of the reproducibility of the determination from experiment to experiment. The analysis is considered more accurate the less the results of parallel determinations differ from each other.
Absolute error is the difference between the obtained result and the true or most reliable value. Relative error is the ratio of the absolute error to the true value.

Lecture No. 4

Sampling

The main task of sampling and its subsequent preparation for analysis is to ensure that the chemical composition and properties of the sample correspond to the average composition and properties of the object under study.

There are general, laboratory and analyzed samples. The general sample is taken directly from the analyzed object. It can be quite large and in some cases amount to tens of kilograms.

From the general sample, a laboratory sample weighing no more than 1 kg is taken by reducing it. One part of the laboratory sample is used for preliminary research, the other is saved for possible arbitration analyses, and the third is used directly for analysis (analyzed sample). During the analysis, the analyzed sample is also divided into several parts, which are analyzed in parallel. This is done in order to increase the accuracy of the analysis. Usually no more than 1 g of the substance is used directly for analysis.

The sampling methods and sample size are mainly determined by the following parameters:

- 1) the physical state of the analyzed object (methods of sampling and sample sizes are different for gases, liquids, solids, plant and animal tissues, etc.);
- 2) the heterogeneity of the analyzed material and the particle size from which the heterogeneity begins;
- 3) the required accuracy of estimating the component content over the entire mass of the analyzed object;
- 4) the possibility of changing the chemical composition of the analyzed object in time and space (composition of flue gases, air, wastewater, etc.).

Lecture No. 5
Basic types of chemical equilibrium

Chemical equilibria in a homogeneous system

The main types of homogeneous equilibria used in analytical chemistry: acid-base, redox, complexation equilibrium. Law of mass action. Equilibrium constant of a reversible chemical reaction. The concept of ideal and real systems. Reasons for deviation from ideality. Activity, activity coefficient, its relationship with ionic strength. Ionic state of elements. The concentration is total and equilibrium. α-coefficient (mole fraction). Thermodynamic constants, real, conditional, their relationship. Acid-base balance. Modern ideas about acids and bases. Protolytic theory of Bronsted-Lowry. Acid-base pairs, acidity and basicity constants, their relationship. Processes of ionization and dissociation. Types of solvents, autoprotolysis reaction. Ionic product of the solvent. Leveling and differentiating effects of solvents. Calculation of pH in solutions of acids, bases and ampholytes. Buffer solutions and their properties. Complexation equilibrium. Classification of complex compounds. Chelates, intracomplex compounds. changes in the potential of the redox system. Quantitative characteristics of the stability of complex compounds - general and stepwise stability constants. Types of complex compounds used in analytical chemistry and their characteristics. The use of complexation for

detection, separation, masking and unmasking of ions, dissolution of precipitates, Theoretical foundations of the interaction of organic reagents with inorganic ions. Functional analytical groups, chromophore groups. Cycle formation rule by L.A. Chugaev. The main factors influencing the stability of chelates are: the nature of the metal ion, the basicity and denticity of the ligand, the spatial factor, etc. The main directions of using organic reagents in chemical analysis (detection, identification and masking of ions). The most common organic reagents: dimethylglyoxime, 8-hydroxyquinoline, etc.

Complexons. General properties of complexones and complexonates. The main uses of disodium ethylenediaminetetraacetic acid (EDTA) for detection, masking and quantification of ions. Redox balance. Reversible and irreversible redox systems. Equilibrium electrode potential. Nernst equation. Standard potential of the redox system. The concept of the real (formal) potential of the system. Factors influencing the magnitude of formal potential. The direction of oxidation - reduction reactions. Equilibrium constants of redox reactions. Relationship between the equilibrium constant and standard potentials. Rate of redox reactions. Catalytic, induced reactions in redox processes. Main oxidizing and reducing agents used in the analysis. Redox reactions in the processes of external dynamics during the formation of sedimentary and metamorphic rocks.

Equilibrium in a heterogeneous system

Equilibrium in the solid phase - solution system. Precipitation - dissolution reactions in analytical chemistry. Thermodynamic equilibrium constant of the precipitation - dissolution reaction (thermodynamic product of solubility). The influence of conditions on the equilibrium state of the precipitation - dissolution reaction (real and conditional products of solubility). Using the solubility product rule in analytical chemistry. Conditions for the formation and dissolution of sediments. Crystalline and amorphous sediments. Dependence of sediment structure on the nature and conditions of deposition. The colloidal state is an intermediate stage of sediment formation. Purity of precipitation. Co-precipitation. Using this phenomenon to concentrate microimpurities. Law V.G. Khlopin. The phenomenon of isomorphism in silicates and other minerals. Calculation of solubility under various conditions (the influence of pH, complexation, oxidation-reduction reactions, ionic strength of the solution and temperature). Influence of the same ion. Salt effect. Equilibrium between two liquid phases. Extraction and its use in analytical chemistry. Law of distribution. Distribution coefficient. Equilibrium constants in the liquid-liquid system (extraction constant). The use of extraction in the practice of chemical analysis.

Lecture No. 6
Activity

Electrostatic interactions lead to significant deviations in the behavior of the system from ideal. Take into account deviations from the ideal, i.e. the influence of electrostatic factors can be predicted using the activity method: instead of the concentrations of reacting particles [A], values called activities aA are used. The numerical values of activities are chosen in such a way that the form of the functional dependence for free energy

$G_A = G_{A0} + nRT \cdot \ln[A]$

was also preserved for real solutions:

$G_A = G_{A0} + nRT \cdot \ln aA.$

Consequently, activity is the concentration that a component of an imaginary ideal solution would have, having the same thermodynamic properties as a given real solution and having a dimension (mol/l).

Then for the general reaction

$aA + bB = cC + dD$

Taking into account the activities, we obtain the equilibrium constant - an expression of the law of mass action:

$K^0 = a_{Cc} \cdot aDd/aAa \cdot aBb,$

applicable to any chemical systems - both ideal and real.

Ratio of particle activity to its equilibrium concentration

$g_{A=}a_A/[A]$

called the activity coefficient. The activity coefficients of ions in electrolyte solutions can serve as a measure of electrostatic interactions in the system. For ideal solutions, electrostatic interactions are negligible, activities are equal to equilibrium concentrations, then g = 1.

There are several methods for determining and calculating activity coefficients. Since electrostatic interactions are very noticeable in electrolyte solutions, we will focus on calculating the activity coefficients of ions. They depend on the ionic strength, calculated using the well-known equation:

$I = (1/2) S[Ai] zi2,$

where zi is the charge of the Ai ion; S is the sum of all ions present in the solution. Ionic strength takes into account the electrostatic influence of all ions in a solution. It has the dimension of concentration and for solutions of strong II electrolytes is numerically equal to it.

One of the most used methods for determining the activity coefficients of individual ions is the estimate using the Debye-Hückel approximation [8]

loggi = -Azi2(I)1/2

in the case when I £ 0.01 M, and

*loggi = -Azi2(I)1/2/[*1+aB(I)1/2],

if I = 0.01-0.1 M, where A and B are constants depending on the temperature and dielectric constant of the solvent (for water at 298 K A » 0.5 and B » 0.33); a is an empirical constant that takes into account the sizes of ions and characterizes the average distance of approach of solvated ions under the assumption that they are rigid spheres. The value of a can be approximately considered constant, independent of the nature of the ion and equal to ~ (3...5)×10-8 cm (although it is difficult to agree with this).

In dilute solutions (I < 0.1 M), the ion activity coefficients are less than unity, but at I ® 0 the value gi ® 1. Solutions with very low ionic strength (I < 0.0001 M) can be considered ideal. At high ionic strengths, activity coefficients begin to depend on the nature of the ions, and then on the overall composition of the solution. In these cases, specific reference data should be used to find activity coefficients. In very concentrated solutions (ionic strength greater than unity), ion activity coefficients can be much greater than unity. The reason for this is thought to be the binding of a significant amount of solvent as a result of solvation of the ions and thus increasing the apparent concentration of the ions. At ionic strengths from 0.1 to 0.5 M, in many cases good results are obtained by calculations using the Davis equation [9]:

loggi = -Azi2(I)1/2/[1+aB(I)1/2]+ CI,

where a and C are constants (selected empirically for each specific electrolyte).

It is impossible to experimentally determine the activity coefficients of individual ions, since it is impossible to obtain a solution containing ions of only one type. Empirically, it was possible to measure only the average activity coefficient g± of the electrolyte ions AmBn, which is related to the activity coefficients of its constituent ions An+ and Bm- as follows:

g± = *(gAm*gBn)(m+n).

The Debye-Hückel and Davis equations are also suitable as a first approximation for calculating the activity coefficients of uncharged molecules (nonelectrolytes). In these cases, zi = 0 and in the Debye-Hückel equations, the activity coefficient of a nonelectrolyte is equal to unity at an

ionic strength I £ 0.1 M; for large values of ionic strength, it is necessary to use the Davis equation, which for nonelectrolytes turns into lgg = CI. The constant C in this case is called the salt coefficient, which depends on the dielectric constant of the nonelectrolyte e. For substances with low e (gases, sugars, proteins) C>0, g > 1. For such substances, the effect of "salting out" is observed, i.e. decreasing their solubility in water in the presence of electrolytes. For substances with high e (for example, for HCN e = 111) C< 0, g < 1.

Everything that has been said above indicates a difficult situation with the activity coefficients of both hydrated or solvated ions and neutral molecules (nonelectrolytes), for which until now a unified, all-encompassing theory has not been developed that allows one to unambiguously calculate g. An unreasonably large number of adjustment parameters are allowed when changing the concentrations of the same solute and the nature of the solvent.

The theory of hydrodynamic fluctuations in solutions of symmetrical and asymmetrical, strong and weak electrolytes, proposed by us, makes it possible to estimate the activity coefficients of both individual ions and undissociated molecules, as well as transport properties over the entire range of concentrations studied (from 0 to 4-5 mol/l) in any solvent.

Relationships between activity coefficients and concentrations of electrolyte solutions

The activity coefficient is a measure of the deviation of real (practical, experimental) parameters from ideal ones, developed as a first approximation for dilute solutions of non-electrolytes. Their values in solutions of high concentrations become virtual. In fact, values of coefficients of several tens, that is, deviations from ideal parameters by tens of times, are difficult to adapt to laws for practical use in solutions where association processes or other intermolecular interactions dominate.

However, there is a number of factual data on the dependence of the activity coefficients of electrolytes on molality, and at some concentrations (from decimolal for some electrolytes to several molalities for others) a minimum point is observed.

Until now, there are no clear explanations in the literature, much less justification for the appearance of this minimum value of the activity coefficient.

This work proposes a model equation for calculating optimal electrolyte concentrations corresponding to the minimum activity coefficient and reasoning [13-18].

It is shown that at the minimum point of the function

g= f(C) (1.22)

at a concentration C0 characterizing gmin, the equality ħw = kBT, w = w0 holds and this characterizes the special point at which the sign of the dielectric response changes. At w = w0 and further at all w > w0, a new structure is formed in the electrolyte solution, the elements of

which are ionic associates. At this special point, the activity coefficient g has the minimum possible value. To combine the solutions before and after the equality ħw = kBT, reducing the exponent and taking into account the universal constants, we come to the form:

g = 0.368·exp[-(245.467/T)·(C0/μ)1/2] , (1.23)

and then - to expression (4):

g = 0.368 exp{[(C0)1/2-(C)1/2]/(C0)1/2} (1.24)

where C0 is the electrolyte concentration at the gmin point.

From equations (1.22), (1.23) and (1.24) by substituting universal constants and dimensions into the SGS: kB = 1.38 10-16, e = 4.8 10-10, ħ = 1.05 10-27, NA = 6.023 1023 , mass in units. GHS is equal to 1.67·10-24, we get:

$$C_0 = 1000 \cdot \mu \cdot 1.67 \cdot 10^{-24} \cdot k_B^2 \cdot T^2 / 64 \cdot Z_{Kt} \cdot Z_{An} \cdot e^2 \hbar^2 N_A$$

C0 = 1.02·10-6·m·T 2/ $Z_{Kt} \cdot Z_{An}$ (1.25)

Equations (1.23) and (1.24) express the activity coefficient for unassociated electrolyte ions, while the literature (experimental) values of g± take into account at this point the actual (real) interactions of solvated ions with the formation of the molecular form of the electrolyte or ionic associates at equilibrium (a). Therefore, one should not expect complete identity of the activity coefficients theoretically estimated from equation (1.24) with the literature ones, but, of course, the nature of the dependence of the activity coefficients on concentrations is important.

Table 1.3 shows the obtained concentrations for 42 electrolytes at gmin.

Table 1.3

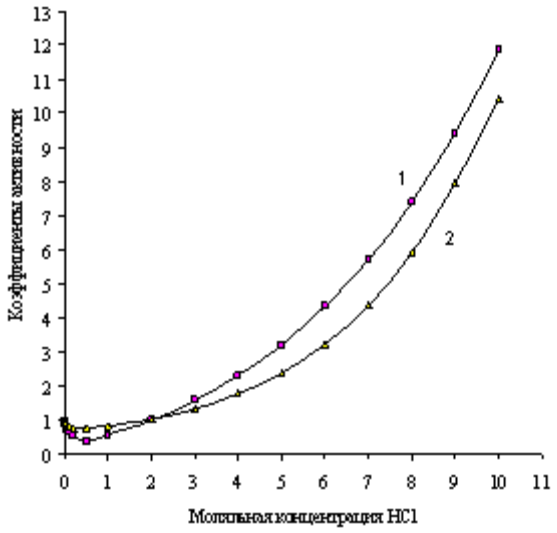
*Electrolyte concentration values C0, mol/l at gmin according to the equation (*1.25)

And he	*Li+*	*Na+*	*K+*	*Rb+*	*Cs+*	*NH4+*
F-	0.46	0.94	1.16	1.41	1.51	0.84
Cl-	0.53	1.26	1.68	2.27	2.54	1.08
Br-	0.58	1.62	2.37	3.74	4.52	1.33
I-	0.60	1.76	2.70	4.63	5.88	1.43

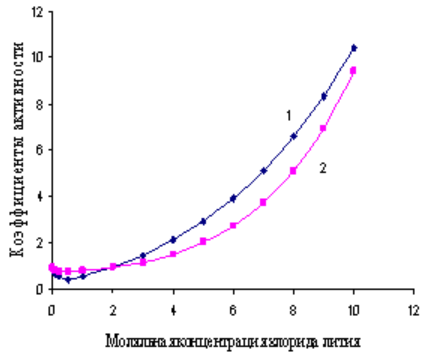
NO3-	0.56	1.52	2.17	3.26	3.83	1.26
ClO4-	0.59	1.69	2.54	4.17	5.15	1.38
CNS-	0.56	1.49	2.11	3.13	3.66	1.24

As for the increase in the activity coefficient g at high electrolyte concentrations, no rational quantitative theory has been proposed that would determine the concentrations of solutions with a minimum g and a significant increase in it with increasing molality. This work provides an explanation for this fact and calculates the optimal concentrations of electrolytes corresponding to the minimum activity coefficient. Thus, beyond the concentration C0 corresponding to the minimum activity coefficient, due to the reduction in the mean free path of solvated ions or molecules, interionic interactions become prevalent, leading predominantly to ionic associates in polar solvents with low dielectric constants or to molecular solvates in nonpolar solvents with low dielectric constants. values of dielectric constants in solvents.

Equation (1.24) allows you to calculate the theoretical values of the activity coefficients of various electrolytes depending on their concentrations. The function passes through a minimum at C0, repeating the contour of the dependence of actual (real) g± on the molality of solutions (Fig. 1.1 and 1.2).



Rice. 1.1. Dependences of calculated (1) and experimental (2) activity coefficients on the molal concentration of an aqueous solution of hydrochloric acid



Rice. 1.2. Dependences of calculated (1) and experimental (2) activity coefficients on the molal concentration of an aqueous solution of lithium chloride

In Fig. 1.1 and 1.2 show the acceptability of the proposed model estimate of the activity coefficient due to the fairly noticeable correspondence of the dependence of the functions g = f (m) and g± = f (m) for aqueous solutions of hydrochloric acid (Fig. 1.1) and lithium chloride (Fig. 1.2).

In table As an example, Table 1.4 presents the experimental (literature) and calculated by equation (1.24) values of the activity coefficients of hydrochloric acid and lithium chloride.

Thus, this work theoretically substantiates the concentration ranges of electrolyte solutions in which a minimum of activity coefficients are observed, explains the phenomenon of dominance of associative phenomena leading to the formation of ionic associates or, depending on the properties and nature of the solvent, to the predominant state of solutions in the form of molecular solvates.

Lecture No. 7
Equilibrium in acid-base reactions

The nature of acids and bases has always interested researchers, and recently interest in them has especially increased due to the fact that the rapid development of chemistry has provided an abundance of new experimental material, which urgently requires broad theoretical generalizations covering the whole variety of acid-base interactions.

The history of the development of the doctrine of acids and bases is one of the interesting and important chapters of chemistry. At the same time, as the historian of chemistry G. Kopp points out, "... in few branches of chemistry there is a change in such opposite and contradictory views as in the doctrine of acids, alkalis and salts. Every step forward that was made for the theoretical knowledge of these substances was achieved through a difficult struggle against surviving prejudices. ...As soon as we believed that we had arrived at a satisfactory solution to the main theoretical problems, we were immediately faced with emerging contradictions."

Arrhenius theory

Concepts about acids and bases have existed for more than three centuries, but there is still no uniform definition of these concepts. The first approximation to modern views on acids and bases was the theory of the Swedish physical chemistArrhenius, put forward by him in 1887, resulting from his theory of electrolytic dissociation. For his development of the theory of electrolytic dissociation, Arrhenius was awarded the Nobel Prize in Chemistry in 1903. While studying the electrical conductivity of aqueous solutions, he drew attention to the fact that their conductivity increases with dilution. Based on this, he suggested that in such solutions substances disintegrate into charged particles - ions, which can move to the electrodes - a negatively charged cathode and a

positively charged anode. This decomposition process was called electrolytic dissociation. This name also suggests that dissociation occurs under the influence of an electric current. Arrhenius's theory, on the one hand, explained why electrolyte solutions conduct current; on the other hand, it explained the increase in the number of particles in the solution. Arrhenius isolated H+ and OH□ ions from all the ions as products of autodissociation of water:

$H2O \rightleftharpoons H+ + OH□$

He then stated that all acids form hydrogen cations (H+) in solution, and all bases form hydroxide ions (OH□):

Acids: HNO3 $\rightleftharpoons$ *H+ + NO3□ and HNO2* $\rightleftharpoons$ *H+ + NO2□*

Grounds: NaOH $\rightleftharpoons$ *Na+ + OH□ and NH3. H2O* $\rightleftharpoons$ *NH4+ + OH□*

Acids and bases for which the degree of decomposition into ions (degree of electrolytic dissociation) has a value close to unity were called strong by Arrhenius (HNO3, NaOH), and all others were called weak (HNO2, NH3. H2O).

Weak acidscould be compared by strength using the law of mass action - by the values of the acid dissociation constants KDC, and weak bases - by the values of the basic dissociation constants KDO. The higher the KD value, the stronger the weak acid electrolyte or the weak base electrolyte was considered.

For polybasic acids (for example, H2CO3 or H3PO4) and polyacid bases such as Ca(OH)2 and La(OH)3, stepwise dissociation occurs - the sequential separation of each H+ cation or OH□ anion:

$$\boldsymbol{H2CO3 \rightleftharpoons H+ + HCO3□,\ HCO3□ \rightleftharpoons H+ + CO32□}$$

$$\boldsymbol{Ca(OH)2 \rightleftharpoons CaOH+ + OH□,\ CaOH+ \rightleftharpoons Ca2+ + OH□}$$

In these cases, a set of KD values was obtained (for acids KDK1, KDK2 ..., for bases - KDO1, KDO2 ...), and the comparison of acids or bases in strength became uncertain.

Strong acidsand the foundations, due to the practical absence of a state of equilibrium according to the law of mass action, were not characterized quantitatively in any way; their strength was simply considered to be the greatest.

Many scientists - contemporaries of Arrhenius, initially did not accept his theory. Many of them at that time did not yet have a clear understanding of how ions differ from neutral atoms. It seemed incredible to them how, for example, sodium chloride in water could exist in the form of separate sodium and chlorine ions: as is known, sodium reacts violently with water, and a chlorine solution is yellow-green and poisonous. As a result, Arrhenius' dissertation received a number of negative reviews. Among the most irreconcilable opponents of Arrhenius was D.I. Mendeleev, who created the “chemical” theory of solutions, in contrast to the “physical” theory of Arrhenius. Mendeleev believed that in solutions there are essentially chemical interactions between the solute and the solvent, while Arrhenius' theory represented aqueous solutions as a mechanical mixture of ions and water. In 1889, Mendeleev published a Note on the dissociation of dissolved substances, which questioned the very fact of disintegration into ions in electrolyte solutions. “Keeping everything that has been acquired in relation to the understanding of

solutions," wrote Mendeleev, "it seems to me that we can leave aside the hypothesis about a special type of dissociation - into ions, which occurs with electrolytes during the formation of weak solutions."

It soon became clear that the qualitative and quantitative limitations of Arrhenius's views on acids and bases were as follows.

Firstly, according to Arrhenius's idea, from the reversibility of dissociation reactions it seemed to follow that the more substances are introduced into the solution, the more the dissociation equilibrium will shift to the right (in accordance with Le Chatelier's principle), and the more this reaction will proceed. But experimental data showed the opposite: in a dilute solution, the degree of dissociation of a weak acid or base became greater than in a concentrated solution.

From this one could draw the false conclusion that highly soluble acids and bases are stronger electrolytes than poorly soluble ones.

Experiments have shown that solubility and the degree of dissociation are in no way related to each other: a well or poorly soluble electrolyte can be both strong and weak.

These experimental facts were explained in 1888Ostwald, who formulated the law of dilution, establishing a mathematical relationship between the degree of dissociation α and the analytical (by preparation) concentration of a substance in solution C, namely:

$K_D = \alpha 2C / (1 - \alpha) = Const = f(T)$

Secondly, according to Arrhenius's idea, water is only a solvent (medium) and does not chemically participate in the dissociation reactions of acids and bases (see the dissociation equations above).

However, we know that this is not always the case.

The theory of chemical bonding divides all substances into ionic and covalent. Salts and alkali hydroxides, being ionic crystals in the solid state, when dissolved in water, naturally decompose (dissociate) into the same ions from which their crystal lattice is built:

$$KNO3 = K+ + NO3□ \quad Ba(OH)2 = Ba2+ + 2\ OH□$$

All salts and alkaline hydroxides are strong electrolytes.

Acidsaccording to Arrhenius, these are substances consisting of polar covalent molecules. After dissolving them in water, it is not a simple decomposition into ions that occurs, but a chemical reaction between the molecules of acid and water. The participation of water in reactions of this kind has been confirmed experimentally, but it is impossible to depict this interaction within the framework of the Arrhenius theory.

Thirdly, according to Arrhenius's idea, acid salts should dissociate in water in the same stepwise manner as polybasic acids:

$$NaHSO4 \rightleftharpoons Na+ + HSO4□, \quad HSO4□ \rightleftharpoons H+ + SO42□$$

$$NaHCO3 \rightleftharpoons Na+ + HCO3□, \quad HCO3□ \rightleftharpoons H+ + CO32□$$

At the same time, they must create an acidic environment in the solution due to an excess of H+ ions.

However, experimental data show that, for example, in a NaHSO4 solution the environment is acidic, and in a NaHCO3 solution, on the contrary, it is alkaline, although

the excess content of OH- hydroxide ions cannot be explained within the framework of the Arrhenius theory.

Fourth, the hydrolysis reactions of salts formed by weak acids or weak bases did not fit into the framework of Arrhenius's definitions, for example:

AlCl3 + H2O ⇄ (AlOH)Cl2 + HCl, Al3+ + H2O ⇄ AlOH2+ + H+

Na2CO3 + H2O ⇄ NaHCO3 + NaOH, CO32□+ H2O ⇄ HCO3□ + OH□

Despite the fact that such salts create an acidic or alkaline environment in solution, they are not acids or bases according to Arrhenius. Since water is included in the hydrolysis equations as a full-fledged reagent, such reactions, according to Arrhenius' ideas, were considered a special type of exchange reactions in an aqueous solution, and the equilibrium state was characterized by hydrolysis constants, calculated according to complex rules, different for different types of salts.

Fifthly, according to Arrhenius's idea, neutralization reactions of the type:

KOH + HNO3 ⇄ KNO3 + H2OOH□ + H+ ⇄ H2O

pass only in aqueous solution. However, many reactions are known that are very similar to neutralization reactions, but occur either in non-aqueous solvents or not in solution at all. For example:

KOH(s) + HCl(g) = KCl(s) + H2O(g);NH3(g) + HBr(g) ⇄ NH4+(g) +

Br□(g);HNO3(s) + CH3COOH ⇄ NO3□(s) + CH3COOH2+(s).

From the point of view of the theory of electrolytic dissociation, these reactions cannot be explained, reflecting their similarity to neutralization reactions in an aqueous solution.

These are the main shortcomings of Arrhenius's definitions for acids and bases.

Brønsted–Lowry theory

In 1923, independently of each other, Bronsted and Lowry proposed a new, so-called protolytic theory of acids and bases, which is more often called simply Bronsted's theory.

The creators of this theory believe that the electrolytic dissociation of acids and bases is not a physical process of the elimination of H+ and OH ions, as it followed from the Arrhenius theory, but is the result of the chemical interaction of a solute with a solvent. For example:

$$HCl + H_2O \leftrightarrow H_3O^+ + Cl^-$$

or

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$$

The phenomenon of decomposition of a substance into nonons as a result of chemical interaction with a solvent can be illustrated by the dissolution of various amines in organic acids. As is known, neither amines nor organic acids in their pure form are practically dissociated. If you mix amines with an organic acid, then (as D.P. Konovalov first showed), the resulting solution conducts electricity well, since during the reaction:

$$R'NH_2 + RCOOH \leftrightarrow [R'NH_3]^+[RCOO]^- \leftrightarrow R'NH_3 + RCOO^-$$

ions are formed.

Taking into account all these facts, Brønsted calls substances that are capable of donating a proton (proton donors) acids:

acid $кислота\ A \leftrightarrow основание\ B + H^+$

For example,

$$HClO_4 \leftrightarrow ClO_4^- + H^+$$

*Reasons*according to Brønsted, are substances that are capable of attaching a proton (proton acceptors):

$$основание\ B + H^+ \leftrightarrow кислота\ A$$

For example,

$$NH^3 + H^+ \leftrightarrow NH_4^+$$

Brønsted represents the acid-base reaction with the following scheme:

$$кислота_1 + основание_2 \leftrightarrow кислота_2 + основание_1$$

For example,

$$HCl + NH_3 \leftrightarrow NH_4^+ + Cl^-$$

This equilibrium involves two pairs of acids and bases, called by Brønsted corresponding, i.e. conjugated, or corresponding. So, in the indicated reaction Cl^--ion is the conjugate base of the acid HC1; NH4+ ion is the conjugate acid of the base NH3.

Thus, a substance can exhibit acidity only when interacting with a base and, conversely, it can exhibit basic properties only in the presence of an acid.

Brønsted draws an analogy between acid-base and redox reactions. In redox reactions, an electron passes from the reducing agent to the oxidizing agent, and in acid-base reactions, the acid donates a proton to the base. Just as an acid, having given up a proton, turns into a base, a reducing agent, having lost an electron, becomes an oxidizing agent:

$$восстанови тель \leftrightarrow окислитель + электрон$$

$$кислота \leftrightarrow основание + протон$$

Just as for a reduction reaction to occur, the presence of an oxidizing agent that accepts an electron is necessary, and for the acidity of a substance to occur, the presence of a base capable of accepting a proton is necessary.

Thus, the same substance, depending on the reaction conditions, can be both an acid and a base. For example, in the reactions below, water behaves as a weak base because it is a proton acceptor:

$$HCl + H_2O \leftrightarrow H_3O^+ + Cl^-$$

$$CH_3COOH + H_2O \leftrightarrow H_3O^+ + CH_3COO^-$$

But water can also exhibit acidic properties, i.e., be a proton donor:

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$$

$$RH_2 + H_2O \leftrightarrow RH_3^+ + OH^-$$

Acetic or nitric acids behave like acids towards weaker acids. For example, when acetic acid reacts with anhydrous nitric acid, acetic acid acts as a base.-

$$CH_3COOH + HNO_3 \leftrightarrow [CH_3COOH_2]^+ + [NO_3]^-$$

In turn, even such an acid as nitric acid in relation to a stronger one, for example, perchloric acid (in an aqueous solution) behaves as a base:

$$HNO_3 + HClO_4 \leftrightarrow [H_2NO_3]^+ + [ClO_4]^-$$

A clear example of the dependence of the properties of a substance on the partner (solvent) is urea, which behaves as an acid in liquid ammonia, as a base in acetic acid, and as a neutral in water.

Substances that can easily attach protons to themselves are called protophilic and are bases. If such substances serve as solvents, they are called protophilic solvents (liquid ammonia, amines). The more pronounced the protophilicity of a solvent, the greater the number of substances dissolved in it that behave like acids, the more clearly the difference in their strength is manifested, and the fewer the number of bases that can exist in this solvent.

Substances capable of donating protons are called protogenic and are acids (sulfuric, nitric, acetic acids). If they are solvents, they are called protogenic solvents. The easier the solvent molecules give up protons, the more

a number of substances will be able to exhibit basic properties in this solvent.

Water is a typical amphoteric solvent. It can add and donate a proton with approximately equal ease:

$$HNO_3 + H_2O \leftrightarrow H_3O^+ + NO_3^-$$

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$$

According to Brønsted, there are also so-called aprotic solvents. These are substances that either do not exhibit acidic and basic properties at all, or exhibit them very weakly. They are unable to give or receive protons. Brønsted includes benzene and most hydrocarbons as such solvents.

Thus, Brønsted's theory of acids and bases significantly expanded the range of substances that can be considered as acids or bases not only in water, but also in non-aqueous media. The protolytic theory explains well acid-base reactions in both aqueous and non-aqueous systems, as well as the interaction between acids of varying strengths, which could not be explained based on the Arrhenius theory.

However, the further development of chemical science showed that this theory is also imperfect, since there was no place for aprotic acids in it. Meanwhile, in practice there are often reactions that are acid-base in nature, while none of the substances participating in the reaction is a proton donor.

Lewis' theory.

A different approach to the interpretation of the properties of acids and bases was proposed by G. Lewis in 1923. Believing that the presence of a proton is not the main sign of acidity, he substantiated the electronic mechanism of acid-base reactions. According to the definition of G. Lewis, an acid is any chemical compound that, during a chemical reaction, is capable of attaching to a pair of electrons of another molecule and forming a new covalent chemical bond through this pair. Such substances have since been called Lewis acids. These substances contain atoms with unfilled (vacant) orbitals and therefore they can be acceptors of a pair of electrons (from the Latin acceptor - accepting). And the molecules or ions that provide electron pairs to Lewis acids are

Lewis bases; they are electron donors (from the Latin donare - to give, donate). Any equilibrium described by an electron-donor mechanism is considered to be acid-base.

A distinctive feature of the Lewis acid-base theory is that an acid and a base interact with each other to form a donor-acceptor (coordination) bond:

A+B=A:B,

where A is a compound, B is a base, A: B is an acid-base complex (neutralization product).

As a result of the acquisition of a pair of electrons by the atom responsible for the acidic properties of the compound in question, a complete electronic configuration often results:

In accordance with the Lewis theory of acids and bases, acids include metal ions (for example, Ag+, Fe3+), oxides of some non-metals (for example, SO3), a number of salts (for example, AlCl3), hydrogen ions themselves - protons (as particles that easily attach a pair of electrons), as well as substances such as BF3, SiO2, Al2O3. All such substances (except hydrogen ions) are now called Lewis acids. And bases, according to Lewis, are ions or molecules that have one or more lone pairs of electrons. These include, for example, ammonium ions, organic amines, oxides of alkali and alkaline earth metals, as well as atoms and molecules carrying negative charges, i.e. anions, including hydroxyl ions OH– (the latter are also not currently classified as Lewis bases). Protic acids are considered in Lewis theory as products of neutralization of a proton with bases (for example, hydrochloric acid is a product of neutralization of H+ with the base Cl-).

When Lewis acids interact with Lewis bases (neutralization reaction), a so-called donor-acceptor bond is formed. It is essentially no different (except for its origin) from an ordinary covalent bond. Typical Lewis ones are, for example, the reaction between ammonia (donor of a pair of electrons) and a hydrogen ion to form ammonium ion; reaction of iron bromide with bromine ion to form the anion FeBr4–; reaction between ammonia and boron trifluoride to form a molecule with a donor-acceptor (coordination) bond H3N:BF3. The donor-acceptor bond is often represented by an arrow pointing from the donor to the acceptor: H3N□BF3. According to Lewis, bonds in numerous complex metal compounds are also donor-acceptor. In them, pairs of electrons bind the metal atom with inorganic or organic electron donors - ligands. Thus, Lewis was the first to use electronic concepts to explain bonds in complex (coordination) compounds, for example, in [Ag(NH3)2]+ ions.

The dissolution of Lewis acids in ionizing solvents leads to an increase in the concentration of solvent cations (for example, SO3+H2O□H3O++HSO-4). Bases increase the concentration of solvent anions [for example, (CH3)3N+H2O□OH-+(CH3)3NH+].

Lewis's theory has a number of weaknesses. Thus, protic acids such as H2SO4, HC1, HC1O4, according to this theory, should have the ability to add electron pairs, forming covalent bonds. The structure of the molecules of these substances indicates the absence of such an ability. In this regard, a rather complex mechanism for the interaction of an acid with a base was proposed, where the formation of intermediate compounds (due to hydrogen bonds) and their subsequent destruction with the formation of the final reaction products was assumed. This has only made the most widely known processes more difficult to explain.

The limitations of Lewis's theory were also evident in the interpretation of the strength of acids. Lewis acids and bases cannot be arranged in a universal series by strength, since their sequence depends on the substance taken as the standard for comparison. According to Lewis, the strength of an acid or base depends on the characteristics of the chemical reaction in which these substances participate. For example, during the formation of fluoride complexes, copper ions act as a weaker acid than beryllium ions. This follows from the fact that the stability of the copper fluoride complex is less than the stability of the beryllium fluoride complex. However, with amines, copper gives more stable complexes than beryllium. In the latter case, increased acidity should be attributed to copper ions. With this approach, it is not possible to quantify the strength of acids or bases.

There is also no consistency in the catalytic action of Lewis acids and protic acids. It has been found that many reactions that are catalyzed by Lewis acids are not catalyzed by protic acids.

Thus, the desire to extend the laws of acid-base interaction to a much wider range of processes has led to a decrease in the number of common features of chemical reactions of substances.

Several classifications of chemical reactions are known from the course of inorganic chemistry. Depending on the quantity and composition of the starting substances and reaction products, they are divided into decomposition, combination, substitution and exchange reactions. We can also distinguish reactions that occur with a change in the oxidation state and without a change, exo- and endo... reactions. From the point of view of an analytical chemist, it is advisable to distinguish the following types of chemical reactions:

1) with proton transfer – acid-base; 2) with electron transfer – redox; 3) with the transfer of electron pairs with the formation of donor-acceptor bonds - complexation reactions. Within each type, a more detailed classification can be further carried out. For example, among acid-base reactions one can distinguish reactions - dissociation, autoprotolysis, etc., in ORR - disproportionation, intermolecular oxidation - reduction, intramolecular oxidation - reduction.

All these equilibria have much in common, however, each type has its own characteristics. Let us dwell in more detail on these types of chemical equilibrium. Equilibria in solutions of

acids and bases are distinguished as a separate type due to the sharp difference between the hydrogen cation and all other ions and the extraordinary importance of reactions involving a proton for most branches of chemistry.

There are several theoretical concepts of acid-base transformations: 1) this is the electrical theory of dissociation by S. Arrhenius, according to which an acid is an electrolyte, the dissociation of which produces H+; and the base is an electrolyte, the dissociation of which leads to the formation of OH–; this theory has a number of disadvantages and is valid only for aqueous solutions;

2) Lewis electron theory;
3) Freyn's theory of solvosystems;
4) Bronsted's protolytic theory;

5) the most general theory of acids and bases is the Usanovich theory, in which acids are substances that donate cations or accept anions (electrons), and bases are substances that donate anions (electrons) and accept cations.

The protolytic theory became more widespread. The protolytic theory is based on the ratio of substances to the proton (H+), devoid of an electrical shell, which is five orders of magnitude smaller than other ions and is very mobile.

According to this theory, an acid is a particle (molecule or ion) capable of donating a proton, i.e. acid is a proton donor.

$CH_3COOH \Leftrightarrow H^+ + CH_3COO^-$ (a) or in general $HB \Leftrightarrow H^+ + B^-$

to-that to-that

A base is a particle (molecule or ion) capable of accepting a proton, i.e. The base is a proton acceptor.

$NH_3 + H^+ \Leftrightarrow NH_4^+$ (b) or in general $H^+ + B \Leftrightarrow BH^+$

basic basic

(a) and (b) are acid-base half-reactions that cannot exist separately (independently).

Proton transfer reactions (acid-base reaction reactions) are called protolytic, and acids and bases themselves are called protolytes.

Such reactions include dissociation, autoprotolysis, hydrolysis, and neutralization reactions. All substances are only potentially acids or bases, and exhibit these properties only in a protolytic reaction.

$CH_3COOH + NH_3 \Leftrightarrow CH_3COO^- + NH_4^+$ $B_1 + HB_2 \Leftrightarrow HB_1 + B_2^-$

k-ta1 $basic_2$ $basic_1$ $to\text{-}that_2$main 1 set 2 set 1 main 2

As a result of the reaction, a new pair of particles is formed, one of which is capable of donating a proton, and the other is capable of accepting a proton, i.e. the acid is in equilibrium with its conjugate base, and the base is conjugate with the acid.

Some particles (molecules or ions) can act as both acids and bases depending on conditions, i.e. can either accept or donate a proton. They are called ampholytes. Ampholytes include water, ammonia, bicarbonate ion, etc.

	NH3 + H+⇔[NH]4+
H2O⇔H+ + OH–	basic lyonium ion
liate ion (hydroxide ion)	NH3⇔H+ + NH2–
	lyate ion
H2O + H+⇔H3O+	HCO3– + H2O⇔CO32– + H3O+
basic lyonium ion (oxanium ion)	k-ta1 main.2 main.1 k-ta2
	HCO3– + H3O+⇔H2CO3 + H2O
	main 1 set 2 set 1 main 2

Within the framework of the protolytic theory, the circle of acids, bases and ampholytes looks different than according to the theory of electrolytic dissociation by S. Arrhenius.

According to the theory of Brenstez and Lowry, acids, bases and ampholytes include

Acids	Grounds	Ampholytes
1. Neutral molecules: H2SO4, HNO3, HCl, CH3COOH, H2O, etc.	1. Neutral molecules: NH3, NH2R, NHR2, N2H4, NH2OH, etc.	1. Neutral molecules: H2O, NH3, Zn(OH)2, etc.
2. Hydroanions: HCO3–, HSO3–, H2PO4–, etc.	2. Anionic bases: OH–, CH3COO–, Cl–, Br–, I–, HCO3–, CO32–, etc.	2. Hydroanions: HSO3–, etc.
3. Cation exchangers: H3O+, NH4+, [Al(H2O)6]3+, etc.	3. Cationic bases: NH2 NH3 – hydrazolium ion, Al(H2O)5OH2+, etc.	3. Complex molecules: Al(H2O)5OH2+, etc.

The solvent in this theory is considered not only as a physical medium, with a certain value of dielectric constantε, but also as a substance that chemically interacts with an acid or base.

Examples:

Dissociation of acid in water:	CH3COOH + H2O⇔H3O+ + CH3COO– k-ta1 basic$_2$ to-that$_2$main 1

Dissolution of NH3 in water	NH3 + H2O⇔NH4+ + OH– main 1 set 2 set 1 main 2

The ability of acids and bases to dissociate in a given solvent depends on:

1. The ability of a base to attach a proton or the ability of an acid to donate a proton.

2. The ability of a solvent to add or donate a proton.

Therefore, the strength of acids or bases can only be compared in solvents of the same chemical nature. The reference tables show Kp and pK in aqueous solutions at 298 K.
Classification of solvents

All solvents can be divided into

Aprotic	**Protolytic**		
(not capable of joining or giving proton, acids and bases in them are not capable of dissociation). These are C6H6, C6H3CH3, CCl4	(capable of attaching or releasing H+) ↓↓↓ Amphiprotic (amphoteric), capable of attaching and donating H+ (H2O, C2H5OH, CH3OH, C6H5OH, NH3). Bases and acids dissociate in them	Protophilic (capable of adding H+) (basic), the dissociation of acids in them is enhanced (pyridine, hydrazine)	Protogenic capable of eliminating H+ (acidic), the dissociation of bases (HCOOH, CH3COOH, etc.) is enhanced in them.

According to proton-donor and proton-acceptor properties, solvents can be arranged in a row:

protogenic	amphiprotic	protophilous
H2SO4, CCl3, CH3COOH,	H2O, C2H5OH, NH3	NH3, C5H5N

"on right" "left"

proton-donating properties are enhanced←————————————

"left" "right"

proton-acceptor properties decrease————————————→

For analytical practice, it is important to classify solvents according to their ability to differentiate and neutralize the strength of acids and bases.

*Leveling solvents*are solvents that smooth out differences in the strength of acids or bases. Leveling solvents for them are CH, NH3, hydrazine. Moreover, the greater the proton-acceptor properties of the solvent, the more it is leveled out.

For bases, leveling solvents are acids CH3COOHbz, HCOOHbz. The stronger the proton-donating properties of the solvent, the more bases in it are leveled.

Differentiating solvents- These are solvents in which there is a sharp difference in the strength of acids or in the strength of bases.

For acids, protonogenic or ampholytic solvents (CH3COOH) are differentiating.

This issue will be discussed in more detail in the topic “Non-aqueous titration”.

For the main differentiation are profile solutions.

The acid-base properties of protoliths can be characterized by equilibrium constants.

Since strong electrolytes in solutions completely disintegrate into ions, and the activity of the ions varies depending on the concentration of the electrolyte, Kp does not have a constant value (its value is large), and it is not used to describe these solutions.

A feature of weak electrolytes is that the dissociation process is reversible and, therefore, ZDM can be applied to it.

a) CH3COOH⇔H+ + CH3COO–

to-that

[H+] [CH3COOH]

Kr= ---------- = Kd or Cl or KA - acidity constant.

[CH3COOH]

[H+] [B–]

NV⇔H+ + B K_{∂}^{c} = ---------- = K_{A}^{c}

[HB]

to-that

b) NH4OH–⇔*OH– + NH4 +*

basic

[NH4+] [OH–]

Kr= ---------- = Kd or Cl or KA – basicity constant.

[NH4OH–]

B + H2O⇔VN+ + OH–

The dissociation constant depends on the nature of the electrolyte and temperature, but does not depend on the concentration, i.e.

[BH+] [OH–]

CA= ----------

[V] [H20]

CD=φ(nature of electrolyte, t0)

The dissociation constant depends on the nature of the electrolyte and temperature, but does not depend on the concentration, i.e.

The relationship between Kd andαexpressed by Ostwald's dilution law.

$$\alpha = \sqrt{\frac{K\partial}{C}}$$

Often it is not the Kd themselves that are used, but the indicators of constants:

pKa = – log Ka

pKB = – log KB

$$K\frac{T}{B} = \frac{a_{cm} \times a_{HB^+}}{a_B \times a_{H_2O}} \qquad K_A^T = \frac{[a_H \times a_{B^-}]}{aHB}$$

*CD*and pK are given in reference tables.

Dissociation constants and also constant indicators are used to compare the strength of acids and bases, as well as the direction of chemical reactions, which is determined by the competition between the strengths of acids and bases participating in equilibrium.

Examples.

KA H3CCOOH = 1.8×10–5
KA NSSOUN = 1.8×10–4

The higher the Kd, the stronger acid.

CO2↑
Na2CO3 + 2HCl⇔2NaCl + H2CO3⟨
H2O
strong one weak one
Kd1 = 4.3×10–7

Reactions used in qualitative analysis most often occur in aqueous solutions. Water is a weak electrolyte and dissociates reversibly to a small extent. The process of water dissociation is called autoprotolysis. Autoprotolysis – self-ionization of a solvent exhibiting acid-base properties

For NH3

NH3 + NH3⇔N2H4 + 2H+
kit1 main.2 kit2 main.1

For water

H2O + H2O⇔H3O+ + OH–

main 1 set 2 set 1 main 2

In a simplified form, the dissociation of water can be written:

H2O⇔H+ OH–

According to the ZDM:

$$Kr = \frac{[H^+]\,[OH^-]}{[H_2O]} = 1.8 \times 10^{-16}$$

*[H+]*and [OH–] – equilibrium parameters in mol/dm3.

KS = Kr [H2O] = KW = [H+] [OH–]= 10–14 (at 298 K)

KW- ionic product of water;

KS- autoprotolysis constant.

In general, KS = [ion-lyonium] [liate-ion].

For a given temperature, the product of the molar concentrations of hydrogen ions and hydroxide ions is a constant value and is called the ion product of water.

pKs(H2O) = – log Ks H2O = 14

In pure water [H+] = [OH–] = 10–7 mol/dm3.

More often, it is not the concentrations of hydrogen ions and hydroxide ions that are used, but the hydrogen index and hydroxide index.

pH = – log [H+] The hydrogen index is the negative decimal logarithm of the polar concentration of hydrogen ions.

pOH = – log [OH–] The hydroxide index is the negative decimal logarithm of the molar concentration of hydroxide ions.

The relationship between them is expressed by the formula pH + pH = 14.

To calculate [H+] or [OH–], use the following formulas:

$$[H+] = \frac{TO_W}{[OH–]}; \qquad [OH^-] = \frac{KW}{[H^+]}$$

The pH value quantitatively characterizes the acidity and basicity of solutions.

Scale pH values	0-3	4-6	7	7-11	12-14
	highly acidic environment	slightly acidic environment	neutral Wednesday	weak main environment	strongly basic environment

Determining the pH value of a solution is an important condition for conducting an analytical reaction.

For example:

a) pharmacopoeial reaction to

K+ + H2C4R4O6⇔KHC4R4O6↓+H+

white precipitate insoluble in acids

pH = 4÷7 for this purpose, the reaction is carried out in the presence CH3COONa

2) pharmacopoeial reaction to Ca2+ c (NH4)2

Ca2+ + C2O42–⇔CaC2O4↓

white precipitate soluble in acids

pH = 6÷7

The pH value can be determined visually using chemical indicators (methyl orange, methyl red, ph/f, litmus - universal indicator paper - so-called pH indicators), or instrumentally (pH meter device), or calculated.

To calculate [H+], [OH–], pH and pOH in aqueous solutions of acids and bases, you can use the following calculation formulas:

For strong acids and bases:

acid: [H+] = Sc-you×acid basicity

pH = – log Sk-ty×acid basicity

base [OH–] = Pine.×acidity of the base

pOH = – log Pine.×acidity of the base

pH = 14 – pOH.

For weak electrolytes:

acid: [H+] =α ×Sk-you =√CA×Sk-you⇒pH = – log [H+] = – log√CA

base [OH–] =α ×Pine=√HF×Pine⇒pOH = – log [OH–] = – log√HF

pH = 14 – pOH.

The converted mathematical formulas are given in the reference tables.

USING ACID-BASE REACTIONS IN QUALITATIVE ANALYSIS

1. Acids (HCl, H2SO4, 2H) and bases (NaOH or NH4OH) are used as group reagents of the acid-base classification, i.e. to distinguish one group of cations from others.

2. A 2M solution of HCl and H2SO4 is a group reagent of the first analytical group of anions. Used to prove their presence and for detection.

3. For detection of cations and anions

NH4+ + OH–⇔NH3↑+ H2O (pharmacopoeial)

characteristic smell

S2– + 2H+⇔H2S↑

rotten egg smell

Ca2+ + H2SO4⇒ISS (pharmacopoeial)

4. Many precipitates are colorless and detection is carried out in relation to acids and alkalis.

PbSO4↓+↓NaOH⇔Na2[Pb(OH)4] + Na2SO4

white solution

PbSO4↓+ H2SO4⇔Pb(HSO4)2

white solution

Ca SO4, BrSO4, BaSO4, white precipitates, insoluble in acids and alkalis.

4a. for dissolving sediments: Al(OH)3↓+3OH–⇒

Zn(OH)2 + 4NH4OH⇒

5. The dissociation of ampholytes as an acid or base is determined by the ratio of [H+] and [OH–], this allows the ion to be analyzed either as a cation or as an anion.

pH < 7 pH > 7

2OH– + Zn2+⇔Zn(OH)2⇔ZnO2 + 2H+

6. Acids and bases are used to create specific pH values in the environment.

7. Based on the pH value of the medium in the preliminary analysis, the presence of certain ions can be assumed.

a) Example: in a strongly acidic medium, anions of analytical group I cannot be present;

b) an acidic environment may cause the presence of hydrolyzable cations.

Quantitative analysis uses the acid-base titration method.

Lecture No. 8
Buffer solutions

Many reactions in solution proceed in the desired direction only at a certain concentration of H+ ions. Changing it in one direction or another from the corresponding optimal value leads to the emergence of new, often undesirable products. In this regard, maintaining a constant pH value throughout the entire reaction is often an important condition for its successful completion.

This is especially true for biochemical processes occurring in living organisms. Most of them are catalyzed by various enzymes or hormones, which exhibit their biological activity only in a strictly defined and fairly narrow range of pH values.

Solutions that can maintain a constant concentration of H+ ions when small amounts of a strong acid or alkali are added to them, as well as when diluted, are called**buffer solutions or buffer systems.**

The property of these solutions to maintain unchanged their inherent pH value under the above circumstances is otherwise called a buffer effect.

Buffer solutions, depending on their composition, are divided into 2 main types: acidic and basic.

Acidic buffer systems are usually formed by a weak inorganic or organic acid and a salt of the same acid with a strong base. For example:

1)	CH3COOH	+	CH3COONa	–	acetate buffer
	weak acid		acid salt		

2)	H2CO3(H2O + CO2)	+	NaHCO3	–	bicarbonate or bicarbonate buffer
	weak acid		acid salt		

From the point of view of the Bronsted-Lowry theory, an acid buffer system is an equilibrium mixture of a weak acid and its conjugate base. Moreover, the role of the conjugate base is played by the anions of weak acids formed during the dissociation of salts. In this regard, the composition of buffer solutions can be written differently:

1)	CH3COOH	/	CH3COO–	–	acetate buffer
	weak acid		conjugate base		

2)	H2CO3(H2O + CO2)	/	HCO3–	–	bicarbonate buffer
	weak acid		conjugate base		

An acid buffer system can also be formed by a mixture of two salts of a polybasic acid, corresponding to different stages of neutralization of this acid. In this case, the acidic residue of one of the salts (less substituted) plays the role of a weak acid, and the acidic residue of the second salt (more substituted) plays the role of its conjugate base.

Examples of such systems include:

1) carbonate buffer system, which is a mixture of acidic (NaHCO3) and intermediate (Na2CO3) salts of carbonic acid

HCO3–	/	CO32–
weak acid		conjugate base

2) phosphate buffer solutions

NaH2PO4 + Na2HPO4	(H2PO4–	/	HPO42–
	weak acid		conjugate base

Na2HPO4 + Na3PO4	(HPO42–	/	PO43–
	weak acid		conjugate base

It should be noted that not only mixtures, but also solutions of some individual salts (for example: sodium tetraborate (Na2B4O7), ammonium carbonate ((NH4)2CO3), etc.) also have buffer properties, which are explained by the strong hydrolysis of these salts and the resulting formation components required for buffering action:

(NH4)2CO3+HOH↔NH4HCO3+NH4OH

Basic buffer systems are formed by a weak inorganic or organic base and a salt of this base with a strong acid.For example:

1)	NH3 H2O(NH4OH)	+	NH4Cl	– ammonia buffer

	weak foundation		salt	
2)	C2H5–NH2	+	C2H5NH3Cl	– ethylamine buffer
	weak foundation		salt	

From the point of view of the Brønsted-Lowry theory, the main buffer system is also an equilibrium mixture of a weak acid and its conjugate base, only the role of an acid in this case is played by the cation formed during the dissociation of the salt:

1)	NH4+	/	NH3	– ammonia buffer
	weak acid		conjugate base	
2)	C2H5–NH3+	/	C2H5–NH2	– ethylamine buffer
	weak acid		conjugate base	

Solutions of many organic substances, whose molecules simultaneously contain functional groups exhibiting both weak acidic (COOH groups) and basic (NH2 groups) properties, also have a certain buffering effect. By their nature, these compounds are ampholytes. These include amino acids, proteins, peptides.

Thus, any acid-base buffer system is an equilibrium mixture consisting of a proton donor and acceptor.

In such a system containing a weak acid, a distinction is made between total, active and potential acidity:

1) total acidity corresponds to the maximum possible concentration of H+ ions in a given solution, if we theoretically assume that all acid molecules present in it will completely disintegrate into ions, and the hydrolysis of the existing salt can be ignored. Total acidity is numerically equal to the molar concentration of the chemical equivalent of the acid in the solution and is determined experimentally (for example, using the titrimetric method of analysis);

2) active acidity is equal to the concentration (or activity) of the contained “free” H+ ions (H3O+), formed as a result of the dissociation of a certain number of acid molecules;

3) potential acidity is determined by the totality of undissociated acid molecules present in the system.

Potential acidity can be calculated by subtracting active acidity from total acidity.

For example, for an acetate buffer, all these types of acidity can be roughly represented as follows:

CH3COOH	Δ	H+	+	CH3COO–
⌣		⌣		
potential acidity		active acidity		
⌣				
total acidity				

+By analogy with solutions of weak acids in solutions of weak bases (basic buffer systems), one can also distinguish between total, active and potential alkalinity or basicity.

Lecture No. 9

Equilibrium in complexation reactions

Structure of complex compounds. Equilibria in solutions of complex compounds. stability constant. Calculation of ionic equilibria in solutions. Types of complex compounds used in analytical chemistry, requirements for them (stability, solubility, color, etc.). Complex compounds of metals with inorganic and organic ligands. Functional-analytical, chromophore and auxochromic groups in organic reagents. The main types of compounds with organic reagents used in the analysis: intracomplex compounds (chelates), ionic associates. Stability of chelate compounds. Use of complex compounds with organic and inorganic ligands in analysis.

Complexometry is based on complex formation reactions. In the most general sense, under*complex (complex compound)*in chemistry we understand a complex particle consisting of constituent parts capable of autonomous existence. It is possible to note the main features that make it possible to distinguish complex compounds into a special class of chemical compounds:

- the ability of individual components to exist independently;

- complexity of the composition;

- partial dissociation into components in solution according to a heterolytic mechanism;

- presence of a positively charged central particle –*complexing agent*(usually a metal ion) bound to ligands;

- the presence of a certain stable spatial*geometry*arrangement of ligands around the complexing agent.
Examples:
Ligands (“toothed structures”) can be bidentate, monodentate, or polydentate. Dentity is the number of donor atoms of the ligand that form coordination bonds with the central atom.

Many monodentate inorganic and organic ligands are known, but their use in complexometry is hampered by the fact that the stepwise stability constants of the corresponding complexes differ little from each other. Therefore, as the amount of added ligand increases, the concentration of metal ions changes gradually and the titration curve does not have a jump.

Chelates (chelo-claw) are compounds that surround the central ion. The most important feature of chelates is their increased stability compared to similarly constructed non-cyclic complexes. That is why polydentate ligands and chelate complexes have found wide application in analytical chemistry.

The rate of complexation is of great importance in analytical chemistry. For example, during direct complexometric titration, the reaction of the ion being determined with the titrant must occur almost instantly, otherwise the indication of the end point of the titration is significantly difficult.

The stability of the complex is determined by both fundamental factors (the nature of the complexing agent and ligands) and external conditions (temperature, nature of the solvent, ionic strength, solution composition).

Trilon B is used in complexometry for the determination of metals in aqueous solutions. Direct titration can detect: Ba, Ca, K, In, Mg, St, Zn, Cd. By back titration method: Al,Bi,Co, Cr,Fe,Mn,Pt, Sc.

Trilon B is used for analytical determinations of water hardness.

$Mg(HCO_3)_2 \quad MgCO_3\downarrow + CO_2\uparrow + H_2O$

$Ca(HCO_3)_2 \quad CaCO_3\downarrow + CO_2\uparrow + H_2O$

Complexometry, as an analysis method, is used in the vast majority of enterprises where it is necessary to analyze the composition of slag, alloys, and various additives.

ecture No. 10

Complex compounds and double salts

When adding any cobalt(II) salt to a solution, 1-2 drops of cyanide solutionpotassiuma red-brown precipitate of cobalt cyanide is observed:

$$CoCl_2 + 2KCN \longrightarrow \downarrow Co(CN)_2 + 2KCl$$

When an excess of the precipitant is introduced, it dissolves to form brown potassium hexacyanocobaltate (II):

$$4KCN + Co(CN_2) \longrightarrow K_4[Co(CN)_6]$$

Its structure is similar.

Hexacyanocobaltate(II)potassiumeasily oxidized by chlorine, bromine, oxygen and other oxidizing agents to form yellow potassium hexacyanocobaltate (III), in whichcobalttrivalent:

$$4K_4[Co(CN)_6] + O_2 + 2H_2O \longrightarrow 4K_3[Co(CN)_6] + 4KOH$$

$K_3[Co(CN)_6]$ аналогичен по своему строению $K_3[Fe(CN)_6]$.

Using ordinary reagents, either cannot be detected in solution or. In solutions of these compounds there are (in addition to -ions) -ions, which differ in a number of characteristic properties that are completely different from the properties of simple cobalt and iron ions.

Simple ions of cobalt and iron can attach not only ions of opposite charge, but also neutral onesmolecules, for example, etc. When simple ions add ions of opposite charge, the initial charge of the simple ions changes. When neutral molecules are added, no change in charge is observed; for example, cobalt (III) ions form dark red ions with molecules:

$$Co^{+++} + 6NH_3 \longrightarrow [Co(NH_3)_6]^{+++}$$

Ions such as etc., in contrast to simple ions, are called complex ions, and the compounds they form are called complex compounds.

When writing formulas, complex ions are enclosed in square brackets.

Complex compounds are certain molecular compounds whose components combine to form positively or negatively charged complex ions that can exist both in a crystal and in solution (A. A. Grinberg). The theory of complex compounds was developed by A. Werner.

The founder of the Russian chemical school, which comprehensively studies complex compounds, is L. A. Chugaev.

In a complex compound, which is a molecular combination of four KCN molecules and onemolecules

$$4KCN + Fe(CN)_2 \longrightarrow K_4[Fe(CN)_6]$$

a negatively charged ion participates in the formation of crystals and exists in solutions of this substance.

In aqueous solutions, complex salts during the primaryelectrolytic dissociationact likestrong electrolytes, and the complex ions themselves dissociate weakly. For example, a complex compound dissociates in an aqueous solution, mainly according to the equation:

$$K_3[Fe(CN)_6] \rightleftharpoons 3K^+ + [Fe(CN)_6]^{---}.$$

This is explained by the fact that between the components of complex compounds belonging to the class of electrolytes, there isionic bond; In complex ions of this type, non-ionic bonds (covalent, electrovalent, coordination, hydrogen) exist between the central atom and its ligands (addends).

Thus, complex compounds differ sharply in their type of connection from simple salts.

In this case, iron (III) ions are part of the anion and cannot be detected, for example, by the action of ammonium thiocyanate. is a complex anirne that hardly dissociates in solution. Similarly, CN ions, being a component of a complex ion, cannot be detected by the formation of silver cyanide.

Complex ions in many cases give new, completely different characteristic reactions. An example is the formation of Turnboule blue during the interaction of ions:

$$3Fe^{++} + 2[Fe(CN)_6]^{---} \longrightarrow \underset{\text{осадок синего цвета}}{\downarrow Fe_3[Fe(CN)_6]_2}$$

However, sometimes the constituent parts of complex ions can still be detected using certain reagents. For example, , which is not destroyed by the action of , reacts with hydrogen sulfide, and silver sulfide precipitates:

$$2[Ag(CN)_2]^- + H_2S + 2H^+ \longrightarrow \downarrow Ag_2S + 4HCN$$

Complex compounds are divided into three main groups:

1) formed by the type of accession, for example:

$$2HCl + PtCl_4 \rightleftarrows H_2[PtCl_6]$$

2) formed by the type of implementation, for example:

$$ZnCl_2 + 6NH_3 \rightleftarrows [Zn(NH_3)_6]Cl_2$$

3) intracomplex (chelate) salts.

The first group includes halo-, cyano-, rhodano-, nitro-, oxygen-containing and other complex compounds.

A general method for obtaining addition-type complexes, or, as they are also called, acid complexes, is the action of an excess of the complexing reagent on the salts of the ionl bound into the complex:

$$Hg^{++} + 2I^- \longrightarrow \downarrow HgI_2$$
$$2KI + HgI_2 \longrightarrow K_2[HgI_4]$$

The second group includes ammonia and aqua complexes (hydrates).

In all cases of complex formation, the complexing agent is a cation. Such ions include mainly cations, etc. A common method for obtaining complexes formed by the insertion type is the action of ammonia or water on the salts of the ion bound into the complex.

During the formation of a complex, the central ion (complexing agent) can attach a different number of atoms, ions, or molecules (ligands, or addends). For example, in a complex: the central ion is a complexing agent and is a ligand. The number of ligands attached to the central ion depends on the individual properties of the complexing agent and the ligands themselves. The highest number of atoms, ions or molecules that a complexing agent can bind into a complex is called the maximum coordination number of that complexing agent. Most complex ions encountered in analyticalchemistry, has coordination numbers equal to 4, 6 and 2. The same ion in different compounds can have different coordination numbers.

The ligands grouped around the complexing agent are located symmetrically. Occupying a planar or spatial position, they form geometric figures (triangles, squares, tetrahedrons, octahedra, etc.), at the corners of which ligands are located, and in the center is a complexing agent.

The charge of a complex ion is expressed by the algebraic sum of positive andnegative chargesthe central ion and the ions (ligands) coordinated around it.

Lecture No. 11

Redox reactions

Redox reactions always consist of 2 processes - reduction, that is, the addition of electrons:

Ox1 + nē ↔ Red1

and oxidation, that is, the release of electrons:

Red2 – nē ↔ Ox2,

where Ox1 and Ox2 are the oxidized forms of the first and second substances, and Red1 and Red2 are the reduced forms of these substances. The oxidized and reduced forms of the substance form a conjugate pair.

The half-reactions of oxidation and reduction are not feasible without the other. In reality, a total redox reaction always occurs:

Ox1 + Red2 → Red1 + Ox2.

In this case, the number of given and received electrons is always the same.

To assess the ability of substances to donate or gain electrons, the equilibrium constant is used

$$K^0 = \frac{a_{Ox_2} \cdot a_{\mathrm{Re}\,d_1}}{a_{Ox_1} \cdot a_{\mathrm{Re}\,d_2}}.$$

Unlike other types of reactions, oxidation and reduction half-reactions can be separated spatially because an electric current is generated when electrons are transferred. Therefore, the energy of the redox reaction can be converted into electrical energy.

The possibility of spatial separation of oxidation and reduction half-reactions makes it possible to quantitatively describe redox reactions not only using the equilibrium constant, but also by the magnitude of the electromotive force of the galvanic cell, which is calculated as the difference in the electrode potentials of the reduction and oxidation processes.

The electrode potential of the half-reaction is calculated using the Nernst equation

$$E = ЭДС - E^0_{H_2} = E^0 + \frac{RT}{nF} \ln \frac{a_{Ox}}{a_{\mathrm{Re}\,d}},$$

If the half-reaction involves solids or gases whose partial pressure is equal to 1, then their activities are also equal to 1 and they are excluded from the equation. At T = 298 K and the transition from the natural logarithm to the decimal one, the multiplier in front of the second term will be equal to 0.059/n, then the equation will take the form:

$$E = E^0 + \frac{0{,}059}{n} \lg \frac{a_{Ox}}{a_{\mathrm{Re}\,d}}.$$

For example, for the half-reaction MnO4- + 8H+ + 5ē → Mn2+ + 4H2O

$$E = E^0_{MnO_4^- / Mn^{2+}} + \frac{0{,}059}{5} \lg \frac{a_{MnO_4^-} \cdot a^8_{H^+}}{a_{Mn^{2+}}}.$$

We do not write the activity value of water molecules into the equation, since the activity of water in an aqueous solution is a constant value.

Because $a = \gamma \cdot C$, then the equation can be rewritten by replacing activities with concentrations

$$E = E^0 + \frac{0{,}059}{n} \lg \frac{\gamma_{Ox}}{\gamma_{\mathrm{Re}\,d}} + \frac{0{,}059}{n} \lg \frac{C_{Ox}}{C_{\mathrm{Re}\,d}} = E^{0'} + \frac{0{,}059}{n} \lg \frac{C_{Ox}}{C_{\mathrm{Re}\,d}},$$

Where $E^{0'}$ - formal electrode potential.

If the total concentrations of oxidized and reduced forms are equal to 1 M, then the formal potential is equal to the equilibrium potential.

The formal electrode potential, in contrast to the standard one, depends on the ionic strength of the solution, the depth of competing side reactions, and the concentrations of particles that are not oxidized or reduced, but take part in the reaction (for example, hydrogen ions).

Measuring the formal electrode potential under various conditions makes it possible to determine the instability constants of complexes, solubility products, and other constants of competing reactions.

In the absence of competing reactions, measuring the formal electrode potential allows us to accurately determine the activity coefficients of electrolytes.

2. The influence of various factors on the value of the electrode potential

a) influence of solution pH

If hydrogen ions take part in the redox reaction, then their concentration is included in the expression under the logarithm in the Nernst equation. For example, for the reaction MnO4- + 8H+ + 5ē → Mn2+ + 4H2O

$$E = E^0_{MnO_4^-/Mn^{2+}} + \frac{0{,}059}{5}\lg\frac{[MnO_4^-]\cdot[H^+]^8}{[Mn^{2+}]} = E^0_{MnO_4^-/Mn^{2+}} + \frac{0{,}059}{5}\lg[H^+]^8 + \frac{0{,}059}{5}\lg\frac{[MnO_4^-]}{[Mn^{2+}]}.$$

If one of the forms - oxidized or reduced - is protonated (that is, it adds a hydrogen ion), this must also be taken into account when calculating the electrode potential.

Let's look at an example where the oxidized form is protonated:

Ox- + H+ ↔ HOx,

This reaction is characterized by the equilibrium constant $K_a = \frac{[H^+]\cdot[Ox^-]}{[HOx]}$. From this equation we express the concentration of the oxidized form: $[Ox^-] = K_a\frac{[HOx]}{[H^+]}$, we substitute this expression into the Nernst equation:

$$E_{HOx/\mathrm{Re}d} = E^0_{Ox/\mathrm{Re}d} + \frac{0{,}059}{n}\lg\frac{K_a\cdot[HOx]}{[H^+]\cdot[\mathrm{Re}d]} = E^0_{Ox/\mathrm{Re}d} + \frac{0{,}059}{n}\lg K_a + \frac{0{,}059}{n}\lg\frac{1}{[H^+]} + \frac{0{,}059}{n}\lg\frac{[HOx]}{\mathrm{Re}d}$$

.

At concentrations of all components equal to 1, we obtain

$E^0_{HOx/\mathrm{Re}d} = E^0_{Ox/\mathrm{Re}d} + \frac{0{,}059}{n}\lg K_a = E^0_{Ox/\mathrm{Re}d} - \frac{0{,}059}{n}pK_a$ - standard electrode potential of the half-reaction taking into account the protonation of the oxidized form.

b) the influence of complex formation of one of the forms on the value of the electrode potential

Let the oxidized form form a complex compound

Ox + mL ↔ OxLm

and the instability constant of this compound is equal to $K_H = \frac{[Ox]\cdot[L]^m}{[OxL_m]}$.

From this equation we express the concentration of the oxidized form:

$$[Ox] = K_H \frac{[OxL_m]}{[L]^m}.$$

Then the half-reaction with the oxidized form will have the form

OxLm + nē ↔ Red + mL

and the ligand concentration must be included in the Nernst equation:

$$E_{OxL_m/\mathrm{Re}\,d} = E^0_{OxL_m/\mathrm{Re}\,d} + \frac{0{,}059}{n}\lg\frac{[OxL_m]}{[\mathrm{Re}\,d]\cdot[L]^m} = E^0_{OxL_m} + \frac{0{,}059}{n}\lg\frac{1}{[L]^m} + \frac{0{,}059}{n}\lg\frac{[OxL_m]}{[\mathrm{Re}\,d]}.$$

If the concentrations of the oxidized complexed form and the reduced form are equal to 1 mol/dm3, then the formal electrode potential is equal to

$$E^{0\,\prime}_{OxL_m/\mathrm{Re}\,d} = E^0_{OxL_m/\mathrm{Re}\,d} + \frac{0{,}059}{n}\lg\frac{1}{[L]^m} = E^0_{OxL_m/\mathrm{Re}\,d} - \frac{0{,}059\cdot m}{n}\lg[L].$$

Taking into account the expression for the instability constant of the OxLm complex, the expression for the electrode potential takes the form

$$E_{OxL_m/\mathrm{Re}\,d} = E^0_{Ox/\mathrm{Re}\,d} + \frac{0{,}059}{n}\lg\frac{[Ox]}{[\mathrm{Re}\,d]} = E^0_{Ox/\mathrm{Re}\,d} + \frac{0{,}059}{n}\lg\frac{K_H\cdot[OxL_m]}{[L]^m\cdot[\mathrm{Re}\,d]} = E^0_{Ox/\mathrm{Re}\,d} + \frac{0{,}059}{n}\lg K_H +$$

$$+\frac{0{,}059}{n}\lg\frac{1}{[L]^m} + \frac{0{,}059}{n}\lg\frac{[OxL_m]}{[\mathrm{Re}\,d]}.$$

If the concentrations of the ligand, oxidized complexed and reduced forms are equal to 1 mol/dm3, then the standard electrode potential under the conditions of complexation of the oxidized form will be equal to

$$E^0_{OxL_m/\mathrm{Re}\,d} = E^0_{Ox/\mathrm{Re}\,d} + \frac{0{,}059}{n}\lg K_H = E^0_{Ox/\mathrm{Re}\,d} - \frac{0{,}059}{n}pK_H.$$

Similarly, if the reduced form takes part in the complexation reaction, the electrode potential of the half-reaction will be equal to

$$E_{Ox/\mathrm{Re}\,dL_m} = E^0_{Ox/\mathrm{Re}\,d} + \frac{0{,}059}{n}\lg\frac{1}{K_H} + \frac{0{,}059}{n}\lg[L^m] + \frac{0{,}059}{n}\lg\frac{[Ox]}{[\mathrm{Re}\,dL_m]}.$$

Thus, binding into a complex compound the oxidized form lowers and the reduced form increases the standard electrode potential, which is widely used for the separate determination of several components that have similar values of standard electrode potentials.

c) the influence of the formation of a poorly soluble compound on the value of the electrode potential

Sometimes one or both forms, oxidized and reduced, are poorly soluble compounds. In this case, it is necessary to take into account the value of the solubility product of this compound.

Let's consider the case if the insoluble compound is the oxidized form OxA↓ + nē ↔ Red + A.

In this case, the equilibrium in the reaction Ox + A ↔ OxA↓ is described by the constant PR = [Ox]·[A].

After transformations similar to those we carried out in parts a) and b), we obtain an expression for the electrode potential

$$E_{OxA/\mathrm{Re}d} = E^0_{Ox/red} + \frac{0{,}059}{n}\lg ИР + \frac{0{,}059}{n}\lg\frac{1}{[\mathrm{Re}d]\cdot[A]},$$

where the first two terms are the standard electrode potential of the half-reaction with the insoluble oxidized form. The concentration of a poorly soluble compound is assumed to be equal to unity.

Similarly, if the reduced form is insoluble, then

$$E_{Ox/\mathrm{Re}dA} = E^0_{Ox/\mathrm{Re}d} + \frac{0{,}059}{n}\lg\frac{1}{ИР} + \frac{0{,}059}{n}\lg[Ox]\cdot[A],$$

where the first two terms are the standard electrode potential of the half-reaction with the insoluble reduced form.

If both forms: reduced and oxidized are poorly soluble compounds, then the potential of the system depends only on the concentration of precipitant ions. For example, in the reaction AgCl↓ + nē ↔ Ag↓ + Cl- the electrode potential will be equal to $E_{AgCl/Ag} = E^0_{Ag^+/Ag^0} + \frac{0{,}059}{1}\lg\frac{1}{[Cl]} = E^0_{Ag^+/Ag^0} - 0{,}059\lg[Cl^-]$. This is the basis for the use of a silver chloride electrode as a reference electrode.

The formation of a poorly soluble compound with the participation of the oxidized form reduces, and with the participation of the reduced form, it increases the standard electrode potential.

3. Redox titration curves

Since the concentrations of the oxidized and reduced forms of the analyte are related, logarithmic curves are constructed in redox titration.

Redox titration curves are plotted in the coordinates “formal electrode potential” - “degree of titration.”

A titrant can be both an oxidizing agent and a reducing agent (depending on the nature of the substance being determined). After adding each portion of titrant, equilibrium is established in the solution, and the potential of the analyte system becomes equal to the potential of the titrant system. Therefore, it makes no difference which of the two systems is used to calculate the equilibrium potential at a given point in the titration. Usually, up to the equivalence point, the potential is calculated using the system of the analyte, and after the equivalence point, using the titrant system.

If the substance being determined is a reducing agent, then up to the point of equivalence

$$E = E^0_{Ox_1/\mathrm{Re}d_1} + \frac{0{,}059}{n_1}\lg\frac{f}{1-f},$$

since the oxidized form of the analyte is as much as we titrated, and the reduced form is as much as remains to be titrated. And after the equivalence point

$$E = E_{Ox_2/\mathrm{Re}d_2} + \frac{0{,}059}{n_2}\lg(f-1),$$

since the oxidized form of the titrant is as much as the excess titrant we added after reaching the equivalence point, and the reduced form of the titrant is as much as it was formed at the equivalence point.

If the substance being determined is an oxidizing agent, then up to the equivalence point the potential of the system is calculated using the equation

$$E = E^0_{Ox_1/\mathrm{Re}\,d_1} + \frac{0{,}059}{n_1}\lg\frac{1-f}{f}$$

and after the equivalence point $E = E^0_{Ox_2/\mathrm{Re}\,d_2} + \frac{0{,}059}{n_2}\lg\frac{1}{f-1}$.

At the point of equivalence, the concentrations of conjugate forms of the half-reaction of the analyte and the half-reaction of the titrant are negligible, therefore we add the equations of both half-reactions, having previously multiplied each to equalize the number of electrons given and received:

$$(n_1+n_2)\cdot E_{T.ЭКВ} = n_1\cdot E_1^0 + n_2\cdot E_2^0 + 0{,}059\lg\frac{[Ox_1]\cdot[Ox_2]}{[\mathrm{Re}\,d_1]\cdot[\mathrm{Re}\,d_2]}.$$

At the equivalence point, the reactants are in a stoichiometric ratio, that is $\frac{[Ox_1]}{[\mathrm{Re}\,d_2]} = \frac{n_2}{n_1}$ And $\frac{[Ox_2]}{[\mathrm{Re}\,d_1]} = \frac{n_1}{n_2}$, from which it follows that under the logarithm sign the expression is equal to 1. Then the electrode potential at the equivalence point is calculated using the equation

$$E_{T.ЭКВ} = \frac{n_1\cdot E_1^0 + n_2\cdot E_2^0}{n_1+n_2}.$$

It should be noted that if polynuclear particles participate in the reaction, then the equation has a more complex form.

Taking into account the influence of side reactions, if a reduced form of the analyte is involved in them, then the potential increases, and the titration jump, accordingly, decreases. if the oxidized form of the analyte is involved in the side reaction, then the potential decreases, the left branch of the curve is lower, and the titration jump increases.

4. Methods for detecting the titration end point

To detect the titration end point in redox reactions, use:

1) disappearance or appearance of color of the titrant or analyte (for example, in permanganatometry);

2) specific and redox indicators (starch in iodometry, diphenylamine in dichromatometry);

3) instrumental methods (potentiometric titration).

Specific indicators are substances that form an intensely colored compound with one of the components of the redox system. Thus, starch gives the solution an intense blue color in the presence of iodine molecules in the solution, thiocyanate ion colors the solution bright red in the presence of ferric ions.

Redox indicators (redox indicators) are organic compounds capable of oxidation or reduction, and their oxidized and reduced forms have different colors. Complex compounds with metal ions, which change their color depending on the degree of oxidation of the metal ion, are also

used as redox indicators. For example, ferroin forms a red complex with divalent iron, and a blue complex with trivalent iron.

Often, before starting redox titration, preliminary oxidation or reduction of the components of the analyzed solution is carried out, since both oxidized and reduced forms of the analyte can be present in the sample.

5.The most common types of redox titrations

a) Permanganatometry

A KMnO4 solution is used as a titrant. This is a secondary standard because the compound is unstable and decomposes in light, especially in the presence of even small amounts of manganese dioxide. Standardization is carried out by titrating an accurate portion of sodium oxalate, ammonium oxalate or an aliquot of a standard solution of Mohr's salt (a mixture of ammonium and ferrous sulfates). The equivalence point is determined by the appearance of a crimson color of the solution when the first excess drops of titrant are added.

$MnO_4^- + 8H^+ + 5\bar{e} \rightarrow Mn^{2+} + 4H_2O$.

Permanganatometry is used to determine iron in ores, minerals, alloys, to determine nitrites (by back titration method), to determine the total oxidability of water or soil.

b) Dichromatometry

A solution of $K_2Cr_2O_7$ or the same sodium salt is used as a titrant. This is the primary standard. The method is used to determine iron, organic components of water or soil. The indicator is diphenylamine.

$Cr_2O_7^{2-} + 14H^+ + 6\bar{e} \rightarrow 2Cr^{3+} + 7H_2O$.

c) Bromatometry

Potassium bromate is used as a titrant. The following reaction occurs:

$BrO_3^- + 6H^+ + 6\bar{e} \rightarrow Br^- + 3H_2O$.

When the first extra drop of titrant is added, the reaction begins

$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$.

Organic dyes (methyl orange, neutral red) are used as an indicator, which react with the bromine released, as a result the color of the solution disappears. Potassium bromate is the primary standard. The method is used to determine antimony, tin, arsenic, iron, and organic compounds.

d) Yodimetry, iodometry

The reaction $I_2 + 2\bar{e} \leftrightarrow 2I^-$ is reversible, $E^0 = 0.62$ V. Molecular iodine is poorly soluble in water, but in the presence of iodide ions it forms complexes that are highly soluble in water. In this case, the potential of the system decreases: $I_3^- + 2\bar{e} \leftrightarrow 3I^-$, $E^0 = 0.54$ V. The system serves both to determine reducing agents and oxidizing agents. In the direct determination of reducing agents (iodimetry), the titrant is a solution of iodine to potassium iodide. The solution is stored in a dark container, standardization is carried out using a sample of As_2O_3. The method is used to determine arsenic compounds.

It is impossible to determine oxidizing agents by direct reaction, since the reaction proceeds very slowly. In addition, KI solutions are unstable. Substitution titration is used, that is, an excess potassium iodide solution is added to the oxidizing agent, and the released iodine is titrated with a standard sodium thiosulfate solution. The method is called iodometry. The indicator is starch. The indicator is added at the very end of the titration, when very little iodine remains in the solution (straw-yellow color of the solution). This is explained by the formation of very strong complexes of iodine with starch.

Sodium thiosulfate solution is a secondary standard because it is easily oxidized by atmospheric oxygen. Standardization is carried out using a standard solution of potassium dichromate. First, a precisely known excess of potassium iodide solution is added to an aliquot of the standard solution, and some time after completion of the reaction, the released iodine is titrated with a thiosulfate solution.

Iodometry is used to determine large quantities of copper (in alloys, ores).

Lecture No. 12

Oxidizing agents and reducing agents used in the analysis

Solutions of substances that have either pronounced oxidizing or reducing properties are used as titrants in redox titration methods. Redox titration is based on the interaction of the analyte with a standard (working) solution of an oxidizing or reducing agent. As in other titrimetric methods of analysis, the quantitative determination of the analyzed component is carried out by accurately measuring the volumes of solutions that enter into a chemical reaction with each other. Redox titration methods are usually classified according to the names of the titrants used: – permanganatometry – a method that uses oxidation reactions with potassium permanganate KMnO4; – dichromatometry – a method that uses oxidation reactions with potassium dichromate K2Cr2O7; – iodometry – a method that uses oxidation reactions with iodine or reduction with iodide ions; – bromatometry – a method that uses oxidation reactions with potassium bromate KBrO3; – cerimetry – a method that uses oxidation reactions with cerium (IV) sulfate Ce(SO4)2; – vanadatometry – a method that uses the oxidation reactions of ammonium vanadate NH4VO3; – titanometry – a method that uses reduction reactions with titanium (III) salts; – chromometry is a method that uses reduction reactions with chromium (II) compounds. Before discussing the features of the most common variants of these methods, we will formulate the most general requirements for titrants. 1. The titrant must be a strong enough oxidizing or reducing agent to react almost completely with the titrated substance. This requirement can be quantitatively characterized by the values of standard electrode potentials of half-reactions. The latter should differ by at least 0.15–0.20 V from the standard half-reaction potentials of the titrated components, in a more positive direction for oxidizing agents and in a more negative direction for reducing agents. 2. The titrant should not be such a strong oxidizing or reducing agent that it reacts with other components of the solution besides the one being determined. In other words, in all cases, the occurrence of the main redox reaction should not be accompanied by side processes. 3. The titrant with the analyte must react quickly. Some reactions may be

thermodynamically allowed, but kinetically inhibited, that is, they will not proceed at the required rate. This is often observed in cases where the reaction involves the transfer of several electrons or the formation (or breaking) of chemical bonds. 4. The method for detecting the titration endpoint (TEP) must be simple and reproducible. For this purpose, visual methods and various instrumental methods are used. These guidelines discuss only visual methods of fixing the CTT. Redox titration also places specific requirements on the substance being determined: it must react sufficiently completely and quickly with the titrant. In practice, the sample component (ion) being determined is often in an oxidation state that is nonreactive with respect to the titrant, or is a mixture of the same substance in which the atoms are in several oxidation states. In these cases, the sample solution must be treated with an auxiliary reagent - an oxidizing or reducing agent - in order to convert the element being determined to the appropriate oxidation state before the final titration. These oxidizing or reducing reagents must quickly quantitatively convert the element being determined to the required oxidation state. In addition, it is necessary to be able to conveniently separate and remove excess reagent (oxidizing or reducing agent) 6 from the sample solution, otherwise it will further react with the titrant. Finally, the reagent must be selective. Since these guidelines are devoted to the problems of practical application of redox reactions for titrimetry purposes, they will not consider general issues of equilibrium of redox reactions, calculations using the values of standard and real redox potentials, as well as calculations of titration curves.

Lecture No. 13

Precipitation reactions

Sequence of operations used in chemical analysis.

Chemical analysis of a substance consists of a number of general sequential operations: sampling of the substance to be analyzed; establishing the qualitative composition of a substance; choosing methods for extraction, concentration, separation and determination of elements and their compounds, i.e. choosing the most appropriate method of analysis; preparing a solution for analysis; determination by the chosen method of the content of certain components in the analyzed substance, etc. Sometimes, in addition to the indicated operations, others are used, and in some cases there is no need to perform all of the listed operations.

To successfully analyze any complex substance that is a mixture of differentchemical compounds, it is often necessary to extract and separatechemical elementsor groups of elements that make up a given analyte.

For this purpose, use:

1. Methods for the precipitation of poorly soluble sediments, based on the chemical interaction of the components of the substance under study with the corresponding reagents.

2. Electrochemical separation methods based on the isolation of metals or some sting-soluble compounds[1] etc.) constantelectric shock, playing the role of a kind of precipitant.

Methods for transferring (extracting) the analyte into a liquid phase that is immiscible with water, based on the use of organic solvents in which this component is dissolved.

4. Distillation methods based on the formation of volatile compounds.

5. Methods of chromatographic separation, etc.

These methods are discussed in more detail in quantitative analysis.

One of the most important operations of chemical analysis is the separation of precipitation from solutions. In chemical analysis, exchange reactions accompanied by the formation of precipitation are widely used.

The process of separating a solid phase from a solution - sediment - is called precipitation.

Crystalline and amorphous sediments. In appearance, sediments can be very diverse: curdled, crystalline, granular, gelatinous, flaky, gelatinous, etc. However, the classification of sediments according to their appearance is unscientific and is random in nature, since the same substance, depending on the conditions of deposition can form various types of precipitation.

All sediments are divided according to their structure into two types: crystalline and amorphous.

The crystalline structure of precipitation differs externally from the amorphous one in that each crystalline compound precipitates in a certain inherent crystalline form, usually clearly visible under a microscope. The shape of large crystals is clearly visible even to the naked eye. When crystals are crushed, the fragments retain the same structure.

The internal structure of crystals is characterized by the fact thatmoleculesor the atoms of a given compound are arranged in a certain order and form a so-called crystal lattice. Structurecrystal latticeinvestigated using X-ray diffraction analysis.

Crystalline precipitates settle relatively quickly during their formation and are easily separated by filtration.

Sediments of an amorphous structure do not reveal particles of a certain shape under a microscope, since with the amorphous structure of the substancemoleculesthey are arranged randomly and do not form a crystal lattice.

Amorphous sediments are loose, flaky, gelatinous, slowly settling masses that are difficult to separate and wash.

Application of precipitation reactions in chemical analysis. A number of operations are carried out using precipitation reactions.

1. The presence of many individual substances in the test solution is detected by the formation of precipitation, characterized by a certain color or structure, solubility in acids, alkalis and other solvents.

For example, it can be detected by the formation of the corresponding characteristic deposits: a dark blue precipitate of Prussian blue, a white crystalline precipitate of sulfatebariumor yellow crystalline precipitate of barium chromate, white amorphous precipitate of silver chloride, chocolate brown precipitate of silver arsenate.

2. Cations and anions are separated from each other; remove substances that interfere with the analysis from the analyzed solutions (co-precipitates with open ions, oxidizing and reducing agents, complexing and masking substances, etc.).

3. Compounds of the elements being determined are isolated from the mixture and concentrated from highly dilute solutions by coprecipitating them with inorganic and organic co-precipitants.

4. Quantitatively determine the individual components of the analyzed mixtures by weighing the separated sediments on a sensitive analytical balance after their appropriate processing (see book 2, section “Weight analysis”) or by measuring the volume of a reagent solution of a precisely known concentration, consumed for the precipitation reaction of a given, quantitatively determined substances (see book 2, section “Volume analysis”).

The precipitates released should, if possible, have extremely low solubility. Therefore, precipitation must be carried out under certain conditions that ensure the least solubility of the substance being deposited.

Saturated, unsaturated and supersaturated solutions. A solution containing the maximum amount of a substance that can dissolve in a given amount of solvent at a certain temperature to form a stable solution is called saturated. When new quantities of a given substance are added to such a solution, the substance no longer dissolves,solution concentrationdoes not change; the solid and liquid phases are in equilibrium.

Any solution containing less solute than a saturated solution is an unsaturated solution. When additional quantities of this substance are added to it, its dissolution continues and the concentration of the solution increases.

Solutions containing more solute than its normal solubility at a given temperature are called supersaturated. When crystals of this substance (seed) are introduced into a supersaturated solution or the flask with this solution is shaken, the excess solute immediately crystallizes and falls out of solution.

Solutions whose concentration is numerically close to the concentration of a saturated solution of a given substance are concentrated, and solutions that differ greatly in composition from saturated solutions are diluted. Extremely dilute solutions are solutions that contain extremely little solute.

Lecture No. 14

Fractional and systematic deposition

*Systematic*analysis is a complete analysis of the object under study, carried out by dividing the original analytical system into several subsystems (groups) in a certain sequence. Analytical groups are divided into different phases.

Analysis of a selected group of substances consists of sequentially carrying out separation reactions until only components remain in one phase that can be unambiguously identified by characteristic specific reactions with selective reagents.

The separation of substances into groups is carried out by the action of group reagents. Groups of ions are divided into subgroups, and then individual ions within the subgroup are separated and detected using characteristic reactions.

Various methods are used to separate ions into groups:

1) precipitation of ions in the form of poorly soluble compounds;
2) reduction of ions by metals in accordance with the RH potentials;
3) selective adsorption of ions.

Fractional analysis is based on the use of reactions that can be used to detect the desired ions in any sequence in individual portions of the original solution. The reactions used in this method are called fractional reactions. The founder of this trend in our country is N.A. Tanaev. According to his definition, fractional reactions are those by which one can separate an ion from other ions that are in solution with it.

Detection of a substance is carried out after creating conditions under which the influence of interfering ions is eliminated. Thanks to this, a large number of separations are not required and it takes 1-10 minutes to detect one component.

Comparison of operations of systematic and fractional methods

qualitative analysis

Table 6

Operation	***Systematic analysis***	Fractional analysis
Separation	The number of divisions is usually large	No separation of operations required
Centrifugation	With every division	Usually excluded
Washing the sediment	With each centrifugation	Usually excluded
Evaporation, calcination	Necessary in some cases	Necessary in some cases

Cation analysis is performed by both systematic and fractional analysis. Analysis of anions - only by fractional analysis.

Fractional methods for detecting some cations

1. Detection of NH_4^+ in the presence of other cations.

When heated, alkalis decompose ammonium salts, releasing ammonia:

$NH_4^+ + OH^- \rightarrow NH_3\uparrow + H_2O$

Smell, blue wetness

litmus test

2. Detection of Pb^{2+}.

$Pb^{2+} + 2I^- \rightarrow PbI_2\downarrow$

yellow precipitate

The precipitate is dissolved by boiling in a solution of acetic acid. When the solution is cooled, golden PbI_2 crystals fall out of it.

3. Detection of Hg_2^{2+}.

$Hg_2^{2+} + 2Cl^- \rightarrow Hg_2Cl_2\downarrow$

white precipitate

$Hg_2Cl_2 + 2NH_4OH \rightarrow [NH_2Hg_2]Cl + NH_4Cl + 2H_2O$

chloride
dimercourt
ammonium

$[NH_2Hg_2]Cl \rightarrow Hg\downarrow + [NH_2Hg]Cl$

mercury chloride
ammonium

4. Detection of Mn^{2+}

$2MnCl_2 + 5NaBiO_3 + 16HNO_3 \rightarrow 2HmnO_4 + 5Bi(NO_3)_3 + 4NaCl + 7H_2O + NaNO_3$

pink

coloring

5. Detection of Hg2+ (droplet reaction).

A drop of potassium iodide solution is applied to the filter paper. The test solution is drawn into the capillary and the tip of the capillary is pressed for 5-10 seconds to the center of the spot.

$Hg^{2+} + 2I^- \rightarrow HgI_2\downarrow$
orange-red

6. Detection of Fe2+ with red blood salt $K_3[Fe(CN)_6]$

$3Fe^{2+} + 2[Fe(CN)_6]^{3-} \rightarrow Fe_3[Fe(CN)_6]_2\downarrow$
intense blue precipitate

7. Detection of Fe3+ with yellow blood salt $K_4[Fe(CN)_6]$

$4Fe^{3+} + 3[Fe(CN)_6]^{4-} \rightarrow Fe_4[Fe(CN)_6]_3\downarrow$
pH < 3 (HCl) intense blue precipitate

Lecture No. 15
Quantitative Analysis

Quantitative Analysisis intended to establish the quantitative composition of components in the analyzed sample. It is preceded by a qualitative analysis, which establishes which components (elements, ions, molecules) are present in the analyzed sample.

There are three types of quantitative analysis: complete, partial, general. With a complete quantitative analysis, the full quantitative composition of all components present in the analyzed sample is established. For example, for a complete quantitative blood test, it is necessary to determine the content of 12 components: sodium, potassium, calcium, glucose, bilirubin, etc. A complete analysis requires a lot of time and labor.

When performing a partial analysis, the content of only the

these components. General analysis determines the content of each element in the analyzed sample, regardless of what compounds they are included in. This type of analysis is usually called elemental analysis.

CLASSIFICATION OF QUANTITATIVE ANALYSIS METHODS

Quantitative analysis methods can be divided into three large groups: chemical, physical, physicochemical.

Chemical methods are based on the use of quantitative chemical reactions of different types: exchange, precipitation, redox and complexation reactions. Chemical methods include gravimetric and titrimetric (volumetric) methods of analysis.

Gravimetric methodanalysis is based on measuring the mass of the determined component after its isolation in the form of a gravimetric form. The method is characterized by high accuracy, but is time-consuming and labor-intensive. In pharmaceutical analysis, it is mainly used to determine the moisture and ash content of drugs.

The titrimetric method of analysis is based on the introduction of a precisely measured volume of a solution of known concentration - titrant - into a precisely measured volume of a solution of the analyte. The titrant is introduced until the analyte reacts completely with it. This point is called the end point of the titration and is established using special chemical indicators or instrumental methods. Among chemical methods of quantitative analysis, this is the most common method.

Chemical methods of analysis, although they are currently the main ones in chemical laboratories, in many cases do not meet the increased requirements for analysis, such as high sensitivity, rapidity, selectivity, automation, etc. Instrumental methods of analysis, which can be divided into three, do not have these shortcomings large groups: optical, electrochemical, chromatographic.

Lecture No. 16

Gravimetric analysis

The gravimetric method is based on the accurate measurement of the mass of a substance of known composition, chemically related to the component being determined and isolated as a compound or as a simple substance. The classic name of the method is weight analysis. Gravimetric analysis is based on the law of conservation of mass of a substance during chemical transformations and is the most accurate of the chemical methods of analysis: the detection limit is 0.10%; accuracy (relative method error) ±0.2%.

In gravimetric analysis, methods of precipitation, distillation (direct and indirect), isolation, thermogravimetry, and electrogravimetry are used.

In the precipitation method, the component being determined enters into a chemical reaction with the reagent, forming a slightly soluble compound. After a series of analytical operations (Scheme 1.1), a solid sediment of known composition is weighed and the necessary calculations are carried out.

Sequence of analytical operations in the gravimetric sedimentation method

1. Calculation of the mass of a sample of the analyzed substance and its weighing

2. Dissolution of the sample

3. Creation of deposition conditions

4. Precipitation (obtaining a precipitated form)

5.Separation of sediment by filtration

6. Washing the sediment

7. Obtaining a gravimetric form (drying, calcination to constant weight)

8. Gravimetric mold weighing

9 . Calculation of analysis results

Distillation methods can be direct and indirect. In the direct distillation method, the component to be determined is isolated from the sample in the form of a gaseous product, captured, and then its mass is determined. In indirect distillation methods, the mass of the gaseous product is determined by the difference in mass of the analyzed component before and after heat treatment. In the practice of pharmaceutical analysis, this method is widely used to determine the moisture content of drugs and plant materials. For some drugs, determination of mass loss Δm during drying (drying temperature tdry) is one of the mandatory pharmacopoeial tests, for example: analgin - tdry = 100...105˚C, Δm < 5.5%; pyridoxine hydrochloride (vitamin B6) - tdush = 100...105 ˚s, Δm < 0.5%; paracetamol - tdry = 100...105 ˚, Δm< 0.5%, etc.

Thermogravimetric analysis records the change in the mass of a substance during the heating process, which makes it possible to judge the transformations taking place and determine the composition of the intermediate products formed. Thermogravimetric analysis is carried out using derivatograph instruments. During the experiment, the change in the mass of the analyzed sample (ordinate axis) is recorded depending on time or temperature (abscissa axis) and is presented in the form of a thermogravimetric curve - a thermogravigram. Thermogravimetry is widely used to study changes in the composition of a substance and to select conditions for drying or calcination of sediments.

Electrogravimetric analysis is based on the electrolytic separation of metals and weighing of the deposit obtained on the electrode. The main physical condition for the electrolytic separation of metals is a certain voltage at which some metals are deposited and other metals are not precipitated.

In analytical practice, gravity is most widely used.

metric deposition method, which will be discussed in more detail.

MECHANISM OF SEDIMENT FORMATION AND SEDIMENTATION CONDITIONS

The formation of a precipitate occurs when the product of the concentrations of the ions included in its composition exceeds the value of the product of solubility PR(KA) of the poorly soluble electrolyte:

$K+ + A^- \leftrightarrow KA$; $[K+][A^-] > PR(KA)$,

i.e., when local (relative) supersaturation of the solution occurs, which is calculated using the formula:

(Q - S)/S,

where Q is the concentration of the dissolved substance at any point in time, mol/cm3; S is the solubility of the substance at the moment of equilibrium, mol/cm3. In this place, the embryo of the future crystal appears (nucleation process). This requires a certain time, called an induction period. With further addition of the precipitant, the process of crystal growth becomes more likely, rather than the further formation of crystallization centers, which combine into larger aggregates consisting of tens and hundreds of molecules (aggregation process). At the same time, the particle size increases, and larger aggregates precipitate under the influence of gravity. At this stage, the individual particles, being dipoles, are oriented with respect to each other so that their oppositely charged sides come closer together (orientation process). If the orientation rate is greater than the aggregation rate, then a regular crystal lattice is formed, but if, on the contrary, an amorphous precipitate precipitates. The lower the solubility of a substance, the faster the precipitate forms and the smaller the crystals. The same poorly soluble substances can be isolated in both crystalline and amorphous states, which is determined by the precipitation conditions.

Based on the concept of relative supersaturation of a solution, it follows that the lower the solubility of the precipitate S and the higher the concentration of reactants Q, the more nuclei are formed and the greater the rate of aggregation. And vice versa: the smaller the difference (Q – S), that is, the higher the solubility of the precipitate and the lower the concentration of the precipitated substance, the higher the orientation rate. Consequently, to obtain large crystals that can be easily filtered and washed, it is necessary to carry out precipitation from dilute solutions by slowly adding a precipitant and heating (Table 1.1).

Lecture No. 17

Amorphous and crystalline sediments

Conditions for the deposition of crystalline and amorphous sediments

Influencing factor	Character of sediment	
	crystal	**amorphous**
Concentration of solutions of the substance and precipitant	A dilute solution of the precipitant is added to a dilute solution of the test substance.	A concentrated solution of the precipitant is added to a concentrated solution of the test substance.
Deposition rate	The precipitant solution is added dropwise	The precipitant solution is added quickly
Temperature	Precipitation is carried out from hot solutions (70 - 80˚C) with a hot solution of a precipitant	Precipitation is carried out from hot solutions (70 - 80˚C)
Mixing	Precipitation is carried out with continuous stirring	
Presence of foreign substances	Add substances that increase solubility (usually strong acids)	Add coagulant electrolytes
Deposition time	The sediment is kept in the mother liquor for a long time for “maturation” (“aging”)	Filter immediately after sedimentation

Table 1.1

Purity of crystalline sediments. The specific surface area of crystalline sediments (the area of the sediment per unit mass, cm2/g) is usually small, so coprecipitation due to adsorption is insignificant. However, other types of coprecipitation associated with contamination within the crystal can lead to errors.

Two types of coprecipitation in crystalline sediments are known:

1) inclusion - impurities in the form of individual ions or molecules are homogeneously distributed throughout the crystal;

2) occlusion - uneven distribution of numerous ions or impurity molecules that have entered the crystal due to imperfections in the crystal lattice.

An effective way to reduce occlusion is the “aging” (“maturation”) of the sediment, during which spontaneous growth of larger crystals occurs due to the dissolution of small particles, the crystal structure of the sediment is improved, its specific surface area is reduced, as a result of which impurities of previously absorbed substances are desorbed and go into solution substances. The time of “ripening” of the precipitate can be reduced by heating the solution with the precipitate.

The purity of amorphous sediments is significantly reduced as a result of the adsorption process, since the amorphous sediment consists of particles with a disordered structure, forming a loose porous mass with a large surface area. The most effective way to reduce as a result of the adsorption process is reprecipitation. In this case, the filtered precipitate is dissolved and precipitated again. Reprecipitation significantly lengthens the analysis, but it is inevitable for hydrated iron (III) and aluminum oxides, zinc and manganese hydroxides, etc. The reverse process of coagulation of an amorphous sediment is its peptization - a phenomenon as a result of which the coagulated colloid returns to its original dispersed state . Peptization is often observed when amorphous precipitates are washed with distilled water. This error can be eliminated by choosing the correct washing liquid for the amorphous sediment.

SEDIMENTARY AND GRAVIMETRIC FORMS.

REQUIREMENTS FOR THEM.

In the gravimetric sedimentation method, there are concepts of sedimentation

and gravimetric forms of matter. The precipitated form is a compound in which the analyte component precipitates from solution. The gravimetric (weight) form is the compound that is being weighed. Otherwise, it can be defined as the precipitated form after appropriate analytical processing of the precipitate. Let us present schemes for the gravimetric determination of SO ions$_{42}$**-, Fe3+, Mg2+**

S0$_{42}$**-+ Ba2+ ↔ BaS0$_4$↓ → BaS0$_4$↓**

detectable precipitant precipitated gravimetric

ion form form

$Fe^{3+} + 3OH^- \leftrightarrow Fe(OH)_3\downarrow \rightarrow Fe_2O_3\downarrow$

detectable precipitant precipitated gravimetric

ion form form

From the above examples it is clear that the gravimetric form does not always coincide with the precipitated form of the substance. The requirements for them are also different.

The deposited form should be:

 slightly soluble enough to provide almost complete

isolation of the analyte from solution. In case of deposition

binary electrolytes (AgCl; BaS04; CaC2O4, etc.) is achieved

almost complete precipitation, since the product of the solubility of these

precipitation is less than 10 - 8;

 the resulting sediment must be clean and easily filterable (which determines the advantages of crystalline sediments);

 the precipitated form should easily transform into the gravimetric form.

After filtering and washing the precipitated form, it is dried or calcined until the mass of the precipitate becomes constant, which confirms the completeness of the transformation of the precipitated form into a gravimetric one and indicates the completeness of removal of volatile impurities. Precipitates obtained by precipitation of the component being determined with an organic reagent (diacetyldioxime, 8-hydroxyquinoline, α-nitroso-β-naphthol, etc.) are usually dried. Precipitates of inorganic compounds are usually calcined

The main requirements for the gravimetric formare:

 exact correspondence of its composition to a certain chemical formula;

 chemical stability in a fairly wide temperature range, lack of hygroscopicity;

 as high a molecular weight as possible with the lowest content

it contains a determined component to reduce the influence of errors

when weighing the analysis result.

CALCULATION OF RESULTS IN THE GRAVIMETRIAL ANALYSIS METHOD

Gravimetric analysis includes two experimental measurements: determining the mass of a sample mn of the analyte and the mass of a product of known composition obtained from this sample, that is, the mass of the gravimetric form mgr.f of the analyte.

Based on these data, it is easy to calculate the mass percentage w, % of the component being determined in the sample:

$$w, \% = m_{gr.f} \cdot F \cdot 100 / m_н,$$

where F is the gravimetric factor (conversion factor, analytical factor) is calculated as the ratio of the molecular weight of the component being determined to the molecular weight of the gravimetric form, taking into account stoichiometric coefficients.

The value of gravimetric factors, calculated with high accuracy, is given in reference literature.

Example 1. How many grams of Fe2O3 can be obtained from 1.63 g of Fe3O4? Calculate the gravimetric factor.

Solution. It must be assumed that Fe3O4 is quantitatively converted into Fe2O3 and for this there is a sufficient amount of oxygen:

$2\ Fe_3O_4 + [O] \leftrightarrow 3\ Fe_2O_3$

From each mole of Fe3O4, 3/2 mole of Fe2O3 is obtained. Thus, the number of moles of Fe2O3 is 3/2 times greater than the number of moles of Fe3O4, that is:

$nM(Fe_2O_3) = 3/2\ nM(Fe_3O_4);$

$m(Fe_2O_3) / M(Fe_2O_3) = 3/2\ m(Fe_3O_4) / M(Fe_3O_4)$

where n is the number of moles of the component being determined, from which one mole of gravimetric form is obtained; m is the mass of the substance, g; M is the molar mass of the substance, g/mol.

From the formula $m(Fe_2O_3) = 3/2\ (m(Fe_3O_4) \cdot M(Fe_2O_3)) / M(Fe_3O_4)$

we get

$m(Fe_2O_3) = m(Fe_3O_4) \cdot 3M(Fe_2O_3) / 2M(Fe_3O_4)$

and substitute numerical values into it:

m(Fe2O3) = 1.63 · (3 · 159.7) / (2 · 231.5) = 1.687 ≈ 1.69 g.

The gravimetric factor F is equal to:

F = 3M(Fe2O3) / 2M(Fe3O4) = 1.035.

Therefore, in the general case, the gravimetric factor is determined by the formula:

F = (a · Mopred.v-vo) / (b · Mgr.f),

where a and b are small integers by which the molecular masses must be multiplied so that the number of moles in the numerator and denominator is chemically equivalent.

However, these calculations are not applicable in all cases. In the indirect determination of iron in Fe2(SO4)3, which consists in the precipitation and weighing of BaSO4 (gravimetric form), when calculating the analytical factor, there is no common element in the numerator and denominator of the formula. Here another way of expressing the chemical equivalence between these quantities is needed:

2 M(Fe3+) ≡≡ l M(Fe2(SO4)3) ≡≡ 3 M(SO42-) ≡≡ 3 M(BaSO4).

The gravimetric factor for the mass percentage of iron will be expressed:

F = 2M(Fe3+) / 3M(BaSO4).

Example 2. A solution of the drug Na3PO4 (mn = 0.7030 g) was precipitated in the form of MgNH4PO4·6H2O. After filtering and washing, the precipitate was calcined at 1000 °C. The mass of the resulting Mg2P2O7 precipitate was 0.4320 g. Calculate the mass percentage of phosphorus in the sample

Solution.

mgr.f (Mg2P2O7) = 0.4320 g;

F = 2M(P) / M(Mg2P2O7) = 0.2782; mн = 0.7030 g;

W,% = mgr.f · F · 100 / mн

w, %(P) = 0.4320 · 0.2782 · 100 / 0.7030 = 17.10%.

Example 3. When calcining a contaminated sodium oxalate preparation mn = 1.3906 g, a residue weighing mgr.f = 1.1436 g was obtained. Determine the degree of purity of the sample. t

$Na_2C_2O_4 \rightarrow Na_2CO_3 + CO\uparrow$

Solution.It should be assumed that the difference between the initial and final masses corresponds to the loss of carbon oxide during calcination. The analysis is based on measuring this quantity:

n(CO) = n(Na2C2O4),

hence,

w, %(Na2C2O4) = (mn - mgr.f) · F · 100 / mn;

F = M(Na2C2O4) / M(CO) = 4.784;

w, %(Na2C2O4) = (1.3906 – 1.1436) · 4.784 · 100 / 1.3906 = 84.97%.

SELECTION OF WEIGHT IN GRAVIMETRY

As is known, the accuracy of the analysis depends both on the mass of the sample and on the mass of the gravimetric form obtained from it. If the sample is taken with great accuracy, and the gravimetric form obtained from it is a small value measured with a large error, then the entire analysis will be performed with the error made when weighing the gravimetric form. Therefore, a sample must be taken such that when weighing it and when weighing the gravimetric form obtained from it, the error does not exceed ± 0.2%. To do this, it is necessary to determine the minimum mass that can still be weighed with an accuracy of ± 0.2% on an analytical balance with an absolute weighing error of ± 0.0001 g, and the minimum error, taking into account the possible spread (±), in this case will be equal to 2 · (±0.000 1) = ±0.0002 g.

100 g - ± 0.2 g

x - ± 0.0002 g

x = 0.1 g

Therefore, with such a minimum mass $m_{min}$is 0.1 g. For a value less than 0.1 g, the error will exceed 0.2%. When calculating the mass of a sample in gravimetric analysis, the mass of the gravimetric form of the component is equated to the minimum mass of the substance:

mgr.f = mmin, mn = mmin · F · 100 / w, %.

If the mass of the sample calculated according to the specified formula turns out to be less than 0.1 g, then the sample should be increased to 0.1 g. Most often, the mass of the initial sample is indicated in the analysis procedure, or for bulk amorphous sediments, the mass of the sample is taken to be about 0.1, and for crystalline ones from 0.1 to 0.5 g.

The calculation of the amount of precipitant is carried out taking into account the possible content of the component being determined in the analyzed sample. To ensure complete separation of the precipitate, a moderate excess of precipitant is used. If the precipitant is volatile (for example, a solution of hydrochloric acid), take a two- or three-fold excess, which is subsequently removed by heating the precipitate. If the precipitant is non-volatile (solutions of barium chloride, ammonium oxalate, silver nitrate, etc.), a one and a half times excess is sufficient.

Lecture No. 18

Analytical balances

Analytical balances are a precise physical instrument, the use of which is permitted subject to strict adherence to the rules that ensure the necessary reproducibility and accuracy of weighing.

Rules for handling analytical balances include the following basic requirements:

1. The scale must be installed on a rigidly fixed surface,

protecting them from various shocks, and in a specially equipped room - a weighing room.

2. Sharp temperature fluctuations, direct sunlight, and exposure to chemical substances on analytical balances are unacceptable.

3. The maximum permissible load of analytical balances should be no more than 200 g.

4. When weighing objects on analytical balances, they must be at the temperature of the weighing room.

5. The substance to be weighed is placed on the left pan of the scale in a special container (juices, crucibles, watch glass). Analytical weights are placed on the right pan of the scale.

6. The objects and weights to be weighed are brought in through the side doors of the scales (curtains). Weighing is carried out only with the scale doors closed.

7. Analytical weights must be handled only with specially designed tweezers. All operations involving weight changes are performed with the scales fully locked.

8. Before and after each weighing, the zero point of the scale must be checked.

9. To avoid distortion of the scales, weights and objects to be weighed are placed in the center of the scales.

10. Recording of weighing results is carried out using empty slots of the analytical weight and according to the data of drums with tenths and hundredths of a gram. The third and fourth decimal places are removed from the illuminated display.

11. At the end of weighing, you must make sure that the scales are locked, completely unloaded and the case doors are tightly closed.

12. To reduce weighing errors, it is necessary to use an analytical balance designed for strictly defined analytical balances.

It should be noted that even if all the mentioned rules are followed

Weighing errors may occur due to various reasons:

 caused by unequal arms of the scales;

 due to changes in body weight during the weighing process;

 due to weighing in air, and not in vacuum;

 caused by the discrepancy between the mass of weights (weights) and their nominal

mass.

Lecture No. 19

Titrimetric methods of analysis

Titrimetric analysis,method*quantitative analysis*,based on measuring the volume of a solution with a precisely known concentration of the reagent required to react with a given amount of the analyte (see also*Volumetric analysis*). In T. a. precipitation, acid-base, redox, complexation, and other reactions are used. Basic requirements for those used in thermodynamics. reactions - interaction is fast, in*stoichiometric ratios*,without adverse reactions that distort the results of the analysis. In T. a. There are several methods.

Direct*titration*consists in titrating a sample of the analyte*standard solution*,or titrant, to the point of equivalence - the moment when the amount of the standard solution is equivalent to the amount of the substance being determined in accordance with*chemical equation*for this reaction. The end of the titration is determined visually by a change in the color of the introduced indicator or instrumentally (see.*Electrochemical methods of analysis*). The more accurately the equivalence point is determined, the smaller the analysis error. The calculation is carried out according to the formula:

P = 0.0001□N □ v □ E,

where P is weight (mass), E is the number*gram equivalents*of the substance being determined, N is normality, v is the volume (in ml) of the standard solution.

Reverse titration, or residue titration, is used when the analyte does not react with a standard solution or does not react quickly enough. In this case, a known excess of a standard solution is added to the sample of the analyte, and the remainder after reaction with the analyte is titrated with another standard solution.

Titration by substitution is used when the direct determination of a given substance is difficult (there is no suitable titrant, there is no necessary indicator, etc.). In this case, the analyte is converted by reaction with an undetermined excess of the appropriate reagent into another compound, which is titrated with a standard solution as described above. For example, this method determines the amount of potassium bichromate in a solution.

In T. a. Along with water, organic solvents are used: hydrocarbons, their halogen derivatives, alcohols, ketones, acids, amines, amides, nitriles, which makes it possible to expand the range of compounds being determined, since T. a. can be carried out on the basis of those reactions that do not proceed in water or do not give sharp titration endpoints, for example, weak acids (bases) or mixtures of acids (bases) of similar strength. The accuracy of determinations in non-aqueous solutions is usually higher, since, due to low surface tension, the size of droplets of organic liquids is smaller than that of aqueous solutions.

Lecture No. 20

Acid-base titration

Acid-base titration, neutralization reactions, titration jump, construction of titration curves, rules for choosing an indicator for acid-base titration, requirements for indicators, methods of amperometric, conductometric and potentiometric titration.

Titration curve

a graphical representation of the dependence of the change in concentration C (X), determined by the substance X or some associated property of the system (solution) on the volume V (T) of the added titrant (T).

The volume of added titrant is plotted along the abscissa axis, and the corresponding pH value is plotted along the ordinate axis. Potentiometric titration - a change in the ion concentration is certainly accompanied by a change in the potential on the indicator electrode immersed in the solution being titrated.

In this case, a potential jump is observed near the equivalence point, which is recorded using a potentiometer. Conductometric titration is a change in the electrical conductivity of the titrated medium between 2 inert electrodes. Amperometric titration - the progress of the titration is monitored using a dripping mercury, rotating platinum or other microelectrode, which acts as an indicator electrode and is paired with a suitable reference electrode.

Coulometric titration is a measurement of the amount of electricity expended to perform an electrode reaction. In this case, the titrating agent (for example, acid-base type) is not added in the form of a standard solution, but is formed in the solution of the electrode reaction, that is, as a result of electrolysis at constant current.

Titration of a strong acid with a strong base:

HC1+KOH =KS1+H2O,
During the titration process, constant, continuous neutralization of the substance occurs. At point “100” complete neutralization occurs. Since the salt of a strong base and strong acid is not capable of hydrolysis, the pH at this point is 7 (titration curve on the back).

With further titration, excess alkali accumulates in the solution and in this case the pH of the solution is calculated using formulas 1 and 2. Titration of a weak base with a strong base:

CH3COOH+KOH=CH3COOC+H2O,
at the zero point, pH is calculated using formula 3. As titration proceeds, sodium acetate accumulates in the medium. A mixture of a weak acid and its salt is an acidic buffer solution. Therefore, in the range of 10-99 ml of added titrant, the pH is calculated using formula 5. At point 100, all the acid is completely bound into salt. The salt of a weak base and a strong base is easily hydrolyzed with the elimination of free hydroxyls.

Therefore, the equivalence point is in the alkaline region (titration curve on the back); The pH is calculated using formula 8. With further titration, excess titrant accumulates in

the solution and the pH in the region of 101-200 ml of the added titrant is calculated using the formula.

Titration of a weak base with a strong acid:

NH4OH+HC1=NH4C1+H2O,
at the zero point, the pH of the solution is calculated using formula 4. As titration proceeds, a salt, ammonium chloride, accumulates in the solution. A mixture of a weak base and its salt is an alkaline buffer solution, therefore, the calculation of pH in the range of 10-99 ml of added titrant is carried out according to formula 6. At the equivalence point (point 100) all the base turns into salt. A salt of a weak base and a strong one is easily hydrolyzed with the elimination of free protons. Therefore, the equivalence point is in the acidic region (titation curve on the back), pH is calculated using formula 7.

With further titration, an excess of titrant accumulates in the solution and the pH in the range 101-200 is calculated using formula 1. Titration of a weak acid with a weak base: CH3COOH + NH4OH = CH3COONH4 + H2O. At the zero point, the pH of the solution is found using formula 3. In the range of 10-99 ml of added titrant, the mixture is an acid buffer and the pH of the solution is calculated using formula 5. At the equivalence point, all the acid is bound into a salt. The salt of a weak acid and a weak base is completely hydrolyzed to form weak acids and a base. Depending on the pKα and pKb values, the pH of the salt solution can be in both the acidic and alkaline regions (titration curve); The pH at this point is calculated using formula 9.

With further titration, the pH at point 101 is found using formula 4. After a sufficient excess of titrant has accumulated in the solution, the titrated mixture will be an alkaline buffer (a mixture of a weak base and its salt) and the pH in the range of 110-200 ml is calculated using formula 6. As we have already said, acidimetry - acidimetric titration is a method for determining strong and weak bases, salts of weak acids, basic salts and other compounds with basic properties, by titration with a standard solution of a strong acid. When titrating strong bases, the following reaction occurs:

OH-+H3O+=2H2O, the medium in the fuel cell is neutral.
When titrating weak bases, such as ammonia, NH3+H3O+= NH4++H2O, weak base cations are formed that undergo hydrolysis:

NH4++H2O= NH3+H3O+
therefore, the environment in the fuel cell is slightly acidic, pH<7. When titrating salts of weak monobasic compounds, for example acetates,

CH3COO-+H3O+ = CH3COOH+H2O in the TE in the solution there is a weak acid, due to the dissociation of which the solution has a weakly acidic reaction, pH<7.
When titrating salts of weak 2-basic acids, for example carbonates, after adding one proton to the anion, an acidic weak acid anion is formed, CO32-+H3O+=HCO3-+H2O,

which undergoes hydrolysis: HCO3-+H2O=H2CO3 +OH-, as a result of which the reaction of the medium in the 1st heating element is slightly alkaline, pH>7. As the titration of the acidic anion of a weak 2-basic acid continues, this weak acid is present in the 2nd fuel cell: HCO3-+H3O+=H2CO3 due to the partial dissociation of which the medium in the 2nd fuel cell is weakly acidic, pH<7. That. during acidimetric titration, the medium in the fuel cell can be neutral, slightly alkaline or slightly acidic, depending on the nature of the substance being titrated.

And then, when titrating to the 2nd TE, the medium contains the anion SO32- of the weak acid HSO3-: HSO3-+OH-=H2O+SO32-, this anion undergoes hydrolysis: SO32-+H2O=OH-+HSO3- and the medium in the 2nd TE - alkaline, pH>7. When titrating acidic salts, medium anions of the corresponding acid are formed, the properties of which determine the pH value of the medium in the fuel cell. For example, when titrating NaHSO4 solution with alkali, the sulfate ion SO42- is formed: HSO4-+OH-=H2O+SO42-. The sulfate ion practically does not undergo hydrolysis, so the environment in the fuel cell is neutral. Salts containing cations of weak bases are titrated with alkalis to release the free base. This base is present in FC, and therefore the reaction of the medium in FC is slightly alkaline. Acid-base titration indicators. An indicator is something that exhibits a visible change at or near the equivalence point. With the visual indicator method of fixing CTT in acid-base titration, the addition of the titrant to the titrated solution is stopped when the color of the solution sharply changes due to a change in the color of the indicator introduced into the titrated solution.

The titration index pT is the pH value at which a change in the color of the indicator becomes noticeable and the titration ends. Acid-basic indicators are weak organic compounds that dissociate in solutions according to the equation H1nd ↔H++1nd-. The color of the molecular (H1n) and anionic (1nd) forms is different. This is due to the fact that during the dissociation of the indicator, a tautomeric rearrangement occurs, leading to a change in the structure of the molecule, which determines the color of the compound. There are several theories explaining the change in the color of indicators, one of them is chromophore, i.e. the color of an indicator depends on the presence of special atomic groups in their molecule - chromophores. A chromophore in organic compounds most often represents a system of conjugated (alternating) single and double bonds. The longer the conjugation chain is, the more strongly colored the substance is.

In acid-base indicators, the most important chromophores are the azo group -N = N-, the quinoid ring and the quinone imine ring. During the process of tautomeric rearrangement, the chromophore group is either destroyed, causing the indicator to become discolored, or transforms into another chromophore, causing the indicator to change color. The first type of tautomeric rearrangement is characteristic of single-color indicators (such as phenophthalein), the second - for 2-color indicators (such as methyl orange). The latter anion, methyl orange, is yellow in aqueous solutions, and red in the presence of acids. In this case, the azo group is destroyed and the benzene ring is converted into a quinone

ring, which is accompanied by a change in the color of methyl orange. The pH region in which the color change occurs is called the indicator transition interval ΔpH=pKн1пd+-1, where pKH1пd is the indicator of the dissociation constant of the indicator.

The selection of an indicator for titration is carried out according to the titration curve in 2 ways:

1. For this titration, the indicator for which the transition interval ΔpH falls within the jump region on the titration curve is most suitable.
2. For this titration, the most suitable indicator is the one whose titration index pT is closest to the pH of the equivalent titration point.

The curve expressing the change in the pH value of the titrated solution depending on the volume of added working solution is called a titration curve. When comparing titration curves, i.e. The branches of the titration curve located above and below the equivalence point show that when titrating strong solutions, the branches are steeper than when titrating weak solutions. Weak solutions have smoothed branches. In the first case, the branches of the curves corresponding to strong components increase the jump area, otherwise the jump decreases.

Therefore, the α curve with both type 1 branches has the largest titration jump. Curves b and c consist of different branches of types 1 and 11 and therefore have a much smaller jump. Thus, in the case of a weak component, the jump always decreases. If you titrate a weak base with a weak acid, then the titration curve will consist of both branches of the 11th type and will not have a vertical part at all, i.e. in this case, a noticeable jump in titration will not be observed. Therefore, when titrating a weak base with a weak acid, the pH of the titrated solution changes so gradually that it is almost impossible to determine the exact moment when titration should be stopped (i.e., the equivalence point).

Therefore, such titration is practically not used. To construct a titration curve means to plot the following points on the graph: 1) the starting point of titration - corresponding to the pH value of the initial titrated solution before the start of titration. This point is always on the vertical line corresponding to 0 ml of the working solution; 2) equivalence point, indicating at what pH value the titration should be completed. This point always lies on the equivalence line; 3) plot intermediate points of the curve showing how the pH of the solution changes during the titration process.

For the titration curve of a strong base, a strong base is characterized by the following features:

- . The starting point of the titration lies in a strongly acidic environment.
- . The equivalence point lies on the neutrality line.
- . At the beginning of the titration, the pH changes very slowly. A sharp change begins only when the last 0.1 part of the working solution is added.

. The titration jump (when titrating a 0.1 N acid solution) is very large - from pH=4 to pH=10. If the titration proceeds in reverse order, i.e. If there were alkali in the flask and alkali in the burette, then the titration curve would retain the same appearance, but the starting point of the titration would be at the bottom of the graph at pH = 13.

Determination of pH using an indicator, pp. 14 -15. When starting titration, you must first calculate the pH value at which the titration of the solution should be completed. In accordance with this pH value, the indicator is selected, since it is necessary for the indicator to change color at the pH value corresponding to the equivalence point of this titration. In reality, this is not necessary, since the titration curves show that TE lies approximately in the middle of the pH jump, and this jump occurs when the pH of the solution changes from adding the last drop of the working solution. Therefore, with the addition of the last drop, all indicators change color, the transition interval of which corresponds to the titration jump. That. The main rule for choosing an indicator: titration in the neutralization method should be performed in the presence of an indicator whose transition interval is the interval of the pH jump on the titration curve of a given substance.

In the case of titration of a weak base with a strong base, the titration jump is from 8 to 10 units. pH, which corresponds to phenolphthalein, in the case of a strong acid and a strong base - a jump from 4 to 10 and the choice of indicator here is quite wide. Titration with a “witness” is used to accurately determine the color of the solution being titrated, i.e. a standard solution is used, which has the same color as the one with which the titration needs to be completed (the same vessel, volume and indicator in the amount of 1 drop per 25 ml of solution). Oxidimetry. Redox methods of volumetric analysis are based on the use of ORR.

The working solutions are solutions of oxidizing agents or reducing agents. A method based on oxidation with permanganate is called permanganatometry, on oxidation with iodine - iodometry, and on oxidation with chromate - chromatometry. ORP is a quantitative characteristic of the intensity of the redox process (in volts) of systems reacting with each other. The OR potential of systems, measured under the condition that the concentrations (more precisely, the activity) of ions of the reduced and oxidized forms are equal to 1, is called the normal redox potential of the system. Any ORR involves at least 2 redox pairs. Red1+Ox2=Ox1+Red2. The reduced form of one substance, Red1, donating electrons, goes into the oxidized form Ox1 of the same substance. Both of these forms form one redox pair Ox1|Red1. The oxidized form Ox2 of the second substance, accepting electrons, goes into the reduced form Red2 of the same substance. Both of these forms also form a redox pair Ox2|Red2. The higher the ORP of the redox pair Ox2|Red2, the oxidized form of which plays the role of an oxidizing agent in this reaction, the greater the number of reducing agents Red1 can be titrated and determined using this oxidizer Ox2.

Therefore, in redoxmetry, oxidizing agents whose standard redox pair potentials are as high as possible are most often used as titrants. About 10 different methods of OM titration are known. They are usually classified as follows: by the nature of the titrant - oxidimetry, methods for determining reducing agents using a titrant-oxidizer; reductometry - methods for determining oxidizing agents using a reducing titrant. By the nature of the reagent that interacts with the substance being determined, for example, iodometry (potassium iodate K1O3), iodimetry (iodine 12), iodometry (potassium iodide K1). As is known from the theory of quality analysis, the dependence of redox potential on the concentration of ions of oxidized and reduced forms is expressed by the Nernst equation. In the case of permanganatometry, the main working solution is potassium permanganate. Oxidation with permanganate for analyte purposes is carried out mainly in an acidic environment.

Therefore, the main level of permanganatometry is MnO4- +5e +8H+---->Mn2++4H2O, i.e. the permanganate ion, which has an intense violet-crimson color, is reduced to manganese cations (11), which have a very weak pinkish color (virtually colorless). According to Nernst's equation: E=E0+(0.059/5)log([MnO4-][H+]5/[Mn2+]. The normal potential of this system, equal to +1.52 V, is significantly higher than other systems, therefore KMnO4 in an acidic environment it has strong oxidizing properties and is capable of oxidizing many substances. The value of the gram equivalent of an oxidizing agent (or reducing agent) is found by dividing its molecular weight by the number of electrons it accepts (or donates) in a given chemical reaction. 5, the molar mass of permanganate equivalent is M/5 = 158.04/5 = 31.68 g. In practice, solutions of various concentrations are used: 0.01 N, 0.05 N, 0.2 N and mainly 0.1 N p- R.

Lecture No. 21

Acid-base titration errors

The results of any analysis, including acid-base titration, are obtained with some errors, i.e. the content value of the component being determined, found during quantitative analysis, is always slightly different from its true value. These errors can be either random or systematic and have a different nature.

A) Errors due to inaccuracy in measuring the volume of solutions.

To carry out titration, an aliquot of the analyzed solution is taken, measuring its volume using a burette or pipette. If the solution is taken using a burette, then two measurements are taken of the volume of the solution in the burette: before and after taking the solution. The random error of each such measurement when using

conventional laboratory burettes is approximately ±(0.01 - 0.02) ml. If the volume of the sampled solution is equal to V, then the maximum random relative error ε of measuring the volume taken for titration will be (in percent):

$\varepsilon = \pm\nu \cdot 100\%/V$, (10)

where $\nu = 0.02 + 0.02 = 0.04$ ml.

The value of ε can be reduced by increasing the volume V of the sampled solution. So, if V = 50 ml, then

$\varepsilon = \pm 0.04 \cdot 100\%/50 = 0.08\%$

On the contrary, as the volume V of the sampled solution decreases, the maximum relative error in its measurement increases. If, for example, only V = 2 ml of solution is taken from the burette, then

$\varepsilon = \pm 0.04 \cdot 100\%/2 = 2\%$

and is a noticeable amount.

Therefore, when performing a titration, a solution of at least 20–30 ml should be taken from the burette.

When performing a titration, one drop of excess titrant is usually added, i.e. the solution is slightly titrated. The volume of one drop of solution added from a burette is often about ~0.05 ml (although this is not always the case). In this case, the error associated with excess titrant consumption will obviously be equal to

$\varepsilon 1 = 0.05 \cdot 100\%/V$

and with a volume of solution spent on titration equal to V = 20 ml, it will be the volume of the sample

$\varepsilon 1 = 0.05 \cdot 100\%/20 = 0.25\%$

The total maximum relative error in titrant volume measurement will be

$\varepsilon = (0.04 + 0.05)100\%/20 = 0.45\%$

The error in measuring the volume of consumed titrant, caused by the overconsumption of one excess drop of titrant, can be eliminated by introducing a correction for the overconsumption of the titrant, i.e. subtracting the volume of one drop of solution from the total volume of titrant consumed.

Errors caused by inaccuracy in measuring the volume of solutions are inherent not only in acid-base titration, but also in all other titrimetric methods of analysis.

B) Indicator errors in acid-base titration.

Systematic errors in acid-base titration include indicator errors. They are caused by a discrepancy between the pH values of the titrated solution in the TE and the pH values of the indicator in the CTT. Almost no it is possible to select an acid-base titration indicator whose pT value would exactly coincide with the pH value in the fuel cell. Therefore, the indicator changes its color in the CTT either before or after the TE. If a change in the color of the indicator occurs before the TE, then the solution is undertitrated, and a certain amount of untitrated analyte remains in the CTT. If the color of the indicator changes after TE, then the solution is titrated in the CTT and there is some excess amount of titrant. Usually they strive to reduce indicator errors to a minimum so that they, in any case, do not exceed 0.2%. This is achieved mainly by choosing an appropriate indicator.

Sometimes it is recommended to call the indicator titration error simply the titration error; it is formulated as follows: this is the difference in the amounts of the titrant or the corresponding difference in the amounts of the titrated substance; the value found at the end point minus the value corresponding to the equivalence point.

This definition of titration error is universal, i.e. This applies to all titrimetric methods, not just acid-base titration.

Indicator errors in acid-base titration are divided into:*1) hydrogen (protic), 2) hydroxide, 3) acidic, 4) basic (formerly the basic error was called an alkaline error).*

1) Hydrogen (proton) error XH3O+. This error is caused by the presence of excess hydrogen ions in the CCP due to either a) undertitration of a solution of a strong acid, or b) overtitration of a solution of the base being titrated with a solution of a strong acid. In the first case the error is negative, in the second it is positive.

$$XH3O+ = \frac{\pm 10^{-pT}\,[V(a) + V(b)]*100\%}{c(a)V(a)}$$

where Ca is the acid concentration,

Va, VB – volumes of acid and base.

2) Hydroxide error CHON-. This error occurs when there is an excess of OH- hydroxide ions in the CTT as a result of either a) undertitration of a solution of a strong base with an acid (negative error) or b) overtitration of an acid solution with a solution of a strong base (positive error):

$$HON- = \pm 10^{-(14 - rT)} \frac{V(a) + V(b)}{c(b)V(b)} \quad 100\% \quad (12)$$

where Cb is the concentration of the base,

C) Other sources of error in acid-base titration.

The indicator present in the solution has acid-base properties and interacts with the titrant, which consumes a certain amount of titrant. The more indicator is introduced into the solution, the more titrant is consumed for interaction with the indicator. Therefore, the minimum amount of indicator should be added to ensure reliable fixation of the CTT.

In addition, with a significant change in the concentration of the indicator, the pH value of the color transition of the indicator also changes slightly, which leads to the appearance of a concentration indicator error.

To account for such errors, a control experiment is carried out in which the same volume of water is titrated as the volume of the titrated test solution, containing exactly the same amount of indicator as the test solution. The volume of titrant consumed in the control experiment is subtracted from the volume of the titrant solution. spent on titration of the analyzed solution.

During the titration process, the ionic strength of the solution can change, which affects the change in activity coefficients and leads to a change in the concentration equilibrium constants and to a shift in the pT of the indicator to one side or another from the TE. As a result, a salt error occurs. True, usually the salt error is small.

Lecture No. 22

Titration based on redox reactions

The redox titration (OR) method is based on a chemical reaction between the component being determined and a standard solution of an oxidizing or reducing agent (titrant). The quantitative content of the analyte is determined by measuring precise volumes of solutions of known concentrations reacting with each other. The possibility and extent of the reaction is characterized by the redox potential.

To carry out OS titration, certain requirements must be met:

- The titrant must react only with the analyzed component, completely and quickly;
- simple and reproducible detection of titration endpoint (TEP).

The dependence of the determined value (potential) on the titrant volume, presented in the form of a graph, is called a titration curve, the construction of which is necessary to find the equivalence point (PE).

Types of redox titration

There are direct, reverse and substitution titrations.

The direct analysis is carried out at an RH potential value ≥ 0.4 V, the reverse method - at a low reaction rate. When using the substitution method, an equivalent amount of the product formed during the reaction of the reagent with the analyzed component is titrated.

Classification of redox titration methodscarried out according to the names of the titrants used.

Permanganatometry. The basis of the method is the oxidation process with potassium permanganate (KMnO4), which forms brightly colored solutions that are a titration indicator. Finds application for the analysis of inorganic and organic substances.

Dichromatometry.The method is based on the oxidation process with potassium dichromate, which reacts with organic compounds less intensely than KMnO4, and therefore is generally not used for their analysis. To find the CTT, additional indicators (diphenylamine or others) are required.

It is used to determine inorganic and a number of organic substances, chemical oxygen demand (COD) in water.

Iodometry.The basis of the method is the process of oxidation with iodine (I2) or reduction with iodide ions. Disadvantages - low solubility of I2 in water.

Bromatometry.The basis of the method is the oxidation process with potassium bromate (KBrO3).

Advantages - the ability to determine unsaturated, aromatic and heterocyclic compounds, the stability of KBrO3 solutions. Disadvantages - by-products, some reactions do not occur strictly in stoichiometric ratios.

Cerimetry.The basis of the method is the oxidation process with cerium (IV) sulfate. Advantages - stability of the reagents, absence of by-products, possibility of use in the presence of hydrochloric acid.

The presented classification describes the most commonly used redox reactions used in titrations.

Indicator and potentiometric titration.

Indicator titration is based on the reaction of an indicator with an oxidizing or reducing agent, which changes the color of the solution as it approaches the TE.

In potentiometry, the establishment of TE is carried out by changing the electrode potential during the interaction of the potential-determining component and the titrant.

The advantages of the method are:

- in obtaining more accurate results, titrating substances for which indicators have not been selected or if their use is impossible;
- in the analysis of several components in one solution;
- in good reproducibility, absence of indicator errors.

Indicators used in redox titration are divided into 4 main groups: specific, redox indicators, complex compounds of certain metals, organic dyes that are irreversibly oxidized.

Titration, carried out using a photometric sensor, makes it possible to determine TE by changes in the optical properties of the titrated solution (optical density, transmittance and absorption values, spectral characteristics). The advantages of this method include the possibility of carrying out reactions in which it is visually impossible to determine the CPT due to a faint color change, as well as the possibility of automating indicator titration methods for regulatory documents that do not describe potentiometry. Oxidimetry is a method of volumetric analysis, which is based on redox reactions. Using titrated solutions of oxidizing agents, the quantitative content of reducing agents is determined and vice versa. Oxidimetry is divided into a number of methods: permanganatometry, iodometry, chromatometry, bromatometry, etc. This volumetric analysis course covers two methods: permanganatometry and iodometry. Oxidation-reduction reactions are more complex than ion exchange reactions. The main features of redox reactions are the following: 1) in many reactions, not only oxidizing agents and reducing agents interact, but also other substances (for example, acids and alkalis); 2) reactions often occur in several stages, each of them proceeding at a different rate; 3) the rate of oxidation-reduction reactions is lower than the rate of ion exchange reactions. While ionic reactions occur almost instantly, redox reactions require a more or less long time and special conditions to ensure the process is quickly completed; 2 4) different directions of reactions are possible with the same starting materials. In addition, during the reaction, substances are often formed that change the course of the reaction itself.

Oxidation-reduction reactions, on the basis of which quantitative analysis is carried out, must meet the following requirements: 1) the reaction must proceed in the desired direction and be practically irreversible; 2) there should be no adverse reactions; 3) reactions must proceed at a sufficient speed. Very often the reaction rate is increased artificially. It can be increased by increasing the temperature, the concentration of the reactants, changing the pH of the solution and using a catalyst. Taking into account the properties of substances, in each analysis conditions are created to achieve the required reaction rate. The indicators used in oxidimetry methods are different. Often these are organic substances that themselves are oxidizing or reducing agents. Such indicators, called redox indicators, easily pass from the oxidized form to the reduced form and back, and both forms have different colors. Such indicators include diphenylamine, the oxidized form of which is blue-violet and the reduced form is colorless, methyl blue (the oxidized form is greenish-blue, the reduced form is colorless), etc. In addition, for some reactions there are specific reagents that change color at the equivalent point of a given titration. For example, such an indicator is starch, which forms a blue adsorption compound 3 with iodine. In some cases, titration without an indicator is possible if the color of the working solution is sufficiently bright and changes sharply as a result of the reaction. An example is titration using a solution of potassium permanganate, the solution of which is crimson in color. Oxidimetry methods are widely used in clinical and sanitary analysis. Permanganatometry is used to determine the amount of calcium in the blood. This method is also used to determine the so-called oxidability of water, that is, to determine the amount of KMn04 required for the oxidation of organic substances in wastewater. Iodometry is used to determine blood sugar, free chlorine in water and active chlorine in bleach. Permanganatometry. Permanganatometry is based on oxidation reactions produced by a solution of potassium permanganate KMnO4, i.e. The working solution – titrant – is potassium permanganate. Oxidation can be carried out in acidic, neutral and alkaline environments. The process proceeds differently in all three cases. 1. Oxidation in an acidic environment. In this case, manganese with an oxidation state of +7 is reduced to an oxidation state of +2, and a manganese salt is formed corresponding to the acid taken.

For example, if FeSO4 is taken as a reducing agent, the reaction proceeds according to the equation 10FeSO4 + 2KMnO4 8H2SO4 = 5Fe2(SO4)3 + K2SO4 + 2Mn SO4 + 8H2O (1) Here the following redistribution of electrons takes place 4 Mn+7 +5ē = Mn+2 2 2Fe +2 - 2ē = 2Fe+3 5 2. When oxidized in a strongly alkaline environment, manganese with oxidation state +7 is reduced to potassium manganate with oxidation state +6. For example, Cr2(SO4)3 +6KMnO4+16KOH = 2K2CrO4 + 6K2MnO4+3K2SO4+8H2O (2) Mn+7 +ē = Mn+6 6 2 Cr+3 - 6ē = 2 Cr+6 1 3. Oxidation in a neutral environment accompanied by the formation of manganese dioxide, i.e. manganese with an oxidation state of +7 transforms into manganese with an oxidation state of +4. 3Na2SO3 + 2KMnO4 + H2O = 3Na2SO4 + 2MnO2 + 2KOH (3) S +4 - 2 ē = S +6 3 Mn+7 +3ē = Mn+4 2 An equivalent of an oxidizing or reducing agent is a real or hypothetical particle that can accept or give away one electron in ORR. Therefore, in the first reaction, one

mole of KMnO4 corresponds to five equivalents, since a mole of permanganate accepts five electrons, and a mole of FeSO4 corresponds to one equivalent, since it accepts one electron.

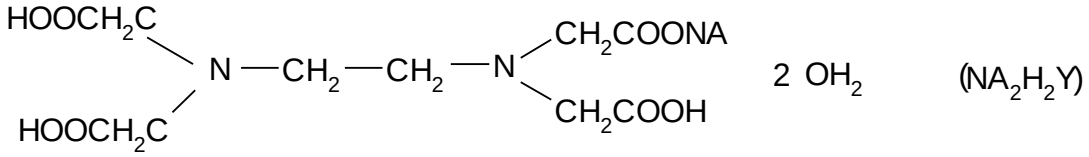
Lecture No. 23

Complexometric titration

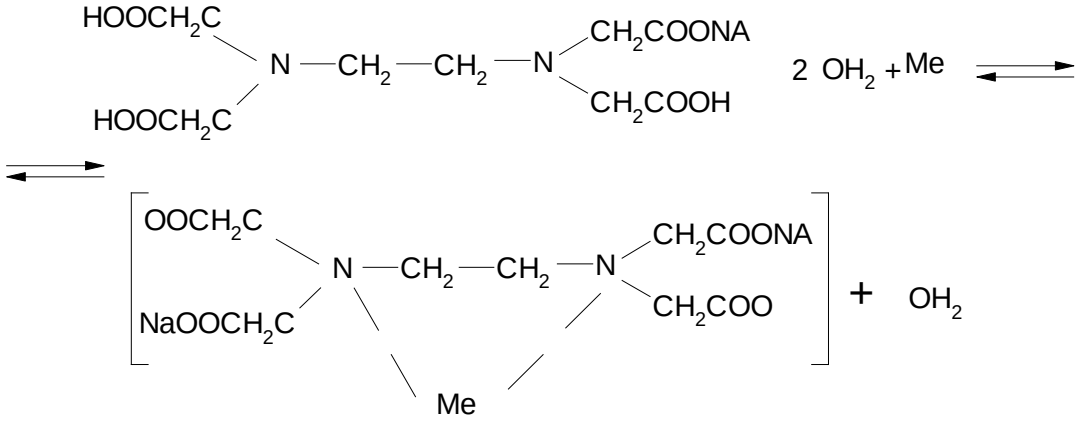
Complexometry (chelatometry) refers to titration methods involving polydentate organic ligands (complexones).

Complexons, in particular, are polyaminocarboxylic acids. The advantage of these reagents is that with many metal ions they form strong soluble complexes in which the ratio of metal to ligand is 1:1.

In titrimetric analysis, one of the representatives of the class of complexons is especially widely used - disodium salt of ethylenediaminetetraacetic acid (EDTA), known under the trade name Trilon B (complexon III):



The reaction of interaction of various cations with EDTA in solution proceeds according to the equation:



Or Me2+ + H2Y2-↔MeY2- + 2H+

The metal replaces the hydrogen ions of carboxyl groups and is simultaneously bonded through coordination bonds with nitrogen atoms. Regardless of the charge of the cation, one H2Y2- anion takes part in the complexation reaction and two hydrogen ions are released.

The completeness of the complexation reaction, as can be seen from the reaction equation, depends on the pH of the solution. Cations that form relatively unstable complexes

(Mg2+, Ca2+) can only be titrated in an alkaline medium. Cations that form very stable complexes with EDTA (for example, Fe3+) can be titrated in a fairly acidic solution.

To establish the stoichiometric point in complexometry, so-called metal indicators are used. Metal indicators are organic dyes that form colored complex compounds with metal ions that are less durable than the complexes of these metals with a complexone.

At the point of stoichiometry, the metal complex with the indicator is completely destroyed, and the solution acquires the color of the indicator itself (metal complexes with complexones are colorless in most cases).

Permanganatometry is a titrimetric analysis method in which the working solution is a solution of potassium permanganate (KMnO4). During the titration of the solution, the crimson-violet color of the permanganate solution becomes discolored. However, after reaching the equivalence point, the very first excess drop of permanganate solution turns the titrated liquid a pale crimson color. The indicator in this case is the permanganate itself. Potassium permanganate exhibits oxidizing properties in both acidic and alkaline environments. When titrating acidic solutions, Mn7+, which is part of KMnO4, is reduced to colorless cations Mn2+. When titrating in an alkaline medium, Mn7+ is reduced only to Mn4+. Permanganatometry is used not only for the quantitative determination of reducing agents, but also oxidizing agents. Reducing agents, with rare exceptions, are determined by direct titration with a working solution of permanganate. When determining oxidizing agents, they use the back titration method, i.e. a known excess of an auxiliary solution of a reducing agent with a known titer is added to the analyzed solution of the oxidizing agent, then the remainder of the reducing agent is titrated with a solution of potassium permanganate and a calculation is made. A titrated solution of potassium permanganate cannot be prepared by dissolving an exact sample; commercial potassium permanganate contains a number of impurities. In addition, the concentration of potassium permanganate transferred into solution decreases noticeably, because it is spent on interaction with ammonia, organic substances and other reducing agents present in water. Therefore, the concentration of the potassium permanganate solution is usually established only 5-7 days after its preparation. Oxalic acid $H_2C_2O_4 \cdot 2H_2O$ or sodium and potassium oxalates are used as the primary standard.

Potassium permanganate reacts with oxalic acid in a sulfuric acid medium according to the equation:

$$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 = 2MnSO_4 + 10CO_2 + K_2SO_4 + 8H_2O$$

Lecture No. 24

Determination of water hardness

To determine hardness the following can be used:

a) visual colorimetric method, suitable for analyzing water with very low hardness of the order of tenths of micrograms - equivalent to a liter;

b) the volumetric oleate method, used relatively rarely, usually in cases where the trilonate method is ineffective.

c) acid-base titration.

Colorimetric method

This method is based on the different intensity of chromium dark blue color depending on the concentration of Ca2+ and Mg2+ ions in the analyzed water and can be used to quickly determine low water hardness (from 10 μg - eq/l).

Oleate method

This method is based on the low solubility of calcium and magnesium oleates. Therefore, adding a solution of potassium oleate to the analyzed water sample and shaking it first causes the precipitation of all calcium and magnesium ions contained in the water in the form of oleate, and only then does the excess of potassium oleate lead to the formation of a stable foam, which serves as a sign of the end of the titration.

The minimum amount of oleate that already causes the appearance of foam when shaking a water sample depends on the concentration of calcium and magnesium ions in it. This dependence is not directly proportional and is more complex, which indicates the absence of simple stoichiometric relationships in the interaction of potassium oleate with alkaline earth metal ions.

The absence of a stoichiometric pattern is not, however, an obstacle to the use of the oleate method for the purpose of determining hardness, since, subject to the exact specified conditions regarding the temperature of the titrated liquid, its volume, pH value, frequency and intensity of agitation, the nature of the foam, the rate of addition of the oleate solution and etc. It is possible to obtain highly reproducible results using this method.

The oleate method for determining hardness is applicable for the analysis of water whose hardness does not exceed 0.5 mg-eq/l. The lowest hardness that can be quite reliably recorded by the oleate method is 2 μg - eq/l. Thus, the sensitivity of this method is almost the same as the trilonometric one.

Acid-base titration method

Acid-base titration in aqueous solutions is based on the interaction reactions between acids and bases:

$H^+ + OH^- = H_2O$

Using this method, direct titration can determine the concentration of an acid or base or the content of elements that form acids or soluble bases (for example, phosphorus - in the form of phosphoric acid, arsenic - in the form of arsenic acid, etc.)

The content of some salts (for example, ammonium salts, calcium salts, etc.) is determined by back titration or indirect methods. Using special techniques, mixtures of acids with their salts, mixtures of acidic and medium salts, etc. are titrated.

1.4.2 Rationale for the complexometric method

The introduction of complexons into analytical practice expanded the capabilities of chemical analysis in general and the volumetric method in particular.

The most valuable property of complexons, widely used in analysis, is their ability to produce intra-complex salts with alkaline earth metal ions: magnesium, calcium and barium, which are known to be difficult or impossible to convert into complex compounds by other means.

The complexes formed by complexons with most metal cations are very stable, which ensures almost complete binding of the metal being determined into the complex.

Volumetric analytical methods of analysis are characterized by simplicity and speed, which is of decisive importance in the practice of industrial laboratories. But before the introduction of complexons, only a limited number of metals could be determined by volumetric analytical methods. Complexons, on the other hand, make it possible to determine almost all metals by volumetric methods. Only EDTA forms complexes with 44 cations, of which only Ag^+, Hg^{2+}, Ba^{2+} and alkali metal cations are usually not determined by complexometry.

The great advantage of complexons is that in some cases it is possible to titrate some cations in the presence of others, without resorting to their preliminary separation.

Complexons, being acids or their acidic salts, when interacting with cations, regardless of their oxidation state, form hydrogen ions, for example:

$$Ca^{2+} + H_2Y^{2-} \rightarrow CaY^{2-} + 2H^+$$

Therefore, titration with complexones can be carried out using the neutralization method using acid-base indicators.

Complexometrically, it is possible to determine not only cations, but also anions. For example, a phosphate ion in the solution being analyzed can be precipitated with a magnesium salt, the precipitate can be separated, dissolved, and magnesium can be titrated in the resulting solution with a working solution of the complexone.

Complexometry places high demands on the purity of the reagents used and distilled water, for which it is better to use bidistillate obtained in a chemical-resistant glass apparatus.

The analytical properties of complexons are not limited to their use in volumetric analysis. They make it possible to facilitate many determinations in gravimetric analysis, since they can bind interfering ions into practically undissociated complexes, freeing the analyst from separating them by precipitation.

In conclusion of the review of the analytical properties of complexons, it should be noted their applicability in physicochemical methods of analysis - in photometry, potentiometry, polarography, etc.

1.5 Theoretical foundations of the complexometric method

The complexometry method is based on the formation of complex compounds of the analyzed cations with organic reagents - complexones.

In complexometric analysis, Trilon B is most often used as a working substance.

Trilon B is the disubstituted sodium salt of organic ethylenediaminetetraacetic acid.

Trilon B is the brand name of the substance; it is also called chelaton, versen, complexon III.

Abbreviated designation for the Trilon B molecule: Na2H2Tr.

This compound easily forms strong intracomplex salts with many cations. Salts are formed, on the one hand, due to the replacement of carboxyl groups with hydrogen by a metal, and on the other, due to the formation of coordination bonds between metal ions and nitrogen atoms.

During complexometric titration, a titrated solution of complexone is gradually added to a solution containing the ions being determined. As titration proceeds, the ions being determined are bound into a complex, and at the equivalence point they are practically absent from the solution. The reaction can be written in general form as follows:

$$Mg^{2+} + Na_2H_2Tp = Na_2MgTp + 2H^+$$

In order for the complexation reaction to proceed to completion, it is necessary to bind the released hydrogen ions. Therefore, during titration, a mixture of ammonium chloride and ammonium hydroxide - an ammonia buffer solution - is added to the analyzed solution.

To determine the end of titration, indicators are used - substances that form colored compounds with calcium and magnesium ions or with one of these cations. Such indicators are acidic chromium blue K, which gives a transition from pink to gray-blue color at pH = 10-11; magnesone and eriochrome black T, also called special black chrome ET00, changing color from wine red to blue; murexide, etc.

Indicators have different sensitivity, i.e. their colored compounds with calcium and magnesium ions occur at different, but specific for a given indicator and for selected conditions, concentrations of these ions (Table 1.1). For example, eriochrome black T forms a colored compound with calcium at a concentration of this ion of about 7 μg - eq/l; in relation to magnesium ions, this indicator is more sensitive, and color appears already at 4 – 5 μg-equiv/l.

At the same time, if you take a series of solutions with different concentrations of magnesium, for example 0; 0.2; 0.5; 0.7; 1.0; 1.5 μg - eq/l, then when adding the indicator chromium dark blue or chromium blue K to such solutions, you can visually distinguish the difference in the shades of the resulting colors.

In this way, small hardness values can be determined by visual colorimetry. To increase sensitivity, you only need to first convert calcium hardness to magnesium hardness. This can be done by adding a solution of magnesium trilonate to the liquid being analyzed. Since the complex with calcium has greater strength (Table 1.1), the following reaction will occur:

$Ca^{2+} + Na_2MgTr. \rightarrow Mg^{2+} + Na_2CaTr.$

and calcium ions will be replaced in the analyzed water by magnesium ions in an equivalent ratio.

The stability of the complex depends significantly on the pH of the solution. Therefore, complexometric titration is carried out in a given pH range using various buffer solutions.

The complexometry method can be used to determine the cations of magnesium, calcium, zinc, aluminum, barium, lead and many others - more than 40 different cations. This method is widely used to determine water hardness.

1.6 Method for determining water hardness using the complexometric method

1.6.1 Essence of the method

The method is based on the formation at pH=10±0.2 of a strong, colorless complex compound of Trilon B with calcium and magnesium ions. At the equivalent titration

point, all calcium and magnesium ions are bound into a complex compound by Trilon B, resulting in a change in the color of the indicator from red to blue.

The sensitivity of the method is 0.5 mg - eq/l with a titration of 0.1 n

1.6.2 Sampling

Sampling is an important part of the analysis, a necessary condition for the correctness of the results obtained.

The main principles that must be observed when collecting water samples are as follows:

1. The water sample taken for analysis should reflect the conditions and location of its collection. When sampling surface water, it is necessary to study the surrounding area and take water samples above and below the wastewater discharge. If there is a fitting, samples from pipelines are taken so that the rate of water flowing out of the pipeline coincides with the sampling rate. According to the purpose of the analysis, single and mixed (average) samples are taken over a certain period, merging single samples taken from the same place at regular intervals. Sometimes average samples are taken simultaneously from different places of the object under study and merged together. The final volume of the average sample must be proportional to the water flow and is determined from the conditions of the given list of definitions.

2. The sample volume must be sufficient and consistent with the analytical method used. For an incomplete analysis, in which only a few components are determined, it is enough to take 1 liter of water. For a more detailed analysis, you should take 2 liters of water.

3. Water samples are taken in glass or polyethylene bottles with a well-selected stopper, and in the presence of large impurities - in tin cans or jars with a wide neck. The dishes used for sampling must be washed with a chrome mixture and rinsed thoroughly with tap water and then with distilled water. Before sampling, the dishes are rinsed several times with the test water.

4. Sampling, transportation conditions and storage periods are determined based on the conditions of no changes in the content of the components being determined or in the properties of water. It must be taken into account that neither preservation nor fixation ensures a constant composition of the sample for a long time.

The purpose of these operations is to maintain the content of the relevant component unchanged for the time required for delivery and processing of the water sample. Analysis should begin as soon as possible after sampling.

Lecture No. 25

Titration by precipitation method

Precipitation titration is a quantitative titrimetric method for analyzing the test sample. The essence of the method comes down to the interaction between the analyzed ions and the titrant with the formation of poorly soluble compounds that precipitate. Precipitation titration makes it possible to determine the content of anions that can be precipitated by metal cations, and vice versa, the content of metal cations that are titrated with anions that give insoluble salts. The presented method is also called sedimetric titration or sedimetry.

Requirements for precipitation titration

To achieve high accuracy of the results obtained by this method, a number of conditions must be met. The requirements for a precipitation titration relate directly to the reaction, the precipitate formed, and the end point of the titration.

Reaction requirements:

- the starting reagents must be completely soluble in an aqueous medium, forming transparent solutions;
- the interaction between the titrant and the analyte should lead to the formation of a precipitate;
- the reaction must proceed practically quantitatively;
- the process must occur quickly and at room temperature;
- no by-products should be formed during the reaction.

Requirements for the resulting sediment:

- low solubility, less than 10-4 mol/l (PR <10-8);
- strict stoichiometric composition;
- The formation of supersaturated solutions should not occur.

Titration end point requirements:

- must be unambiguously recorded in the presence of indicators or using physicochemical methods.

Precipitation titration curve

The data obtained during the analysis is displayed in the form of a precipitation titration curve, which graphically shows the change in the concentration of the analyte as a function of the amount of titrant added. For convenience, the concentration of the component being determined is expressed as a logarithmic function.

If the original compound contains several compounds that interact with the titrant, then the titration curve will have several inflection points.

Types of precipitation titration

Precipitation titration methods can be classified:

- by types of analyzed compounds;
- by titration method;
- according to the titrants used;
- according to the method of recording the end of the analysis.

Classification of methods by types of analyzed compounds

Using precipitation titration, you can determine the quantitative content of the following cations and anions: Ag+, Ba2+, Hg2+, Pb2+, Zn2+, Cl-, CN-, SCN-, SO42-, PO43-.

This type of classification shows which substances are determined by precipitation titration.

The most popular studies in various industrial sectors are analyzes to determine the content of chlorides, sulfides and silver.

Classification of methods according to titration method:

- direct;
- the opposite.

When performing precipitation titrations, both forward and reverse titration methods can be used. In direct titration, the solution being analyzed is titrated, and calculations are performed in accordance with the volume of titrant consumed. In the case of back titration, a precisely known excess of a substance is added to the test solution, which forms an insoluble precipitate with the component being determined, and then the resulting mixture is titrated and the amount of unreacted substance is determined.

Classification of methods according to the titrants used

Depending on the titrants used, the following precipitation titration methods are distinguished:

- mercurometry
- ferrocyanidometry
- thiocyanometry
- bariometry
- argentometry

- nitritometry

Methods for fixing the titration end point:

- without indicator (clarification method and equal turbidity method);
- with metallochromic indicators (they form colored complexes with the titrant);
- with adsorption indicators (organic substances that are adsorbed by the sediment at the equivalence point and color it);
- physicochemical determination (potentiometry).

The advantage of potentiometry

Various methods of precipitation titration, with or without the use of various indicators, make it possible to quite accurately determine the content of individual ions in the composition of the sample being studied. But only the potentiometric method allows for differentiated titration of a mixture of compounds being determined (for example, a mixture of halides). In addition, the results of the analysis are not influenced by the human factor, as happens in the presence of an indicator, when the result can be influenced by the operator's individual perception of the color transition.

Acid-base (pH indicators) are organic acids or bases that change color when the acid or base is neutralized at or near the equivalence point.

Requirements for them:

1. The color change of the indicator must occur within a narrow pH range.
2. The color should change sharply and near the equivalence point.
3. The coloring should be intense.
4. The color change must be reversible.
5. The amount of working solution that changes the color of the indicator should be small so that the analysis results are not distorted.

The reason for the change in the color of the indicator during titration could not be explained for a long time.

And only in 1894 Oswald, based on the theory of electrolytic dissociation of Arrheunius, created*ion theory*indicators, according to which acid-base indicators are weak organic acids HInd or bases IndOH, dissociating in solutions, and the colors of the molecular and ionic forms are different.

$$HInd \Leftrightarrow H^+ + Ind^-$$

$$IndOH \Leftrightarrow Ind^+ + OH^-$$

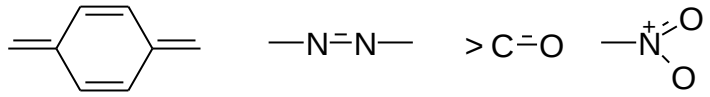
$$HInd \Leftrightarrow H^+ + Ind^-$$

The color of a solution in which the indicator is in molecular form (HInd) differs from the color of a solution in which the indicator is in ionic form (Ind -). Thus, the molecules of phenolphthalein HInd are colorless, and its Ind anions are colored crimson. It is enough to add 1-2 drops of alkali to a solution containing phenolphthalein, and the introduced OH- ions will begin to bind H+ cations to form a weak electrolyte - water molecules. In this case, the dissociation equilibrium of the indicator will shift to the right, and the accumulation of Ind anions will cause the solution to turn crimson.

Methyl orange is a two-color indicator, a sulfonic acid whose non-ionized molecules are red and the anions are yellow. The ionic theory of indicators very simply and clearly explains the reason for the change in the color of indicators under the influence of the introduction of H+ or OH- into the solution. An important advantage of it is also the fact that it allows for quantitative interpretation. However, it does not explain all the properties of indicators. For example, it turned out that the color of organic compounds depends on the structure of their molecules and that, therefore, it can only change as a result of some intramolecular rearrangement that changes the structure of the indicators. As a result of a number of studies, another, the so-called chromophore theory of indicators, emerged.

But at the same time, it did not answer the question - why, when the color changes, the structure of the indicator also changes.

The next stage was*chromophore theory*Hantzsch indicators, created on the basis of the theory of color of organic compounds, according to which the color of organic substances is explained by the presence in their structure of certain functional groups called chromophores (usually containing double bonds):



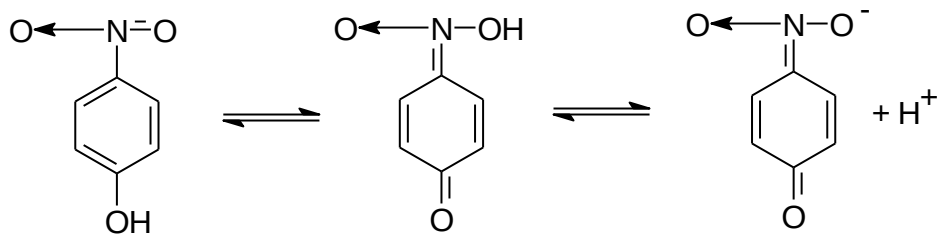
xenon azo group carbonyl nitro group

as well as auxochromes, which by themselves are not capable of imparting color to the compound, but, present together with chromophores, they enhance their effect, deepening the intensity of the color caused by them:

-HE, >NH, >N–$(CH_3)2$, $–NH_2$, $–OC_2H5$

According to Ganch, the change in color of the indicator is explained by a change in its structure due to intramolecular rearrangement, which is reversible and is called tautomeric isomerism. If during this rearrangement groups (chromophores, auxochromes) appear (or disappear) that affect the color, then it changes. According to the chromophore theory, in a solution of any acid-base indicator there are various tautomeric forms of it, which have different colors and are in equilibrium with each other.

We illustrate the theory under consideration using the example of the paranitrophenol indicator, the structure of which is much simpler than the structure of other commonly used indicators. In this case, the following tautomeric transformation occurs:



Colorless yellow
- nitrophenyl alkaline
in an acidic environment Wednesday

As can be seen from the above diagram, the essence of this transformation is that the benzene structure of the indicator transforms into a quinoid one. It is the formation of the quinoid structure that causes the color change of paranitrophenol when the solution is alkalized. When it is acidified, the equilibrium between both tautomers shifts in the opposite direction and theThe diluted indicator solution becomes discolored.

The change in color of other indicators is explained in the same way from the point of view of the chromophore theory.

As can be seen from the above, the ionic and chromophore theories cover the processes occurring with indicators in completely different ways, and at first glance seem incompatible with each other. However, they do not exclude, but, on the contrary, complement each other quite successfully.

Indeed, it can be considered firmly established that a change in color in indicators is associated with a change in their structure. Why does a change in structure occur when acids or alkalis are added to solutions? To explain this, we will have to turn to the ion theory of indicators. In full agreement with this theory, one (and sometimes both) tautomeric forms of indicators turn out to be either a weak acid, or a weak base, or an amphoteric substance. Thus, in the case of p-nitrophenol, its yellow tautomer is an acid. This will become obvious if we pay attention to the fact that the -OH group in the molecule of this tautomer is part of the O←N-OH group, i.e., it is associated with oxidized nitrogen, as in nitrogen molecules (O←N-OH) or nitrous (O=N—OH) acid. Analogies in structure must also correspond to analogies in properties, which is reflected in the fact that all three compounds have acidic properties, that is, they are capable of eliminating the hydrogen atom of the hydroxyl group in the form of an H+ ion in aqueous solutions.

Therefore, in a solution of p-nitrophenol, along with equilibrium (I), there must also be an ionization equilibrium (II) between both tautomers.

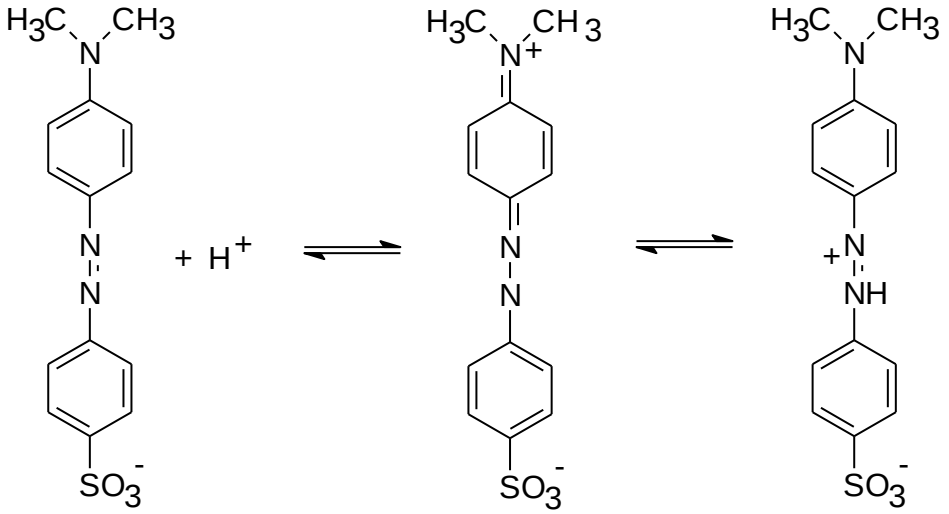
In the process of development of science, both theories are combined into a single ion-chromoform theory of indicators, according to which acid-base (pH) indicators are organic substances of an acidic or basic nature, which are weak electrolytes, which, at a strictly defined pH value of the environment, shift their dissociation equilibrium to side of accumulation of ionic or molecular forms and simultaneously undergo intramolecular rearrangement, and therefore change their color.

It should be borne in mind that while the ionization equilibrium of the indicator is established almost instantly, the process of tautomeric transformation occurs over time.

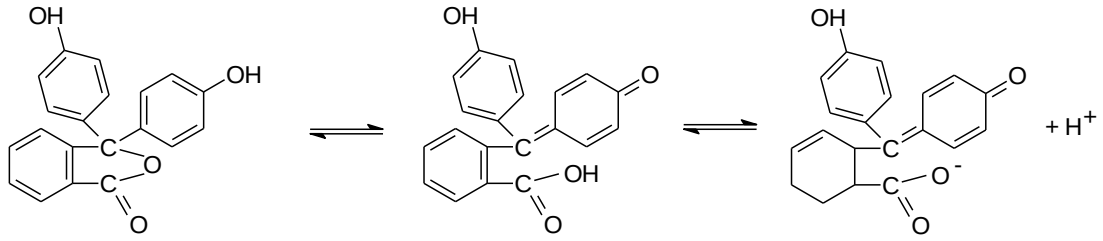
Therefore, the change in color of indicators does not always occur quickly enough. This circumstance is one of the most convincing evidence of the presence of a tautomeric transformation when the color of indicators changes; it would be completely incomprehensible from the point of view of the ion theory of indicators. It is obvious that only those indicators that change color at a sufficient rate can be used in titrimetric analysis.

Methyl orangerefers to the main indicators, more precisely, it is amphoteric, since its molecules contain both acidic SO3H and basic N(CH3)2 groups. When ionized, methyl orange molecules form amphoteric ions ("amphions"), which simultaneously carry both positive and negative charges:

These ions accumulate when the solution becomes acidic and give it a pink color. When the solution is alkalized, the indicated amphoteric ions interact with OH-ions, accompanied by a change in the structure of the indicator and a transition in its color from pink to yellow:



yellow uniform red uniform
in an alkaline environment in an acidic environmentPhenolphthalein



colorless raspberry quinoid form
lactone form in an alkaline environment
in an acidic environment

Acid-base indicators are characterized by a certain color transition interval, since their color change occurs in a narrow pH range, depends on the nature of the indicator itself and does not depend on the nature of the regulating acids and bases.

For titrimetric analysis, two quantitative characteristics are important: the pH range of color measurement and the titration index. Let's consider both characteristics.

The pH value at which the most dramatic change in the color of the indicator occurs and the titration ends is called the titration index pT (usually located in the middle of the color transition interval, constant for the indicator).

pH indicators	transition interval	pT	color change
methyl orange	3.1-4.4	4.0	Red Yellow
methyl red	4.2-6.2	5.0	Red Yellow
litmus	5.0-8.0	7.0	Red Blue
bromothymol blue	6.0-7.6	7.0	yellow --- blue
neutral red	6.8-8.0	7.0	Red Yellow
phenolphthalein	8.2-10.0	9.0	colorless --- bright pink
thymolphthalein	9.4-10.6	10.0	colorless blue

To enhance the contrast of the color transition, mixed indicators are used: methyl orange + methylene blue (2, 5, 1) → green → violet.

The indicator readings may be influenced by the following factors:

1. Temperature. When it changes, the ionization constant and, accordingly, pT change.
2. The presence of non-electrolytes (organic solvents, protein substances), which cause a change in the Kn of titratable acids and bases, changing their effect on indicators.
3. Quantity of indicator. The higher its concentration, the slower the transition from one form to another.
4. Titration order. For example, with methyl orange it is more convenient to titrate a base with an acid, and not vice versa, since the color transition from yellow to red is much clearer than from red to yellow.

To accurately establish the equivalence point in acid-base methods, it is necessary to select the correct indicator.

The rule for selecting an indicator is: pT=pHt.e., that is, it is necessary to select an indicator with a titration index equal to the pH of the equivalence point. It is possible to approximately select an indicator empirically, based on the properties of the neutralization reaction products. Your product is acidic in nature - you need an indicator that changes color in an acidic environment; if the product is of a basic nature - in the main environment.

$CH_3COOH + NaOH \Leftrightarrow CH_3COONa + H_2O$ pH > 7

phenolphthalein from colorless to pink (pT = 9)

$NH_4OH + HCl \Leftrightarrow NH_4Cl + H_2O$ pH < 7

methyl orange from yellow to orange (pT = 4)

$NaOH + HCl \Leftrightarrow NaCl + H_2O$ pH = 7

bromothiol blue from blue to yellow (pT = 7)

neutral red from red to yellow (pT = 7)

A more accurate choice of indicator can be made using the titration curve - a graph of the change in pH of the solution depending on the volume of added titrant.

The titration curve allows you to:

1. Monitor the change in pH during the titration process.
2. Study the influence of concentrations of reactants and temperature on the titration process.
3. Set the end of the titration.
4. Choose the right indicator.

To construct a graph, the amount of added titrated solution is plotted on the abscissa axis, and the pH value corresponding to a given titration point is plotted on the ordinate axis.

The pH value is found using the formula for calculating pH in aqueous solutions of acids and bases, buffer mixtures and hydrolyzing salts.

When constructing titration curves, four main areas are distinguished:

1. Before titration begins, where the pH value is determined by the concentration of the compound being analyzed.
2. To the point of equivalence.
3. At the point of equivalence.
4. After the equivalence point, where the pH value is determined by the concentration of the titrant.

At intermediate points, the factors determining the pH of the system are different and depend on what substance is being titrated.

Depending on the relative strength of the acids and bases involved in the neutralization reaction, several titration cases are distinguished, each of which is modeled by its own titration curve:

1. A strong acid is a strong base.
2. A weak acid is a strong base.
3. A strong base is a strong acid.
4. A weak base is a strong acid.

Objects of titration can be salts of various acids and bases, as well as polybasic acids and polyacid bases.

Lecture No. 27

Optical analysis methods

The task of analytical chemistry is to determine the content of certain substances in the system under study using the fastest, most accurate and rational methods. Depending on the tasks assigned, a reaction is used that either only detects their presence or allows one to

determine their quantity in the system. In the first case, we are dealing with qualitative, and in the second, with quantitative analysis.

Physicochemical methods of analysis are based on the relationship between the composition of the system and its physical and physicochemical properties.

Physicochemical methods of analysis are classified according to the properties of the system used. Optical analysis methods use the relationship between the optical properties of a system:

1. Light absorption.
2. Light scattering.
3. Refraction of light.
4. By rotating the plane of polarization of plane-polarized light.
5. The secondary glow of the substance – and its composition.

These include respectively:

1. Colorimetric analysis.
2. Nephelometric and turbidimetric analysis.
3. Refractometric analysis.
4. Polarimetric analysis.
5. Luminescent analysis.

Optical methods of analysis include physicochemical methods based on the interaction of electromagnetic radiation with matter. This interaction leads to various energy transitions, which are recorded experimentally in the form of absorption of radiation, reflection and scattering of electromagnetic radiation. Optical methods include a large group of spectral analysis methods.

In the methods of atomic spectroscopy we deal with narrow line spectra, and in the methods of molecular spectroscopy we deal with wide, weakly structured spectra. This determines the possibility of their use in quantitative analysis and the requirements for measuring equipment - spectral instruments.

Colorimetric method of analysis

An analysis method based on a comparison of the qualitative and quantitative changes in light fluxes as they pass through the test and standard solutions is called the colorimetric method of analysis.

It is more correct to call this type of chemical analysis absorption spectral analysis, since it is essentially based on measuring the attenuation of the light flux resulting from the selective absorption of light by the substance being determined. There are spectrophotometric and photometric methods of absorption analysis. The spectrophotometric method is based on measurements in a monochromatic flow of light (light of a certain wavelength). The photometric method is based on measurements in a non-strictly monochromatic beam of light. The instruments used for measurements are photoelectric colorimeters and spectrophotometers.

A photoelectric colorimeter is a universal instrument and is intended for determining the concentration of colored solutions, suspensions, emulsions, and colloidal solutions by comparing two light fluxes passing through the reference and test sample. The schematic diagram of the FEK-M photocolorimeter is shown in Fig. 1.

Spectrophotometers are devices that make it possible to measure the light absorption of samples in beams of light with a narrow spectral composition (monochromatic light). Spectrophotometers allow you to decompose white light into a continuous spectrum, select from this spectrum a narrow interval of wavelengths, within which the light beam can be considered monochromatic (the width of the allocated spectrum band is 1 - 20 nm), pass the isolated beam through the analyzed solution and measure the intensity with a high degree of accuracy this bunch.

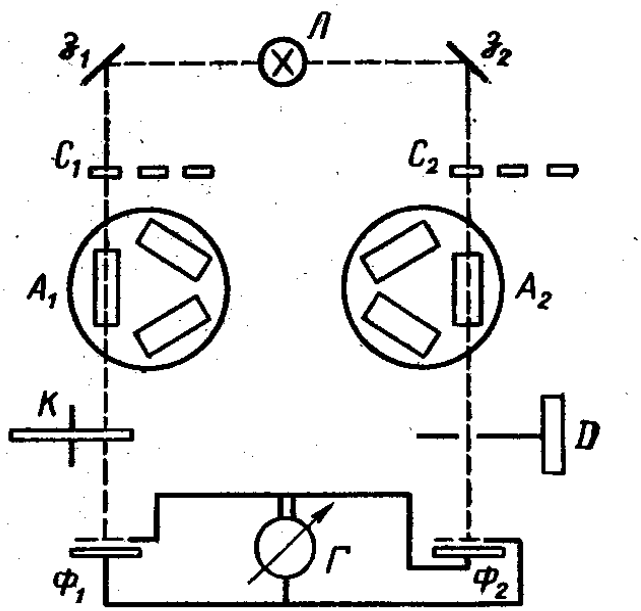
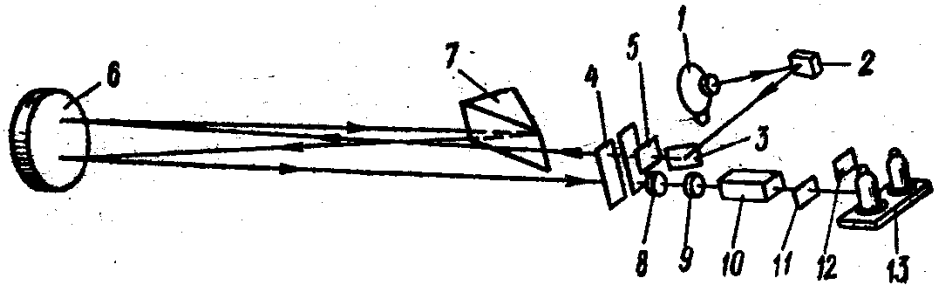


Рис. 35. Принципиальная схема фотоколориметра ФЭК-М:

Л—лампа, $з_1$ и $з_2$—зеркала, C_1 и C_2—светофильтры, A_1 и A_2— кюветы в кюветодержателях, *К*—оптический клин, *D*—диафрагма. $Ф_1$ и $Ф_2$ — фотоэлементы, *Г*—гальванометр

Rice. 1

The absorption of light by a colored substance in a solution is measured by comparing it with the absorption of a zero solution. As an example, Figure 2 shows the optical diagram of the SF-4 spectrophotometer.



Оптическая схема спектрофотометра СФ-4:
1—источник света, *2*—конденсор, *3*—зеркало, *4*—щель, *5*—кварцевая пластинка, *6*—объектив, *7*—призма, *8*—линза, *9*—светофильтр, *10*—кювета, *11*—кварцевое стекло, *12*—шторка, *13*—фотоэлементы

Rice. 2

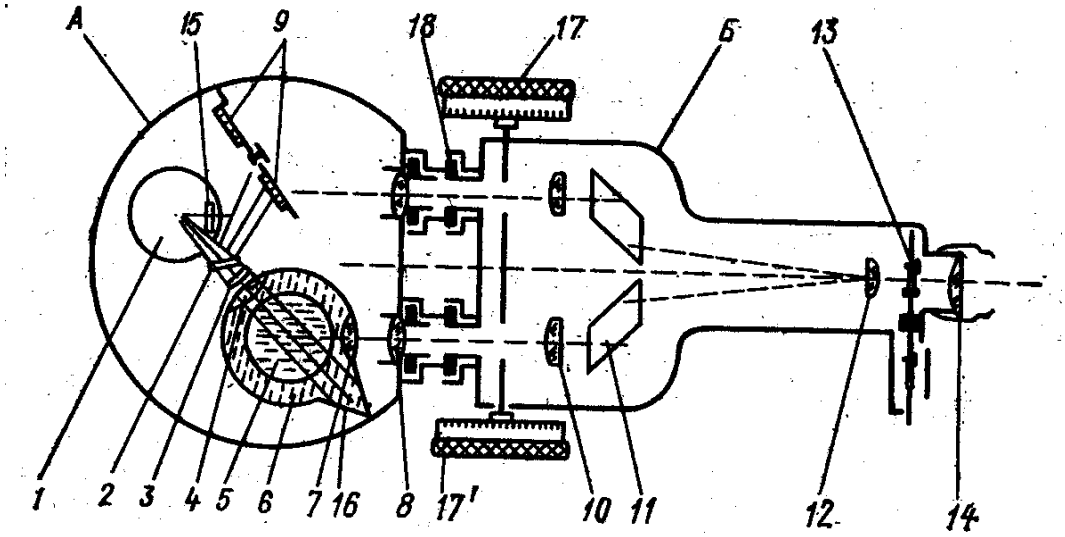
Nephelometric and turbidimetric methods of analysis

When a beam of light passes through a suspension of tiny solid particles in a solvent, i.e. through a dispersed system, lateral scattering of light is observed, due to which the light passing through the medium has the appearance of a cloudy strip. Its turbidity is explained by the scattering of the light beam due to various reasons and depends on the size of the suspended particles. If the linear dimensions of the particles are greater than the length of the incident light wave, then the scattering of light is due to the refraction of light at the particle-solvent interface and the reflection of light by the particles. If the length of the incident light is large compared to the linear dimensions of the particle, then diffraction of the light wave is observed, bending it around the particle. Two related analytical methods for determining the concentration of a substance are based on this fact, that the intensity of scattered light increases with the number of scattering particles: nephelometry and turbidimetry.

The nephelometric method of analysis is based on measuring the intensity of the light flux resulting from the scattering of light incident on a suspension.

The turbidimetric method of analysis is based on measuring the attenuation of the light flux passing through the suspension.

Nephelometric measurements are mainly carried out using nephelometers - instruments similar in design to photometers, but with a device for observing scattered light at an angle of 90°to the direction of the incident beam. Figure 3 shows the optical diagram of the NFM nephelometer



Оптическая схема нефелометра НФМ:

А—нефелометрическая приставка, *Б*—фотометрическая головка, *1*—лампа на 8 *в*, *2*—пластинка, разделяющая световой поток, *3*—цилиндрическая линза, сужающая световой поток при исследовании малых объемов, *4*—конденсор, *5*—кювета, *6*—камера с дистиллированной водой, *7*—объектив нефелометрической приставки, *8*—линзы приставки, *9*—рассеиватели, *10*—объективы фотометрической головки, *11*—призмы, *12*—призма, сводящая световые пучки к одной оси, *13*—светофильтры, *14*—окуляр, *15*—красный светофильтр (вводится в ход лучей при исследовании флюоресцирующих образцов), *16*—светоловушка, *17*, *17'*—барабан правой и левой диафрагмы, *18*—промежуточная трубка с насадкой

Rice. 3

For turbidimetric measurements, any photoelectric colorimeters and spectrophotometers can be successfully used.

Refractometric method of analysis

Refraction, or refraction, is the change in the direction of the rectilinear propagation of light when passing from one medium to another.

Refractometry is the measurement of the refraction of light. The refraction of light is assessed by the value of the refractive index, which depends on the composition of individual substances and systems, on the concentration and which molecules the light beam encounters on its path, since under the influence of light the molecules of different substances are polarized differently. It is on this dependence that refractometric analysis is based.

Refractometers are devices used to measure the value of the refractive index equal to 90°. As an example, Figure 4 shows the optical diagram of the IRF-454 refractometer.

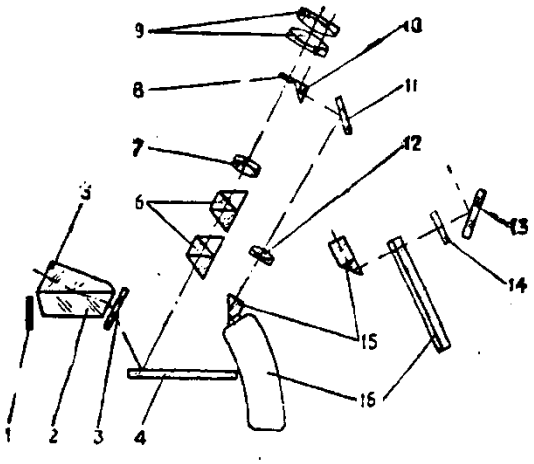


Схема оптическая рефрактометра ИРФ-454:

1—зеркало; 2—призма измерительная; 3—стекло защитное; 4—зеркало; 5—призма осветительная; 6—компенсатор; 7—линза склеенная; 8—сетка; 9—окуляр; 10—призма АР-90°; 11—зеркало; 12—объектив; 13—зеркало; 14—светофильтр; 15—призма; 16—шкала

Rice. 4

Polarimetric method of analysis

The polarimetric method of analysis is based on measurements related to the phenomenon of light polarization (the direction of light vibrations). The plane passing through the lines corresponding to the direction of oriented oscillations and the direction of oriented oscillations and the direction of propagation of the light wave is called the plane of oscillation, the plane perpendicular to it is called the plane of polarization.

It is known that substances are called optically active, the passage through which plane-polarized light is associated with the so-called rotation of the plane of polarization, with its rotation through a certain angle.

The polarimetric method of analysis is based on the dependence of the rotation angle of the plane of polarization of plane-polarized light on the concentration of an optically active substance in solution.

Optically active substances are found in two modifications - dextrorotatory and levorotatory.

A device for measuring the angle of rotation of the plane of polarization (polarimeter) must combine a device for producing polarized light (polarizer) with a device that would allow analyzing the phenomenon (analyzer) - finding the direction of rotation and the magnitude of the angle by which the plane of polarization turned out to be rotated as a result of passage light through an optically active substance.

Luminescent method of analysis

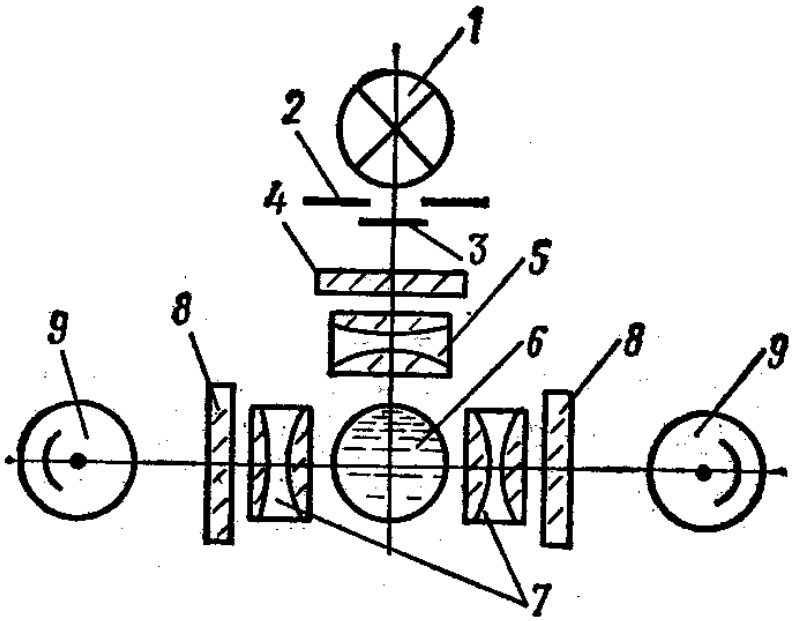
The ability of atoms and molecules to absorb energy coming to them from the outside causes a new energy state of the substance, which is called excited. Excess energy of atoms

or molecules obtained during excitation can be spent on the removal of electrons - ionization of the substance; for any photochemical reactions; to heat the substance; in addition, excited atoms or molecules are capable of all or part of the excess energy in the form of light. Some substances glow without heating at room temperature, which is called cold glow or luminescence. Luminescence phenomena are diverse in properties and origin.

In analytical practice, the most widely used is photoluminescence, or fluorescence, based on the glow of a substance upon absorption of radiant or light energy.

To excite luminescence, various sources of ultraviolet radiation are used. The most widely used sources of ultraviolet light are mercury and mercury-quartz lamps.

The fluorimeter is designed for quantitative analysis of fluorescent substances in solution. The optical design of the EV-3M fluorimeter is shown in Figure 5.



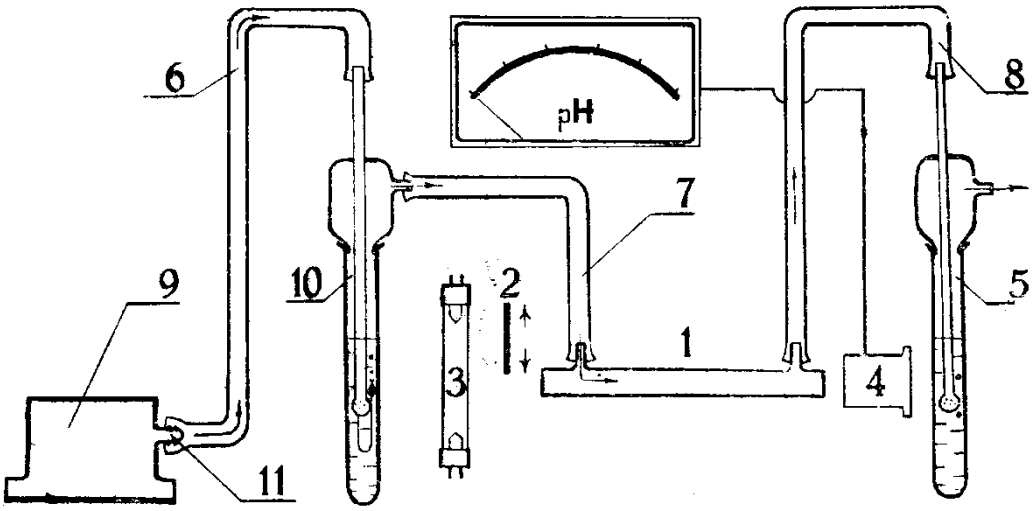
Флуориметр ЭФ-3М:
1 — кварцевая лампа, *2* — диафрагма, *3* — заслонка, *4* — первичный фильтр, *5* — кварцевая оптика, *6* — пробирка с испытуемым раствором, *7* — кварцевая оптика, *8* — вторичные светофильтры, *9* — фотоэлементы

Rice. 5

A photoelectric luminescent photometer is designed to measure the glow intensity of crystal phosphors.

Carrying out the most critical luminescent analyzes that require high accuracy, reproducibility and study of the spectral characteristics of the analyte is possible using modern photoelectric methods for measuring light intensity in combination with spectral instruments.

Mercury analyzer “Yulia – 2”



Функциональная схема

1 — кювета; 2 — шторка лампы; 3 — лампа; 4 — фотоэлемент; 5 — пробирка с барботером для поглощения отработанной ртути; 6, 7, 8 — воздуховоды; 9 — микрокомпрессор; 10 — пробирка с барботером для пробы; 11 — штуцер микрокомпрессора

Lecture No. 28

Molecular spectroscopy methods

For atomic spectroscopy, it is necessary to destroy a substance into individual atoms, but for molecular spectroscopy it is impossible, so absorption spectra are usually studied in the UV, visible and IR ranges at ordinary temperatures. Atoms and molecules obey the laws of quantum mechanics. They can be in states with different energies due to transitions of electrons to higher levels, and for molecules also due to vibrations and rotations. The energy levels of each type of movement are discrete and characterized by quantum numbers. The energy of a diatomic molecule consists of electronic, vibrational and rotational energy,

E = Eel + Ekol + Ev.

and

Eel >> E oscillation >> Evrashch

The figure shows an example of the energy levels of a diatomic molecule. Two electronic states are shown - the main one and the first excited one. Each state has sublevels due to vibrational states, including sublevels due to rotational ones. There are many levels compared to atoms, many transitions are possible between them, close in frequency, they merge with each other and instead of lines, stripes are observed. Atomic spectra are linear, molecular spectra are striped.

Molecular spectra are studied using two types of spectrometers - UV (combined with visible) and IR.

UV and visible spectroscopy

Electronic absorption spectra associated with the transition of electrons to higher energy levels are studied. Spectra of organic molecules are observed that contain double or triple bonds, or atoms

with lone electron pairs (absorbing groups are called chromophores). An example in the table, which shows the wavelengths corresponding to the maximum band of the UV spectrum.

Chromophore	molecule	□max (mmk)
-Cl	CH3Cl	173
-Br	CH3Br	204
-I	CH3I	259
-N<	CH3NH2	215
-O-	CH3OH	184
-S-	(CH3)2S	210
C=C	RCH=CH2	175
C≡C	RC≡CH	187
C=C=C	C2H5CH=C=CH2	225
C=O	CH3CHO	294
N=O	C4H9NO	665
N=N	CH3N=NCH3	340

The detection of such bands in the spectra reveals the groups included in the molecule, which is important for qualitative analysis. Quantitative analysis is based on measuring the light absorption coefficient of the test solution at certain frequencies.

A UV spectrophotometer consists of a radiation source, a prism, a slit and a photocell. The source is a hydrogen lamp, that is, a direct current arc in a hydrogen atmosphere at low pressure, producing continuous radiation in a wide frequency range. Light passes through a prism and then through a slit, which selects a narrow region of wavelengths (frequencies). Next, the light passes through a cuvette - a vessel with plane-parallel transparent walls, filled with the solution under study - and hits the photocell. Light absorption coefficient is the ratio of the intensities of the light rays incident on the sample and those passing through it from the source. To correct for light absorption by the solvent, use a reference sample with pure solvent. Light absorption is measured using a two- or single-beam scheme. In the first case, the light flux of the source is divided into 2 fluxes of equal intensity and one is passed through the test solution, the other through the standard one, then the intensities of the output fluxes are compared. With a single-beam scheme, both solutions are installed in turn.

The same device is used to record spectra in the visible region; an incandescent lamp is used as a source.

For all methods of molecular spectroscopy, the Bouguer-Lambert-Beer law is valid:

$I=I0 \exp(-\square lc)$

or

$\ln(I0/I)=\square lc$

where □□□□molar absorption coefficient (l/mol cm), c is the concentration, l is the thickness of the cuvette, I0 is the intensity of the incident flow, I is the intensity of the outgoing flow; the ratio I0/I is called transmittance, and log(Io/I) is called optical density. If several absorbing substances are

present in a solution, then the optical density of the solution is equal to the sum of the contributions of each component.

The Bouguer-Lambert-Beer law is strictly satisfied for monochromatic radiation,

Sometimes photocolorimeters are used for measurements, which use a limited set of replaceable broadband glass filters; these devices are not spectral devices.

UV-visible spectrophotometry is widely used in substance analysis; in particular, for the determination of colored compounds of a number of metals, as well as As, P, for the determination of some functional groups of organic compounds, such as phenols and compounds with multiple chemical bonds.

To increase the selectivity of the determination, photometric reagents are used that selectively interact with the substance being determined to form a colored product. For example, when determining Fe, Mo, W, Nb, Co, etc., thiocyanates are used, and when determining copper, ammonia is used. Organic dyes are widely used as photometric reagents that form colored complexes with metal cations. Preliminary separation of components is also used.

The advantages of this spectrophotometry are the relative simplicity of the equipment and extensive experience in use. The disadvantage is low selectivity.

The minimum concentration determined by the spectrophotometric method is not lower than 10-7 M, that is, the sensitivity of the methods is average.

Vibrational spectroscopy (IR and Raman).

Infrared spectroscopy (IR)

The absorption of IR light is associated with the excitation of vibrations of atoms and groups in the molecule. In diatomic molecules, the atoms vibrate around an equilibrium position. If we assume that the restoring force is proportional to the magnitude of the displacement, as in the case of two balls connected by an elastic spring, we obtain sinusoidal oscillations and the IR spectrum of a diatomic molecule should consist of one sharp line. In fact, the oscillations are not strictly harmonic, and also appear in the spectra overtone bands with doubled, tripled, etc. frequencies, as well as with composite frequencies, and the spectra are not lined, but striped. Polyatomic molecules undergo many vibrations, during which bond lengths and angles between bonds (“stretching” and “deformation” vibrations) change, so the IR absorption spectrum is even more complex.

In many cases, the vibration frequencies of different functional groups (for example, C=O, C-C, C-H, O-H, NH) change relatively little when moving from one substance to another and are therefore called characteristic. For example, the carbonyl group C=O absorbs in the region of 1820 – 1620 cm-1, in saturated ketones about 1720, in unsaturated ketones about 1680 cm-1. The characteristic bands of different groups have different intensities, which facilitates the interpretation of the spectra. Such frequencies are used for structural group analysis of a substance.

The design of an IR spectrometer is the same as that of a UV spectrometer, but the sources of IR radiation are a ceramic rod heated by an electric current passing through it or a nichrome wire. A NaCl prism or a diffraction grating is used as dispersing elements, and photoresistors, thermistors or bolometers are used as detectors. A modern version of the IR spectrometer is the Fourier transform infrared spectrometer, which uses a fast computer process to obtain spectra with increased resolution.

IR spectrometers are used for the analysis of gaseous, liquid and solid organic and inorganic substances. Advantages of IR spectroscopy:

1) universality, that is, applicability for a very wide range of objects
2) extensive application experience;
3) relative ease of interpretation of spectra;
4) high sensitivity;
5) low-perturbation effect on the substance
6) low cost of devices.

Disadvantages: average selectivity due to the noticeable width of the bands, as well as the inability to analyze aqueous solutions, since water itself absorbs IR in a wide area, masking signals from dissolved substances.

Raman spectra

These spectra arise when a substance is irradiated with monochromatic UV or visible light. If we observe a sample through a tube, perpendicular to the direction of the incident and transmitted light, we see scattered light of the same frequency □ as the incident light - this is ordinary, or Rayleigh scattering. However, scattered light with other frequencies can also be detected □±□i, where □ is the frequency of the source radiation, □i is the vibration frequency of the molecule.

The reason for light scattering is that the incident wave induces an oscillating electric dipole in the molecule, which emits the wave. Let us consider the cause of Raman scattering. There are two electronic levels in the figure, each with vibrational sublevels. When absorbing a quantum, there are three options:

Frequencies □-□0i are called Stokes, □□□0i are called anti-Stokes. The former arise due to the transition of molecules to a higher vibrational level, the latter - to a lower one. Bands of the second (□±2□i) and higher orders also appear in the spectra. Thus, a new opportunity arises to detect molecular vibrations.

Various vibrational transitions are observed in the IR and Raman spectra. Vibrations associated with changes in the electric dipole moment of the molecules are observed in the IR spectra. Raman spectra reveal vibrations associated with changes in the polarizability of molecules, for example, vibrations of covalent bonds in H2, O2, Cl2 molecules. Therefore, the IR and Raman spectra complement each other.

Lasers (He-Ne, Ar, Kr) are used as a radiation source in Raman spectrometers. Scattered radiation is recorded at right angles to the incident laser beam. Raman spectra are presented in the form of curves of the dependence of the intensity of scattered light on the magnitude of the frequency shift of the exciting light. Laser Raman spectrometers make it possible to obtain spectra of solid, liquid and gaseous samples.

Vibrational spectra are specific and are used to identify substances. There are atlases of IR and Raman spectra for various classes of organic and inorganic substances. Since superposition of the spectra of several substances greatly complicates interpretation, preliminary separation of mixtures is necessary.

The detection limits of substances in the analysis of gases, liquids and solids by IR and Raman spectroscopy are 10-1-1% by mass.

3.3. Luminescence spectroscopy

Luminescence is the glow of a substance with a duration of at least 10-10 s, which is excessive over temperature. Called cold glow. In English-language literature the term "fluorescence" is used. In our literature, they are sometimes divided into types: when the glow stops almost simultaneously with the exciting radiation, it is fluorescence; if it continues, it is phosphorescence. The cold glow of atoms, molecules, ions, and complexes occurs as a result of the return of electrons from an excited state to a normal one. Excitation methods:

1. UV and visible radiation (photoluminescence);
2. energy of chemical reactions (chemiluminescence);
3. electron flow (cathodoluminescence);
4. radioactive radiation (radioluminescence);
5. X-ray radiation (x-ray luminescence);
6.mechanical effect (triboluminescence);

To obtain spectra, a UV source with a monochromator transmitting the selected wavelength is usually used. The luminescent radiation observed in the perpendicular direction is scanned by a monochromator, and the luminescence spectrum is recorded using a photomultiplier.

The luminescence spectra of some organic compounds have a clearly defined structure and can be used for qualitative analysis, but often the spectra consist of broad overlapping bands. The shape of the spectrum does not depend on the frequency of the exciting radiation. Advantages: high sensitivity, it is possible to determine compounds with a concentration of less than 10-3 μg/ml. The disadvantage is low selectivity.

Applications:

1) Analysis of inorganic substances. Uranium and lanthanides are determined. Organic reagents are used that form a complex with metals. For example, 8-hydroxyquinoline forms luminescent complexes with more than 25 elements (Li, Ca, Mg, Ba, Al, etc.). Rhodamine dyes are used to determine Au, In, Ga, Hg, B, Te, etc. Salicylic acid forms a luminescent complex with zinc.

2) Determination of vitamins, hormones, antibiotics.

3) Determination of carcinogens. Diagnosis of diseases.

4) Determination of seed viability (yellow and brown leaves).

5) Determination of the initial stage of rotting of fruits and vegetables.

Lecture No. 29

Methods of photometric analysis.

Photometric method of analysis

Photometric analysis refers to absorption methods, i.e. is based on measuring the absorption of light by a substance. It includes spectrophotometry, photocolorimetry and visual photometry, which is commonly called colorimetry.

Each substance absorbs radiation with certain (characteristic only for it) wavelengths, i.e. The wavelength of absorbed radiation is individual for each substance, and a qualitative analysis of light absorption is based on this.

The basis of quantitative analysis is the Bouguer-Lambert-Beer law:

$A = \varepsilon lc$

where A = –log (I / I0) = –log T – optical density;

$I_0$and I is the intensity of the light flux directed at the absorbing solution and passed through it;

With– concentration of the substance, mol/l;

l– thickness of the light-absorbing layer;

 - molar light absorption coefficient;

T- transmittance.

To determine the concentration of the analyte, the following methods are most often used: 1) molar light absorption coefficient; 2) calibration chart; 3) additives; 4) differential photometry; 5) photometric titration.

Molar absorption coefficient method. When working using this method, the optical density of several standard solutions of Ast is determined, for each solution = Ast / (lcst) is calculated and the resulting value of is averaged. Then the optical density of the analyzed solution Ax is measured and the concentration cx is calculated using the formula

$With_X$= Ax /(l).

A limitation of the method is the obligatory subordination of the analyzed system to the Bouguer-Lambert-Beer law, at least in the region of the studied concentrations.

Calibration graph method. A series of dilutions of a standard solution is prepared, their absorption is measured, and a graph is plotted in Ast – Cst coordinates. Then the absorption of the analyzed solution is measured and its concentration is determined from the graph.

Additive method. This method is used when analyzing solutions of complex composition, since it allows you to automatically take into account the influence of “third” components. Its essence is as follows. First, the optical density Ax of the analyzed solution containing the analyte component of unknown concentration cx is determined, and then a known amount of the analyte component (cst) is added to the analyzed solution and the optical density Ax + st is measured again.

The optical density Ax of the analyzed solution is equal to

A_X= l cx,

and the optical density of the analyzed solution with the addition of standard

A_{x+st}= l (cx + cст).

We find the concentration of the analyzed solution using the formula:

$With_X$= sst Ax / (Ax+st – Ax).

Method of differential photometry. If in conventional photometry the intensity of light passing through an analyzed solution of unknown concentration is compared with the intensity of light passing through a solvent, then in differential photometry the second ray of light passes not through the solvent, but through a colored solution of known concentration - the so-called reference solution.

The photometric method can also determine the components of a mixture of two or more substances. These definitions are based on the additivity property of optical density:

A_{cm}= A1 + A2 + …+ An

where Asm is the optical density of the mixture; A1, A2, An – optical densities for various components of the mixture.

Photometric analysis methods are used to monitor a variety of production processes. These methods can be used to analyze large and small contents, but their especially valuable feature is the ability to determine impurities (up to 10-5...10-6%). Absorption spectroscopy methods are used in the chemical, metallurgical, pharmaceutical and other industries, as well as in medicine and agricultural production.

The industry produces instruments for absorption spectroscopy: colorimeters, photometers, photoelectric colorimeters, spectrophotometers, etc., which use various combinations of illuminators, monochromators and light receivers.

Lecture No. 30
Atomic absorption spectrometry

Based on absorption coefficient measurement. Atoms absorb emitted quanta at the same frequencies at which they emit. A radiation source with a line spectrum is used - a lamp with a hollow cathode on which the element to be determined is deposited. Therefore, the emission spectrum of the source contains its lines. The substance under study is usually introduced in the form of a solution into the burner flame, where at a temperature of 2000 - 30000C the molecules dissociate into atoms. The absorption coefficient of gaseous atoms obeys the exponential law of intensity decrease depending on the thickness of the absorbing layer and the concentration of the substance. The concentration is determined using calibration graphs, that is, the absorption coefficient is measured for several standard solutions with different concentrations of the element being determined and a graph of the dependence of the absorption coefficient on the concentration is plotted.

The sensitivity of atomic absorption spectroscopy exceeds the sensitivity of emission spectroscopy. It is used for the analysis of many elements in various objects (steels, alloys, ores, natural waters, soils, biological samples).

Atomic absorption spectrometry is a method of quantitative elemental analysis based on measuring the absorption (absorption) of the characteristic radiation of the element being determined by unexcited atoms of the element being determined, which are in the state of atomic vapor.

During the analysis, part of the analyzed sample is transferred to the state of atomic vapor. Radiation characteristic of the element being determined is passed through this vapor. Free, unexcited atoms located in an atomic vapor absorb part of the light quanta of the transmitted radiation. Moreover, the greater the concentration of atoms of the element being determined in the atomic vapor, the greater the absorption intensity. By measuring the absorption intensity, it is possible to determine the content of the element being determined in the analyzed sample.

Thus, the analytical signal in the atomic absorption spectrometry method is the absorption intensity, i.e., a decrease in the radiation intensity.

The dependence of the intensity of the light flux passing through atomic vapor I on the concentration of absorbing sample particles c is expressed by the Bouguer-Lambert-Beer law:

$$I = I_0 \cdot 10^{-\varepsilon_\lambda l c}$$

or, introducing the value A, which is called optical density:

$$A = \lg \frac{I_0}{I} = \varepsilon_\lambda l c$$

where I0 is the intensity of incident radiation; ε_λ- absorption coefficient at wavelength λ; l is the length of the optical path.

Under controlled atomization conditions, the concentration of absorbing particles in the atomizer is directly proportional to the concentration of the element being determined in the analyzed solution, therefore the calibration curve in the atomic absorption spectrometry method can be constructed directly in the coordinates absorption intensity - concentration of calibration solutions.

1.1.2. Atomization of the analyte.

To produce atomic vapor in the atomic absorption spectrometry method, flames or electrothermal atomizers are used SLIDE 2.

A flame is produced by a chemical reaction between a combustible gas and an oxidizing gas. Methane, propane and acetylene are most often used as flammable gases, and air, oxygen, dinitrogen monoxide are used as oxidizing gases.N2O. As a result of the exothermic reaction between these substances, a large amount of energy is released in the form of heat of combustion. Flames usually burn at atmospheric pressure.

1.1.2. Absorbed radiation.

Atomic absorption lines are very narrow (10^{-3}– 10-2 nm). Therefore, when atoms are irradiated with non-monochromatic radiation, only a very small part of the light quanta is absorbed, and most of the light flux passes through the atomic vapor without changes. A technically very difficult task arises of determining a small change in the luminous flux. For this reason, atomic absorption spectroscopy cannot use radiation sources that produce a continuous spectrum.

Atomic absorption spectrometry uses radiation sources that produce line spectra. The width of the lines in the emitted spectrum must be less than the width of the lines in the absorption spectrum of the atoms of the element being determined.

The width of lines in the atomic spectrum depends on the following factors:

1) natural broadening, which is approximately 10-5 nm and is explained by the Heisenberg uncertainty relation;

2) Doppler broadening, which is approximately 100 times greater than natural. The reason for this broadening is the Doppler effect, which, as applied to atomic absorption

spectrometry, is that atoms moving in the direction of propagation of radiation absorb at lower frequencies, and those moving towards the radiation absorb at lower frequencies. Doppler broadening $\Delta\lambda$ depends on temperature T, radiation wavelength λ and atomic mass m:

$$\Delta\lambda = \frac{2\lambda}{c}\left(\frac{2kT}{m}\ln 2\right)^{1/2} \quad (1\text{-}1)$$

3) Lorentz broadening, which is two to three orders of magnitude greater than the natural broadening. This broadening is caused by collisions of atoms with other atoms or ions. The number of collisions depends on the pressure: the higher the pressure, the greater the likelihood of a collision. As a result of collisions, the spectral lines broaden due to the splitting of the energy levels of atoms.

1.1.3. Absorption of light quanta by free atoms.

In accordance with Boltzmann's law SLIDE 3

$$Nk = N\frac{g_k}{g_0}\, e^{-\frac{E_k}{kT}} \quad (1\text{-}2)$$

where Nk is the number of atoms in the excited state; N is the total number of atoms in the plasma; gk and g0 are the statistical weights of the excited and normal states; Ek is the excitation energy of the kth level, k is Boltzmann's constant; T is the absolute temperature; even at high temperatures (up to 5000 K), the overwhelming majority of free atoms are in the ground state.

Absorbing a quantum of light with energy $h\nu$, the free atom A goes from the ground state to the excited state A*:

$$A + h\nu \rightarrow A^*$$

Typically there is a transition from the ground state to a level closest to the ground state. This transition is called resonant. If unexcited atoms are exposed to radiation with a frequency ν, equal to the resonant transition frequency for atoms of a given element, then such radiation is effectively absorbed by the atoms and its intensity decreases.

The excited state of free atoms is unstable. They quickly return to the ground state, emitting light quanta. If the frequency of radiation emitted by atoms is equal to the frequency of absorbed radiation, then this process is called resonant fluorescence.

In atomic absorption spectrometry, transitions of atoms from the ground state to the energy level closest to the ground state are used, i.e. resonant transition.

1.1. Design of atomic absorption spectrometers.

1.2.1. Schematic diagram of an atomic absorption spectrometer.

The main components of the atomic absorption spectrometer are shown in Fig. 1.2.1.

Rice. 1.2.1. Main components of an atomic absorption spectrometer.

An atomic absorption spectrometer consists of a primary radiation source that produces absorbed radiation, a device for converting the analyzed sample into atomic vapor, a sample injection system, an optical dispersing system, a detector and electronic devices for collecting and processing the obtained data.

1.2.2. Sources of primary radiation.

The following requirements apply to primary radiation sources:

1) they must emit the spectrum of the element being determined;

2) the lines in the emission spectrum should be narrow;

3) the radiation must have a constant intensity;

4) background radiation should be minimal.

Considering the line width in the absorption spectra of atoms, in atomic absorption spectrometry it is necessary to use radiation sources with line widths less than 10^{-3} – 10-2 nm.

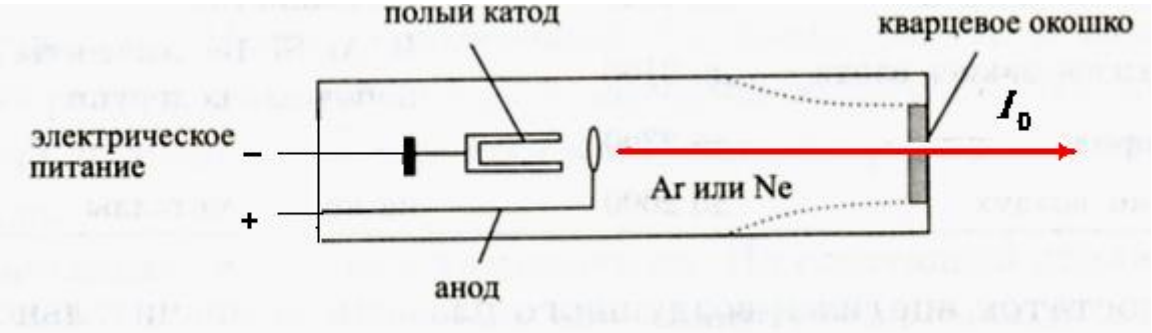
Most often, hollow cathode lamps are used to obtain absorbed radiation. Hollow cathode lamps are among the low-pressure discharge radiation sources. In such sources, light is emitted by an electrical discharge between two electrodes at a pressure of less than 100 kPa.

The width of the lines of the emission spectrum of lamps with a hollow cathode is less than the width of the lines of the absorption spectrum of the atoms being determined. It is 10^{-4} – 10-3 nm. The reasons for smaller line widths are as follows:

1) excitation of atoms occurs at lower temperatures than the temperature of atomic vapor, thereby reducing Doppler broadening (see section 1-1);

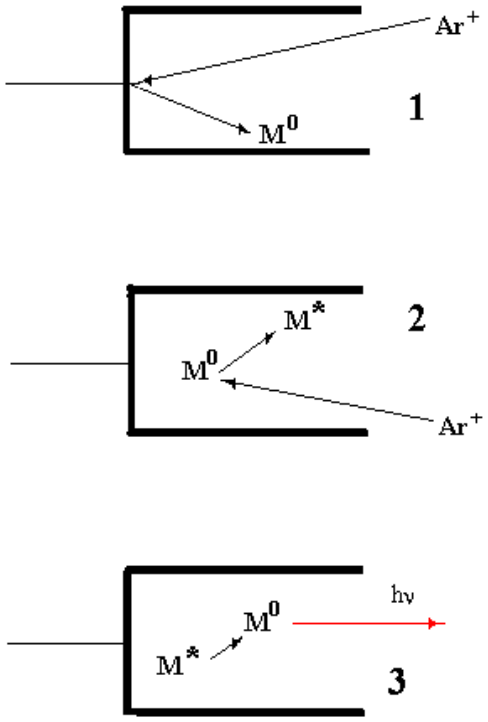
2) the internal space of the lamp is filled with a noble gas at reduced pressure (200-800 Pa), thereby reducing the Lorentz broadening.

A diagram of the device of a hollow cathode lamp is shown in Fig. 1.2.2.



Rice. 1.2.2. The device of a hollow cathode lamp.

The SLIDE 6 lamp has a cylindrical shape and is made of glass. Inside the lamp there is a cathode and anode. The cathode has the shape of a small cup with an internal diameter of 2-5 mm. The cathode is made from the element being determined in high purity. If elements have low melting points, then graphite cathodes impregnated with salts of the elements being determined are used. The anode is a metal rod. It is placed next to the cathode. To power the lamp, a high direct voltage of about 600 V and a current of up to 30 mA are used. The internal hermetically sealed chamber of the lamp is evacuated and filled with a noble gas (argon or neon) at reduced pressure (200-800 Pa). Neon is best used for the manufacture of lamps with cathodes made from elements with high ionization energies. The pressure of the noble gas inside the lamp is chosen such that an electrical discharge occurs inside the hollow cathode. When voltage is applied to the electrodes, cations collide with the surface of the cathode and cause its sputtering (Fig. 1.2.3). As a result, atoms of the element being determined appear in the electrical discharge, a small part of them goes into an excited state and emits resonant radiation. A quartz window is used to transmit this radiation.



Rice. 1.2.2. Processes in a lamp with a hollow cathode: 1 – noble gas cations knock out metal atoms from the cathode; 2 - metal atoms under the influence of noble gas cations go into an excited state; 3 – returning from an excited state to the ground state, atoms from the metal emit quanta of light

To increase the radiation intensity, hollow cathode lamps with increased voltage are used, which have auxiliary electrodes. A high-voltage discharge occurs between these electrodes, under the influence of which the number of atoms that pass into an excited state increases. When using such lamps, the radiation intensity increases by 5-15 times.

To determine some elements, mainly nonmetals, such as arsenic As, antimony Sb, bismuth Bi, selenium Se and tellurium Te, electrodeless discharge lamps are used instead of hollow cathode lamps. Their use may be due to various reasons:

1) it is impossible to make cathodes from some elements;

2) the radiation produced by non-metals belongs to the short-wave region of the spectrum; its production requires large amounts of energy, and its intensity is low.

An electrodeless discharge lamp is a quartz tube into which a small amount (1-2 mg) of the element being determined or its salt is placed. Inside the electrodeless discharge lamp there is also the noble gas argon at reduced pressure. The evaporation of an element and the transfer of its atoms to an excited state is carried out using a high-frequency field.

To increase the sensitivity of the method, it is necessary to distinguish the light emitted by the source of primary radiation from the radiation emitted by excited atoms of the element being determined in the atomizer. To do this, modulate the source voltage with a fixed frequency. Most often, pulsed power supplies for lamps with a hollow cathode are used for this purpose and the intensity of the light flux passed through the atomic vapor is measured not continuously, but only during the passage of pulses.

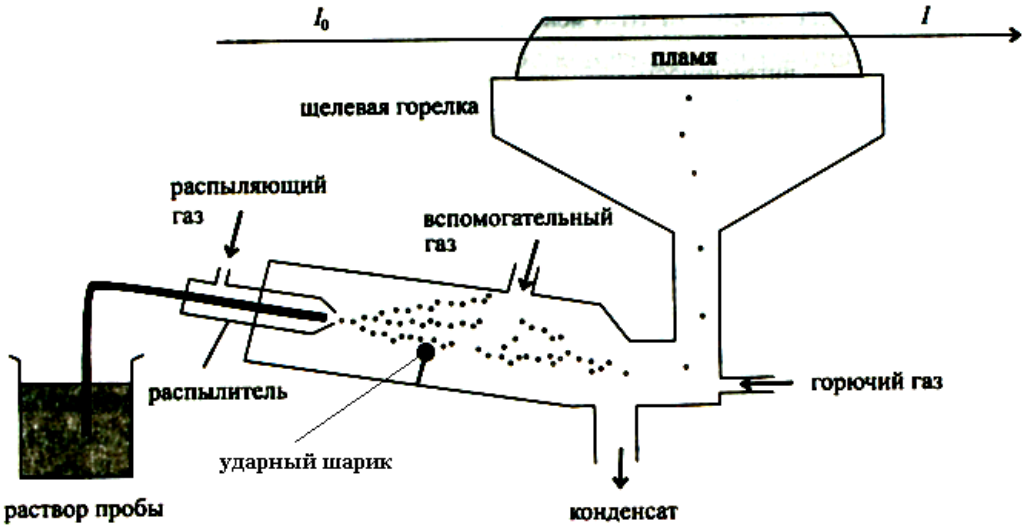
High-pressure xenon arc lamps, which emit an intense continuous spectrum that does not contain lines, are also used as radiation sources in atomic absorption spectrometry. Such continuous spectrum sources are used in multielement atomic absorption spectrometry, since they provide greater versatility in the choice of primary emission lines.

An ideal radiation source for atomic absorption spectrometry would be diode lasers that produce narrow lines of high intensity. However, at present, they can only be used to obtain spectra with wavelengths greater than 620 nm, which limits their use.

1.2.3. Atomizers are sources of free atoms SLIDE 7.

Atomizers are designed to transform the analyzed sample into an atomic state, and most of the atoms in the resulting atomic pair should be in the ground state.

The first method developed to transform a sample into an atomic state was the use of a flame. For atomic absorption spectrometry, SLIDE 8 slot burners have been developed, producing a laminar flame (Fig. 1.2.3).



Rice. 1.2.3. Atomizer – slot burner.

The gas mixture to maintain the flame consists of a combustible gas and an oxidizer gas. The oxidizer can simultaneously serve to spray the analyzed solution (atomizing gas) or be supplied to the burner separately. The most common gas mixtures for atomic absorption spectrometryare presented in table. 1.1.

Table 1.1

Compositions of gas mixtures for atomic absorption spectrometry

Gas mixture	Temperature,	Definable

Flammable gas	Oxidizing gas	K	elements
acetylene C2H2	Air	up to 2500	Majority
acetylene C2H2	dinitrogen oxide N2O	up to 3100	boron B, aluminum Al, silicon Si, beryllium Be, elements of IIIB-VB subgroups
hydrogen H2	air	up to 2300	arsenic As, selenium Se
methane CH4	air	up to 2000	alkali metals

To determine elements whose oxides easily decompose in a flame, a flame of an acetylene-air gas mixture is usually used. These elements include calcium Ca, chromium Cr, iron Fe, cobalt Co, nickel Ni, magnesium Mg, molybdenum Mo, strontium Sr and many others. However, the flame of this gas mixture has a significant drawback: it exhibits significant intrinsic absorption at wavelengths less than 230 nm. The gas mixture of acetylene - dinitrogen oxide provides a higher flame temperature than the acetylene - air mixture, therefore it is used to determine difficultly atomized and difficultly volatile elements, such as aluminum Al, silicon Si, tantalum Ta, titanium Ti, vanadium V, zirconium Zr. It should be noted that extreme caution is required when working with this gas mixture to avoid flashover. The disadvantages of the flame of this gas mixture also include high self-emission. For elements whose atoms absorb at very short wavelengths, a hydrogen-air gas mixture flame is used, in which no noticeable absorption occurs up to 210 nm. These elements include arsenic As and selenium Se. Easily atomized alkali metals can be determined using a low-temperature methane-air flame.

An integral part of the burner is a sprayer, which produces an aerosol from an oxidizing gas and small drops of the analyzed solution. To separate larger droplets, an impact ball is placed in the spray chamber. After this, flammable gas is introduced into the aerosol. An aerosol consisting of a mixture of flammable gas, oxidizing gas and small drops of the analyzed solution enters the gas burner nozzle and from it into the flame.

The following processes occur in the flame SLIDE 10:

1) evaporation of sample components;

2) dissociation of compounds into free atoms;

3) the combination of atoms of the element being determined with other atoms or radicals (an undesirable side process)

4) excitation of atoms under the influence of radiation from a primary source;

5) ionization of atoms (an undesirable side process).

When evaporating, the solvent is the first to pass into the gas state. Then the solid components evaporate. If evaporation does not occur directly, but through a melting stage, then difficultly volatile compounds can be formed: mixed oxides and phosphates. In this case, you need to use a flame of a gas mixture of acetylene - dinitrogen oxide, which has reducing properties and produces a high temperature.

For example, in the determination of calcium, the interfering influence of phosphates can be eliminated using lanthanum chlorideLaCl3 or EDTA. Lanthanum chloride binds phosphate ions into lanthanum phosphate LaPO4 and thus prevents the formation of difficultly volatile calcium pyrophosphate. With EDTA, calcium forms a complex compound that is stronger than calcium phosphate. In the flame, the organic ligand burns, releasing calcium atoms.

Evaporated compounds dissociate into free atoms. The degree of dissociation of a compound into atoms depends on the flame temperature, the dissociation energy of the compound, its concentration and the influence of foreign components.

Free atoms in the ground electronic state absorb radiation; the method of atomic absorption spectrometry is based on this phenomenon.

At high temperatures, an undesirable side process intensively occurs - the ionization of free atoms:

$$M \rightleftarrows M^+ + e^-$$

The lower the ionization energy, the greater the proportion of ionized atoms in the flame. To shift the ionization equilibrium to the left, towards non-ionized atoms, it is necessary to increase the number of free electrons in the flame. For this purpose, spectroscopic buffers are added to the analyzed solution, that is, salts of easily ionizable elements, for example, sodium or potassium.

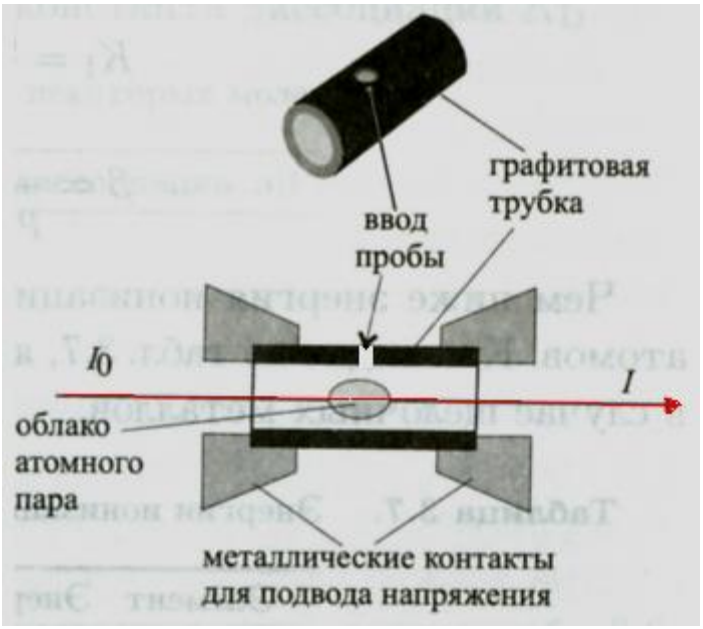
Along with flame atomic absorption spectroscopy, electrothermal atomic absorption spectrometry has become widespread over the past two to three decades. In this type of atomic absorption spectrometry, atomization is achieved by heating the refractory material on which the sample is applied using an electric current. It does not replace flame atomic absorption, but complements it in cases where the sensitivity of the method with flame atomization is insufficient.

In the practice of atomic absorption spectrometry, two types of electrothermal atomizers are used SLIDE 11:

1) graphite;
2) metal.

Graphite atomizers are graphite tubes (furnaces) heated by electric current SLIDE 12 (Fig. 1.2.4). Graphite furnaces are made of electrographite coated with a layer of pyrolytic graphite approximately 30 microns thick. A dense solid layer of pyrolytic graphite is applied

to a graphite base using thermal decomposition of methane from an argon-methane mixture at low pressure and a temperature of 2200°WITH.



Rice. 1.2.4. Scheme of a graphite furnace for electrothermal atomization

As a result of applying a pyrolytic coating, graphite furnaces acquire the following advantages:

1) permeability for hot gases and atoms decreases;

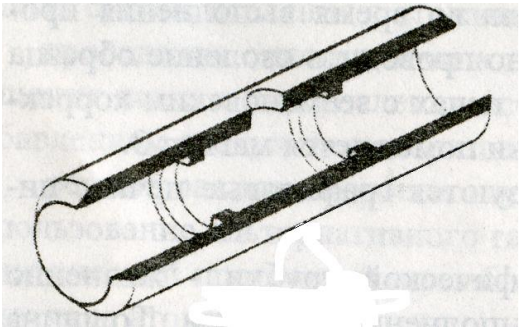
2) oxidation and destruction of graphite is prevented;

3) chemical stability increases, the likelihood of the formation of vanadium, titanium, and molybdenum carbides decreases;

4) the service life of the furnace increases;

5) for some elements the analytical sensitivity increases.

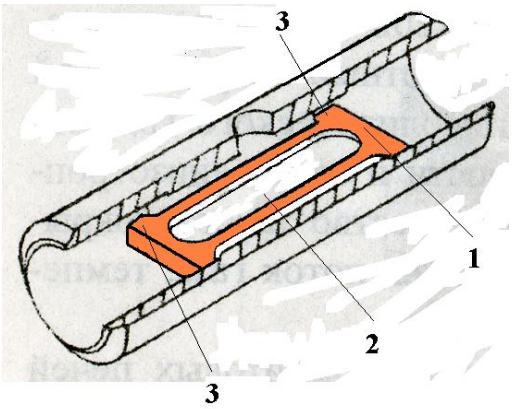
In atomic absorption spectrometers of the Varian company and in the Kvant deviceZETA" from the domestic company "Kvant" uses pyrolytically coated divided tubes (Fig. 1.2.5):



Rice. 1.2.5. Pyrolytically coated split tube

The partitions in the divided tube keep the sample solution in the central part of the tube, enable large volumes of organic solvents to be dried with good reproducibility, and prevent concentrated acids from spreading along the surface of the tube.

An important improvement was the invention of the graphite platform, which is a thin solid graphite plate made of pyrolytic graphite with a central recess capable of holding up to 40 µl of liquid sample (Fig. 1.2.6):



Rice. 1.2.6. Pyrolytically coated tube with a pyrolytic platform: 1 – graphite pyrolytic platform; 2. sample recess; 3 – cams for fixing the platform

At the ends of the platform there are cams for fixing it inside the oven. The contact area between the platform and the graphite tube is very small, so the platform is heated mainly by radiation from the walls of the tube. As a result, the evaporation of the sample is delayed until the tube and gas phase are heated to a constant temperature. This achieves an increase in the degree of sample dissociation and a decrease in interfering influences.

In a heated graphite furnace, the formation of free atoms is possible as a result of the following processes:

1) MO (TV)→MO(g); 2MO(g)→2M(g) + O2;

2) 2MO (TV)→2M (tv) + O2; M (TV)→M(g);

3) MO (TV) + S (TV)→M (s) + CO (g); M (TV)→M(g);

4) MO (TV) + 2S (TV)→MS (sv) + CO (g); MS (TV)→M(g) + S.

The dimensions of the graphite tubes have a significant influence on the atomization process. For example, reducing the size of the tube in the Kvant ZETA device made it possible to significantly increase the rate of temperature rise compared to Varian furnaces. The dimensions of graphite tubes for atomic absorption spectrometers of some companies are given in Table. 1.2.

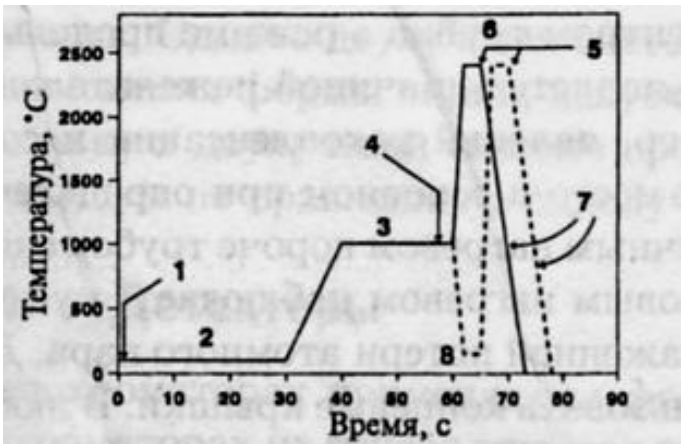
Table 1.2. Graphite tube sizes

Device	Length, mm	Inner diameter, mm	External diameter, mm

GTA from Varian	25.0	5.1	6.8
Grfit-2	28.0	5.8	7.6
Quantum ZETA	16.5	4.0	6.0

To protect the inner and outer surfaces of the graphite tube from oxidation and to remove sample components from the atomizer, a noble gas (usually argon) is passed through at each stage of the analysis.

Modern atomic absorption spectrometers with a graphite furnace provide the ability to implement a multi-step SLIDE 13 program to ensure the required temperature and the rate of its increase at the stages of drying, ashing and atomization (Fig. 1.2.7).

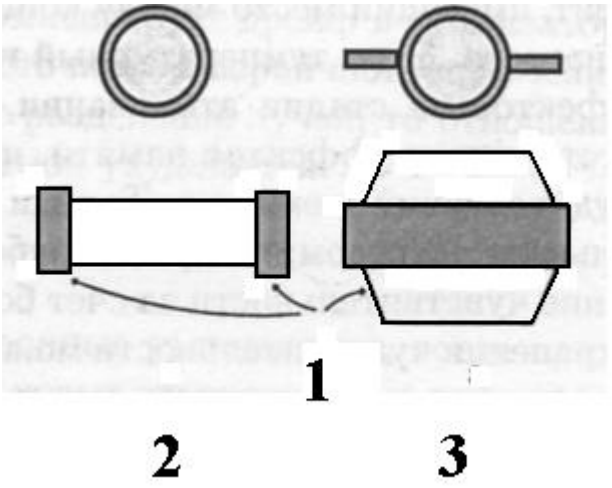


Rice. 1.2.7. Scheme of the electrothermal program: 1 – argon flow is on; 2 - drying; 3 – ashing; 4 – argon flow is turned off; 5 – argon flow is on; 6 – atomization; 7 - cooling period; 8 – cooling procedure.

The drying temperature should be such that the solvent evaporates quickly and, at the same time, there is no intense splashing and spreading of the solution. Ashing temperatures for organic matrices are usually in the range of 400 - 800°C, and the ashing time is comparable to the evaporation time. After the ashing step, only the analyte element in a suitable molecular form and a small amount of matrix in the form of inorganic salts that are thermally stable at the ashing temperature used should remain. The first two stages are usually carried out under argon flow to avoid oxidation. At the atomization stage, the gas flow rate can be reduced to zero to increase the sensitivity of determination due to an increase in the residence time of the atomic vapor on the path of radiation from the primary source. The atomization temperature is determined by the nature of the element being determined and the matrix. Then a cooling period occurs. After the atomization stage, it is necessary to clean the graphite tube from the remains of the element being determined and the matrix using the maximum possible flow of protective gas.

Two types of heating are used to heat furnaces: longitudinal heating, when the furnace is heated from the ends, and transverse heating, when the furnace is heated from the sides

(Fig. 1.2.8) SLIDE 14. Lateral heating is designed to reduce the temperature gradient that occurs between ends and the middle of the tube in longitudinal heating mode.



Rice. 1.2.8. Types of heating of graphite furnaces: 1 – electrical contacts; 2 – longitudinal heating (top – side view, bottom – top view); 3 – transverse heating (top – side view, bottom – top view)

Metal atomizers include tungsten spiral atomizers and graphite furnaces lined with foil made of various metals (tantalum Ta, lanthanum La, zirconium Zr, etc.). Tungsten spiral atomizers were used in domestic devices “Spiral” of the Yekatrinburg company “ITMA” and SA-10PM of the Kazan Optical-Physical Plant. The advantages of metal atomizers include low power consumption and the possibility of more active atomization of elements forming carbides, for example, barium Ba and vanadium V, than in a graphite furnace. These devices have not found widespread use due to their inherent disadvantages: a decrease in mechanical strength after prolonged heating; possibility of formation of intermetallic compounds; low chemical resistance, high brightness at elevated temperatures.

1.2.4. Optical dispersive systems.

In atomic absorption spectrometry, the role of the monochromator is to cut off unnecessary emission lines from a hollow cathode lamp, molecular bands, and extraneous external radiation. The use of light filters in atomic absorption spectrometry is impossible, since their spectral transmission bands are too wide.

Most optical dispersive systems used in atomic absorption spectrometry are designed for single-element determination. To select lines, they use a monochromator based on a rotating flat grating. A flat diffraction grating consists of periodic streaks or lines on a flat surface. These streaks or lines impose a periodic variation on the amplitude and phase of the incident wave. Each stroke acts like a narrow mirror, re-emitting light. When a parallel beam falls on a flat grating (Fig. 1.2.9) at an angleα, then to calculate the angle of the diffracted beamβat a given monochromatic wavelengthλuse the lattice equation:

$\sin\alpha-\sin\beta= kn\lambda$

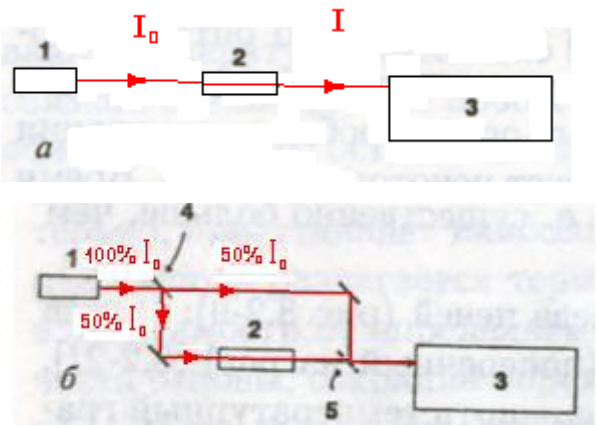
where k is a positive or negative integer called order, n is the density of strokes.

Rice. 1.2.9. The principle of operation of a flat diffraction grating: the distance between two consecutive lines AB = a; this distance is related to the stroke density n by the relation n = 1/a; the normal (perpendicular) to the surface of the stroke forms an angle θwith the normal to the grating surface; on the grating bars at an angleαa parallel ray (shown in green) is incident on its normal; light is reflected from the surface of the grating so that the angle between the direction of the reflected ray and the normal to the surface of the grating is equal toβ.

Numerous reflected rays (shown in green) interfere and create the phenomenon of diffraction. All beams will be amplified when the path difference results in constructive interference, i.e. when the path difference is equal to an integer number of wavelengthsλ.

Typically, diffraction gratings containing 1200-1800 lines per millimeter are used. The useful spectral range is 180-860 nm. The inverse linear dispersion ranges from 0.1 to 2 nm/mm.

The optical systems of an atomic absorption spectrometer can be either single-beam (Fig. 1.2.10 a) or double-beameducational (Fig. 1.2.10 b).

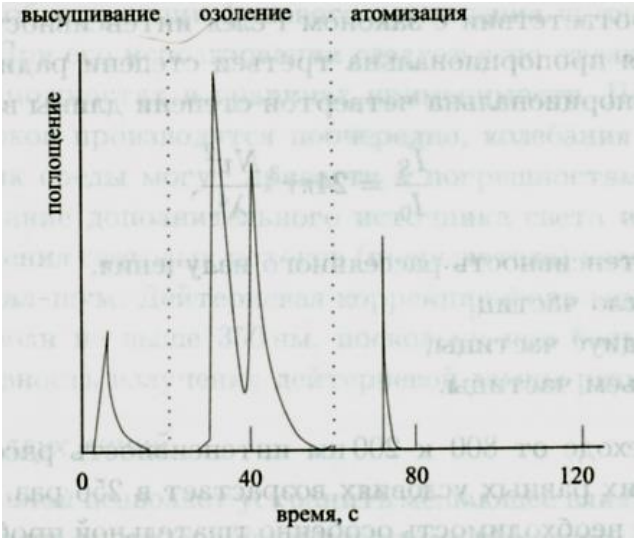


Rice. 1.2.10. Single-beam (a) and double-beam (b) optical systems: 1 – source of primary radiation; 2 - atomizer; 3 – dispersing system; 4 – translucent mirror; 5 – rotating disk.

In dual-beam systems, the beam from the primary radiation source is divided. One part of the beam passes through the atomizer, and the second part goes directly to the input of the dispersing system. Before entering the dispersive system, both beams are combined again. The dual beam device is designed to compensate for any drift occurring in the primary radiation source. However, the two-beam system does not compensate for the change in the shape of the line emitted by the source of primary radiation and the drift in the atomizer. The signal-to-noise ratio in a double-beam system is greater than in a single-beam system.

1.2.5. Receiver and registration of analytical signal.

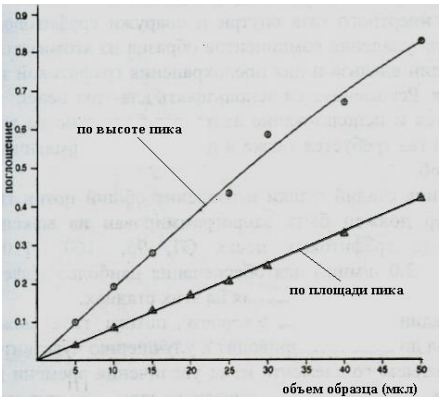
Monochromators use photomultipliers, and polychromators use new solid-state detectors, which consist of a set of photodiodes. In flame atomic absorption spectrometry, a constant signal is obtained for several seconds. In graphite furnace atomic absorption spectrometry, a transient signal in the form of a peak is obtained (Fig. 1.2.11).



Rice. 1.2.11. Change in atomic absorption signal during sample atomization in a graphite furnace.

Modern atomic absorption spectrometers allow absorption measurements in peak height or peak area modes. In some cases, the choice of mode may be straightforward, in others it is necessary to carry out experimental measurements to decide which method is best suited for a given analysis.

Peak area measurement extends the range of calibration linearity. For example, the calibration graph for copper based on peak area is linear over the entire range of sample volumes shown in Fig. 1.2.12. The peak height graph for the same range has curvature.



Rice. 1.2.12. Calibration chart for copper.

Possibilities of the atomic absorption spectrometry method.

1.1.1. Determined elements and their detection limits.

The method of atomic absorption spectrometry can determine about 70 elements, mainly metals. This method is used for mass, fast, selective and fairly accurate determination of metals. Most often, small contents are determined by this method: with flame atomization - about 10-6 - 10-^{9}Gper milliliter, with electrothermal atomization – 10-9 – 10-^{12}Gper milliliter (see Table 1.3). With electrothermal atomization, very small masses can be determined - down to several femtograms (1 femtogram = 10-^{15}G), since the sample volume is very small. It ranges from 10 to 200 μl.

Table 1.3. Comparison of detection limits of elements (ng/ml) by atomic absorption spectrometry using flame and electrothermal atomization methods

No. n\n	Item name	Element symbol	Flame Detection Limit atomization	Detection limit for electrothermal atomization
1	Aluminum	Al	20	0.01
2	Barium	Ba	8	0.04
3	Beryllium	Be	1	0.003
4	Bor	B	700	15
5	Vanadium	V	20	0.1
6	Bismuth	Bi	0.02	0.1
7	Tungsten	W	500	
8	Gadolinium	Gd	1000	8
9	Gallium	Ga	50	0.01
10	Hafnium	Hf	2000	

eleven	Germanium	Ge	50	0.1
12	Holmium	Ho	40	0.7
13	Dysprosium	Dy	50	
14	Europium	Eu	20	0.5
15	Iron	Fe	3	0.01
16	Gold	Au	6	0.01
17	Indium	In	20	0.02
18	Iridium	Ir	500	0.5
19	Ytterbium	Yb	5	0.1
20	Yttrium	Y	50	10
21	Cadmium	Cd	0.5	0.0002
22	Potassium	K	1	0.004
23	Calcium	Ca	0.5	0.01
24	Cobalt	Co	2	0.008
25	Silicon	Si	20	0.005
26	Lanthanum	La	2000	0.5
27	Lithium	Li	0.3	0.01
28	Lutetium	Lu	700	
29	Magnesium	Mg	0.1	0.0002
thirty	Manganese	Mn	0.8	0.0005
31	Copper	Cu	1	0.005
32	Molybdenum	Mo	10	0.02
33	Arsenic	As	0.02	0.08
34	Sodium	Na	0.2	0.004
35	Neodymium	Nd	600	
36	Nickel	Ni	2	0.05
37	Niobium	Nb	1000	
38	Tin	Sn	10	0.03
39	Osmium	Os	80	2
40	Palladium	Pd	10	0.05
41	Platinum	Pt	40	0.2

42	Praseodymium	Pr	2000	
43	Rhenium	Re	200	10
44	Rhodium	Rh	2	0.1
45	Mercury	Hg	0.001	0.2
46	Rubidium	Rb	0.3	
47	Ruthenium	Ru	70	
48	Samarium	Sm	500	
49	Lead	Pb	10	0.007
50	Selenium	Se	0.02	0.05
51	Sulfur	S	20	10
52	Silver	Ag	0.9	0.001
53	Scandium	Sc	20	6
54	Strontium	Sr	2	0.01
55	Antimony	Sb	0.1	0.08
56	Thallium	Tl	9	0.01
57	Tantalum	Ta	9	
58	Tellurium	Te	0.002	0.03
59	Terbium	Tb	600	
60	Titanium	Ti	10	0.3
61	Thulium	Tm	10	
62	Uranus	U		thirty
63	Phosphorus	P		0.3
64	Chromium	Cr	2	0.004
65	Cesium	Cs	8	0.04
66	Zinc	Zn	0.8	0.0006
67	Zirconium	Zr	350	
68	Erbium	Er	40	0.3

The main disadvantage of the atomic absorption spectrometry method is that it is a single element method. Each element requires its own hollow cathode lamp. To reduce the time spent on analysis, several lamps are installed on a rotating drum.

1.1.2. Sensitivity.

Sensitivity in atomic absorption spectrometry using a graphite furnace as an atomizer is defined as the characteristic mass (in picograms) that gives an atomic vapor optical density of 0.0044, which is equivalent to 1% absorbance. Depending on the nature of the element being determined, the characteristic mass varies from 0.3 pg for cadmium, magnesium and zinc to 2000 pg for phosphorus. The characteristic mass depends not only on the element being determined, but also on the method of measuring the signal (by height or by peak area).

Electrothermal atomic absorption spectrometry is used to determine trace elements when the sensitivity of flame analysis is insufficient. However, it does not apply to all 67 elements that can be analyzed by flame atomization. The inability to determine some elements using electrothermal atomization is due to the fact that the flame contains chemically active radicals, for example, C, C2, CH, O, CN, NH, which contribute to the dissociation of metal compounds. There are no such particles in a graphite furnace, so dissociation and atomization of the compounds of certain metals cannot be carried out in it. When using a graphite furnace, it is difficult to determine metals that form thermally stable carbides at high temperatures. Elements that cannot be analyzed using a graphite furnace give a significant residual signal when re-atomized without sample addition or are said to exhibit high memory.

1.1.3. Chemical interference.

With both methods of sample atomization, the results obtained using atomic absorption spectrometry may depend on the chemical nature of the matrix, which may influence the formation of free atoms.

For example, during atomization in the flame of a gas burner, the phosphate content in the matrix causes the formation of thermally stable calcium phosphate, which can interfere with the determination of calcium. When using an acetylene-air flame, it is necessary to use a buffer (lanthanum), which forms a thermally stable compound with phosphate ions and thereby promotes the formation of free calcium atoms. This obstacle can be overcome in another way: using a higher temperature acetylene-dianitrogen oxide flame.

To eliminate possible losses of easily volatile compounds of the elements being determined during the ashing process during atomization in a graphite furnace, chemical modifiers are used. Chemical modifiers are intended:

1) to increase or decrease the volatility and, consequently, the atomization temperature of the element being determined;

2) to increase or decrease the volatility of the matrix;

3) to prevent interaction of the element or matrix being determined with the graphite surface.

The most common reason for using modifiers when determining highly volatile compounds is the need to obtain a compound of the element being determined with a highdecomposition temperature, which makes it possible to increase the ashing temperature and achieve complete removal of the matrix material before atomization.

To date, a large amount of experimental data on the selection of modifiers affecting matrices has also been accumulated. Some modifiers of this kind are given in table. 1.5.

Table 1.5. Chemical modifiers for some matrices in a graphite furnace (from the book Ermachenko L.A., Ermachenko V.M. “Atomic absorption analysis with a graphite furnace”)

1.1.4. Spectral Interference

The most important cause of spectral interference in atomic absorption spectrometry is background absorption SLIDE 16. Background absorption is caused by light scattering and nonspecific absorption of radiation by molecules and radicals.

Light scattering occurs in the atomizer, mainly on solid and less often on liquid particles. The intensity of scattered radiation IS is proportional to the particle radius r taken to the third power and is inversely proportional to the wavelengthλ, taken to the fourth power (Rayleigh’s law):

$$I_S = I0 24\pi r^3 \frac{NV^2}{\lambda^4}$$

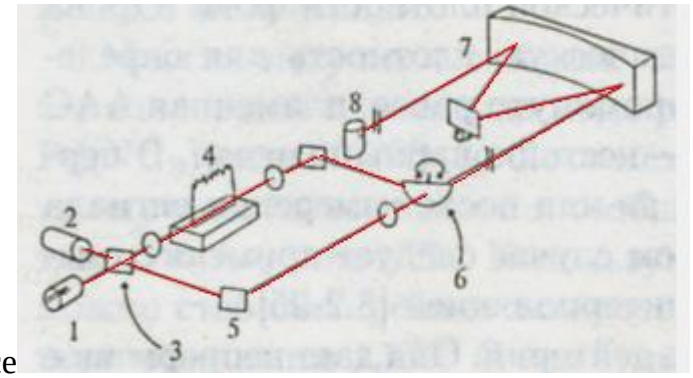
where I0 is the intensity of incident radiation; N – number of particles; V is the volume of the particle. According to Rayleigh's law, the intensity of light scattering increases as the wavelength decreases. Therefore, when working in the short-wavelength region of the spectrum, it is necessary to carry out sample preparation especially carefully. Typically, light scattering makes a smaller contribution to background absorption than absorption by molecules and radicals.

Molecular absorption spectra contain broad bands ranging in width from several nanometers to hundreds of nanometers.

Background absorption leads to overestimation of optical density values, so background correction is necessary. Background correction can be done in four ways:

1) using a source of continuous spectrum radiation (deuterium lamp);
2) two line method;
3) using the Zeeman effect;
4) Smith-Hiftje method.

When correcting the background using a deuterium lamp, two light sources are used: one of these sources is a hollow cathode lamp or an electrodeless discharge lamp, which give a line spectrum, the second source is a deuterium lamp, which gives a continuous spectrum in the region of 200 - 380 nm with a maximum in the region of 250 nm. The intensities of both sources are adjusted so that they are equal (Fig. 1.3.1).

Atomic vapor is alternately irradiated with light fluxes from the primary source 

Rice. 1.3.1. Diagram of a double-beam atomic absorption spectrometer with background correction using a deuterium lamp: 1 – source of primary radiation; 2 – deuterium lamp; 3 – translucent mirror; 4 – atomizer; 5 – mirror; 6 – semi-rotating mirror; 7 – dispersing system; 8 – detector.

radiation and deuterium lamp. Absorption of radiation from a primary source consists of specific absorption by atoms of the element being determined, i.e. absorption at the wavelength of the resonance line, and nonspecific background absorption. When irradiated with a deuterium lamp, only background absorption occurs. Therefore, the attenuation of the radiation from a deuterium lamp corresponds to the optical density of the background and can be subtracted from the optical density obtained by irradiating atomic vapor with the primary radiation source:

$$A_{\text{specialist}} = \text{API} - A_{D_2} = \log \frac{I_0}{I_{\text{ПИ}}} - \lg \frac{I_0}{I_{\text{D}_2}} = \log \frac{I_{\text{D}_2}}{I_{\text{ПИ}}}$$

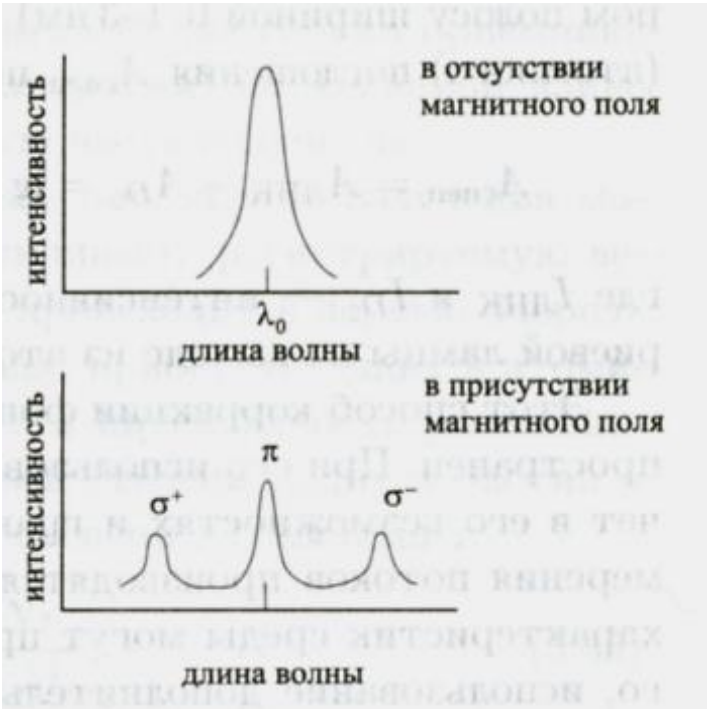
where IPI and I_{D_2} - intensity of light fluxes of the primary radiation source and the deuterium lamp at the exit from the atomizer.

The deuterium lamp method is applicable to both flame and graphite furnace atomization. However, its use is limited to wavelengths less than 360 nm, since at longer wavelengths the radiation intensity of a deuterium lamp drops sharply.

The two-line method is based on simultaneous measurement of absorption at two wavelengths. To do this, next to the resonant absorption line of the atoms of the element being determined, another emission line of a hollow cathode lamp is selected, the wavelength of which corresponds only to the background absorption. By subtracting the absorption intensity at the second wavelength from the absorption intensity corresponding to the resonance line, correction is carried out. The use of this method is limited by the difficulty of choosing a wavelength at which the absorption intensity does not depend on the concentration of the element being determined and corresponds to the background absorption at the wavelength of the resonance line. To use this method, a specially designed spectrometer is required.

The third method for correcting background absorption is based on the Zeeman effect. The Zeeman effect is the splitting of the electronic levels of an atom under the influence of a magnetic field. As a result of the Zeeman effect, a spectral line can split into three or more closely spaced lines, which are called components (Fig. 1.3.2). In the simplestIn this case, under

the influence of a magnetic field, the spectral line is split into three components: π-component whose wavelength coincides with the wavelength of the original line λ_0, and two σ-components located symmetrically relative to π-components in the region of longer and shorter wavelengths. Radiation π- And σ-component is polarized differently:



Rice. 1.3.2. Splitting of excited electronic levels in atoms under the influence of a magnetic field (manifestation of the Zeeman effect).

π-components are parallel to the magnetic field vector, and σ-component – perpendicular to it. π-The component is absorbed both by atoms of the element being determined and by particles, the presence of which in the atomic vapor causes background absorption. σ-Components are absorbed only last. By passing the light flux through a polarizing filter, it is possible to separate the components and perform background subtraction.

In most commercially produced atomic absorption spectrometers, the magnetic field is applied to the atomizer (graphite furnace), although it can also be applied to the primary radiation source. Most often, an alternating magnetic field with a frequency of up to 10 kHz is used. If a magnetic field is applied perpendicular to the beam (transverse mode of the magnetic field), then when the field is turned off, the total absorption (of the atoms of the element being determined and the background) is measured, and when the field is turned on, only the background absorption is measured. If the magnetic field is applied parallel to the beam (longitudinal mode), then when the field is turned on π-component is not observed and there is no need to polarize the light flux.

Unlike deuterium correction, Zeeman background correction is effective for any wavelength and for a structured background, i.e. in the presence of a number of narrow molecular bands near the line of the element being determined. It is especially effective in the case of strong background absorption that occurs when analyzing biological samples.

The Smith–Heftje method is based on the use of hollow cathode flash lamps. When a high current (up to 500 mA) passes through the lamp, self-absorption of the line of the element

being determined occurs, and only the background absorption is measured. The advantage of thisThe method is its simplicity, it does not require additional equipment and can be used in spectrometers with any type of atomization.

The possibility of interference as a result of spectral lines of two different elements of similar wavelengths entering the passband of a dispersive system in atomic absorption spectrometry is not great. The pairs of elements listed in Table 1 can interfere with each other. (Table 1.6). This interference can be prevented by selecting a different sensitive wavelength in deuterium correction or by using background correction using the Zeeman effect.

Table 1.6. Elements having spectral lines close in wavelength

Element	Wavelength, nm	Element	Wavelength, nm
Cadmium, Cd	228,802	Arsenic, As	228,812
Aluminium, Al	308.215	Vanadium, V	308.211
Antimony, Sb	217,023	Lead, Pb	216,999

It should be noted that when developing an atomic absorption analysis technique, it is necessary to use optimal temperature programming and chemical modification, and not rely only on background correction.

Lecture No. 31

Atomic emission spectrometry

Atomic emission spectroscopy is based on thermal excitation of free atoms or monoatomic ions and recording the optical emission spectrum of the excited atoms. Light emitted by hot gases or vapors passing through the prism of a spectrograph is refracted and decomposed into components. Therefore, the experimenter observes a number of individual colored lines that together make up a line spectrum. The line spectrum of each element is characterized by constant spectral lines corresponding to rays with a certain wavelength and vibration frequency. By the presence of these lines, one can judge the presence of a particular element in the analyzed substance. To observe and record emission spectra, the sample must be transferred to the atomic state.

If the conditions for atomization of the sample and excitation of atoms are constant and not complicated by extraneous physicochemical and optical phenomena, then the intensity of the Ie line in the atomic emission spectrum is directly proportional to the substance content in the sample (c):

$Ie = a \cdot c$

In the presence of optical or physicochemical interference, this dependence may be violated. The most important optical interference in atomic emission spectroscopy is self-absorption - the partial absorption of photons emitted by excited atoms of a sample by unexcited atoms of the same element. If there is self-absorption, then the dependence of Ie on c is satisfactorily described by the Lomakin-Shaibe equation.

$Ie = a \cdot cb,$

where a and b are constants for given conditions.

The main physicochemical interference in atomic emission spectroscopy is the formation of difficult-to-dissociate compounds involving the element being determined, as well as the ionization of its atoms. To eliminate such interference, they usually use the introduction of special additives (spectroscopic buffers) into the sample, which suppress undesirable processes, and optimization of the temperature regime of the atomizer.

Types of atomizers

There are flame, electrothermal and plasma atomizers (inductively coupled plasma).

Flame atomizermade in the form of a burner into which the components of a combustible mixture are supplied - combustible gas (methane, propane, acetylene, hydrogen) and an oxidizer (air, nitrogen oxide (I) or oxygen). The operating temperature of the flame atomizer depends on the nature of the combustible mixture and ranges from 1000° to 3000°C. These atomizers are used mainly for alkali and alkaline earth metals.

Electrothermal atomizers -These are arc or spark discharge generators that allow operation in the temperature range of 3000–7000°C and 10,000–12,000°C, respectively. The test sample is placed between carbon electrodes through which an electric discharge is passed.

Inductively coupled plasma– the most modern and having, in a number of indicators, the best analytical capabilities and metrological characteristics. The ICP atomizer is a specially designed plasma torch into which argon is supplied. The temperature of the argon plasma varies with the height of the burner and ranges from 6000 to 10,000°C. The method is universal, since most elements are excited at such temperatures, has high sensitivity (10–8 – 10–2 mass) and reproducibility, and a wide range of determined concentrations. The main disadvantage is the high cost of equipment and consumables (high purity argon)

Lecture No. 32

Molecular luminescence

Luminescence is the glow of a substance with a duration of at least 10-10 s, which is excessive over temperature. Called cold glow. In English-language literature the term "fluorescence" is used. In our literature, they are sometimes divided into types: when the glow stops almost simultaneously with the exciting radiation, it is fluorescence; if it continues, it is phosphorescence. The cold glow of atoms, molecules, ions, and complexes occurs as a result of the return of electrons from an excited state to a normal one. Excitation methods:

1. UV and visible radiation (photoluminescence);
2. energy of chemical reactions (chemiluminescence);
3. electron flow (cathodoluminescence);
4. radioactive radiation (radioluminescence);
5. X-ray radiation (x-ray luminescence);
6.mechanical effect (triboluminescence);

To obtain spectra, a UV source with a monochromator transmitting the selected wavelength is usually used. The luminescent radiation observed in the perpendicular direction is scanned by a monochromator, and the luminescence spectrum is recorded using a photomultiplier.

The luminescence spectra of some organic compounds have a clearly defined structure and can be used for qualitative analysis, but often the spectra consist of broad overlapping bands. The shape of the spectrum does not depend on the frequency of the exciting radiation. Advantages: high sensitivity, it is possible to determine compounds with a concentration of less than 10-3 μg/ml. The disadvantage is low selectivity.

Applications:

1) Analysis of inorganic substances. Uranium and lanthanides are determined. Organic reagents are used that form a complex with metals. For example, 8-hydroxyquinoline forms luminescent complexes with more than 25 elements (Li, Ca, Mg, Ba, Al, etc.). Rhodamine dyes are used to determine Au, In, Ga, Hg, B, Te, etc. Salicylic acid forms a luminescent complex with zinc.

2) Determination of vitamins, hormones, antibiotics.

3) Determination of carcinogens. Diagnosis of diseases.

4) Determination of seed viability (yellow and brown leaves).

5) Determination of the initial stage of rotting of fruits and vegetables.

Luminescence is the glow of atoms, molecules and other particles resulting from an electronic transition upon returning from an excited state to the ground state.

Luminescence phenomena are varied in properties and origin. Different types of luminescence are determined by the nature of the energy and excitation, the duration of the glow and the chemical properties of the luminescent substances.

Based on the type of excitation, the following types of luminescence are distinguished.

- PHOTOLUMINESCENCE - a glow that occurs under the influence of light rays in the optical frequency range (ultraviolet and visible rays); observed in gaseous, liquid and solid systems.
- CATHODOLUMINESCENCE - a glow that occurs under the influence of cathode rays - electrons moving rapidly under the influence of an electric field. This type of excitation is widely used in gas-discharge tubes, where an electron accelerated by an electric field along its path can ionize thousands of gas atoms, thereby causing them to glow. Cathodoluminescence is also used to excite powders, thin films and surface layers of single crystals.
- ELECTROLUMINESCENCE - glow under the influence of radioactive decay products (α-, β-particles and γ-rays), as well as cosmic radiation.
- CHEMILUMINESCENCE - the glow of a substance during a chemical reaction. The excitation energy of luminescence in this case is drawn from the energy reserves of the reacting substances (for example, the glow of phosphorus oxide that occurs during its oxidation). The glow that occurs in various plant and living organisms is also due to the chemical processes occurring in them (for example, the glow of fireflies, mollusks, etc.).
- TRIBOLUMINESCENCE - a glow that occurs when certain substances rub together.

- CRYSTAL LUMINESCENCE - a glow that occurs during mechanical compression of crystals.

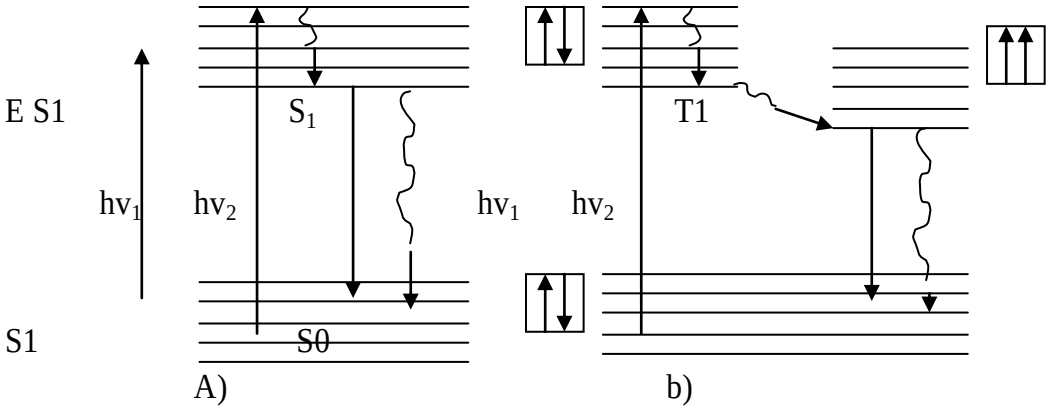
Based on the duration of the glow, two types of luminescence are distinguished: fluorescence and phosphorescence.

Fluorescence is luminescence with a duration of the order of 10-8 –10-10 s.

Phosphorescence is a glow that lasts a noticeable period of time after the cessation of excitation from 10-8 s to several hours.

All luminescent substances have a common name -phosphors. Inorganic phosphors are simply called phosphors, and organic phosphors are called organoluminophores, and they differ significantly in the nature of their glow. In inorganic phosphors, crystals are usually involved in the glow process, and they are also called crystal phosphors. In oragnoluminophores, the processes of absorption and emission of light occur within each molecule capable of luminescing.

The molecule, absorbing a light quantum, passes from the ground state S0 to the excited state S1. At room temperature the molecules are inground vibrational state. Upon transition to an excited state, the molecule enters one of the vibrational levels of the vibrational state.



Rice. 5. Scheme of energy transitions of a molecule during fluorescence - (a) and phosphorescence - (b)

The absorption of a light quantum by a molecule occurs in a very short time - 10-15 s. Then, within a time of 10-12 s, the electron transitions to the lower vibrational sublevel of the excited state (Fig. 5a - short wavy line). This process is called vibrational relaxation. The return of a molecule from the lower state Si to the unexcited state S0 can occur in three ways.

1 - The loss of energy by a molecule in the form of heat as a result of collisions with other particles is the process of internal conversion.

2 - Return of a molecule to any vibrational sublevel of the ground state with the emission of energy in the form of a light quantum without changing the electron spin - fluorescence.

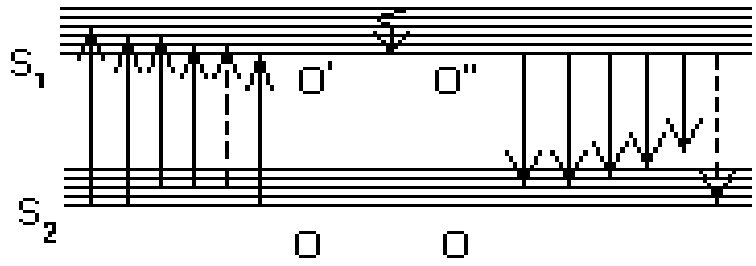
3 - The transition of a molecule from the excited state Si to the metastable state T1, and then to the ground state S0, either as a result of internal conversion with the release of heat (Fig. 6 - long wavy arrow), or with the release of a light quantum - phosphorescence. In the metastable state, the spins are parallel ↑↑.

Fluorescence is observed more often than phosphorescence, especially in liquid solutions. Intense phosphorescence is observed in organic compounds in a frozen or glassy state.

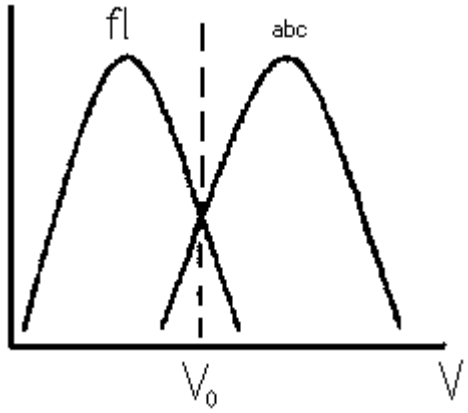
Luminescence output. The dependence of luminescence intensity on the wavelength or frequency of radiation is called the luminescence spectrum. The type of spectrum does not depend on the wavelength of the exciting electromagnetic radiation. The loss of part of the energy of absorbed light quanta to non-radiative processes leads to the fact that the emitted quantum has lower energy and, therefore, a longer wavelength than the absorbed one. According to the Stokes-Lommel law, the fluorescence spectrum as a whole and its maximum are shifted in comparison with the absorption spectrum and its maximum towards long waves.

The difference in wavelengths at the maxima of the fluorescence and absorption spectra is called the Stokes shift (or shift).

The absorption and fluorescence spectra intersect at the point at v0, which corresponds to the excitation of an electron and the emission of a quantum without losses due to non-radiative transitions (O→O', O'→O).



A)



b)

Rice. 6. Diagram illustrating the Stokes-Lommel law:

a - energy transitions; b - absorption and fluorescence spectra.

The vibrational structure of many large organic molecules practically does not change upon excitation, therefore the “normalized” absorption and fluorescence spectra depicted as a function of frequencies are mirror symmetrical relative to the straight line passing through the intersection point perpendicular to the frequency axis (V.L. Levshin’s rule). Compliance with the rule of mirror symmetry for substances in which it is observed makes it possible to construct a fluorescence or absorption spectrum, having only one of them.

A direct relationship has been proven between luminescence intensity and phosphor concentration in solution up to 10-4 mol/l.

Ilum = k*C, where k is the proportionality coefficient.

The higher the quantum yield of luminescence, the lower the amountphosphor can be detected by the luminescent method.

Vkv = Nlum/Nlight,

Where IN_{kv}- quantum yield;

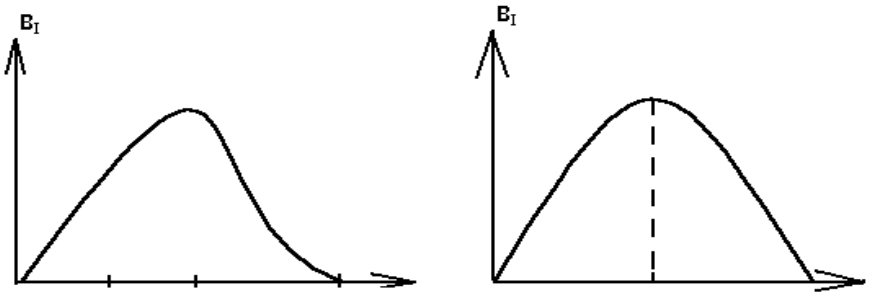
Nlum is the number of quanta emitted during luminescence;

Nlight is the number of quanta absorbed during excitation.

The luminescence yield depends on a number of factors: the wavelength of the exciting light, the phosphor concentration, temperature, and the presence of impurities in the solution.

The dependence of the luminescence yield on the wavelength of the exciting light obeys S.I. Vavilov's law:

When going from short to long waves, the luminescence yield increases to a certain limit in proportion to the wavelength. Starting from a certain wavelength, the luminescence output reaches its maximum and becomes independent of the wavelength of the exciting light, and then quickly decreases.



O 200 400 600 λ, nm 10-4 10-5 s,%

Rice. 7. Dependence of luminescence output:

a - on the wavelength of the exciting light; b - on the phosphor concentration.

The luminescence yield at small amounts of phosphor is proportional to its content in the solution, which is used for quantitative luminescent analysis. An increase in phosphor concentration leads to a decrease in the brightness of the glow. When a certain concentration of a luminescent substance is reached, a gradual and complete quenching of luminescence occurs - concentration quenching.For most phosphors, the concentration barrier lies in the concentration range of 10-4-10-5 mol/l.

Lecture No. 33

Electrochemical analysis methods

These methods are used for the analysis of drinking water, natural and waste water and food. Any electrical parameter - potential E, current I, resistance R, charge - depends on the composition of the solution being analyzed and can serve as an analytical signal.

Classification of electrochemical methods according to the measured parameter.

Measured parameter	Conditions of use	Method

Potential E, V	I=0	Potentiometry
Current I μA	I=f(E)	Voltammetry
Amount of electricity Q, C	I=const or E=const	Coulometry
Mass m, g	I=const or E=const	Electrogravimetry
Electrical conductivity	Alternating current	Conductometry

POTENTIOMETRY

This analysis method is based on the Nernst equation. Measuring the electrode potential under equilibrium reversible conditions, that is, in the absence of current, allows one to determine the activity of the ions. The EMF of a circuit composed of indicator and reference electrodes is measured. Metal or ion-selective (membrane) electrodes are used as indicator electrodes.

Ionometry- a promising and rapidly developing field of potentiometry based on ion-selective electrodes. The main part of the ion-selective electrode is a membrane that is permeable to one type of ion. The membrane separates the internal solution with a known ion concentration and the external, test solution with an unknown concentration. Each solution contains a metal electrode. The ions under study pass through the membrane towards a lower concentration, accumulate, dynamic equilibrium is established, and a membrane potential arises on the surface of the membrane, counteracting further movement of the ions. The measured potential difference between metal electrodes is described by the Nernst equation and allows one to calculate the activity (concentration) of ions in a wide range (up to 5 orders of magnitude). Even a thousandfold excess of foreign ions does not affect the operation of the electrodes.

Membranes are:

1) Solid:

a) from a crystalline substance that is slightly soluble in water and has ionic conductivity, ions move along defects in the crystal lattice. Example -

b) Glass - H+ ion exchange occurs in a thin gel-like surface layer of glass, formed after aging in an aqueous solution. Glass electrodes are widely used for pH measurements.

c) heterogeneous from different crystals.

2) Liquid (a solution of an ion exchange compound in an organic solvent held by a porous partition). These are chelating compounds, crown ethers, etc. They selectively complex the type of ion being studied and transfer it from one aqueous solution to another. Organic solvent (benzene, toluene) should not be mixed with water.

3) Plasticized - from the Navy.

The industry produces ion-sensitive electrodes for many ions: halide ions, nitrite and nitrate ions, cyanide ions, lithium cations, sodium, potassium, calcium, silver, copper, cadmium, lead, for general (Ca-magnesium) hardness water, surfactant. There is a variety - gas-sensitive electrodes - for NH3, NO2, CO2. Inside there is a buffer solution with a certain pH value. Gas molecules penetrate the membrane, react with the buffer solution and change its pH, and the pH is measured by an auxiliary glass electrode. Advantages of ionometry: simplicity, small size, low cost, rapidity, possibility of continuous measurement.

The second option for potentiometry is potentiometric titration. Measuring the dependence of the electrode potential on the composition of the solution is used to determine the end point of the titration. Near the equivalence point, a potential jump occurs (associated with the replacement of one electrochemical reaction by another).

COULOMETRY

Electrolysis is a chemical reaction of oxidation or reduction at an electrode under the influence of an electric current. To measure the amount of charge passed through the cell, coulometers or electronic integrators are used. A known reaction occurs in the coulometer with 100% current efficiency. Measuring the mass of the substance formed in the coulometer allows one to calculate the transferred charge.

The coulometric analysis method uses Faraday's laws of electrolysis:

1. The amount of substance reduced or oxidized as a result of electrolysis is directly proportional to the amount of electricity passed.

2. The masses of various substances released on the electrode during the passage of 1 Coulomb of electricity are equal to their electrochemical equivalents.

Electrolysis begins at a certain voltage between the electrodes, called the decomposition potential. In order for electrolysis to proceed quickly, the voltage in the circuit is maintained above the decomposition potential. If a solution contains several components with different decomposition potentials, they can be separated from the mixture in a certain sequence by adjusting the voltage. As the voltage increases, metals with a lower decomposition potential are first released at the cathode. For example, from a solution of Pb+2 and Cd+2 ions (with single activities), lead ions will first be reduced at the cathode (E0Pb= - 0126 V, E0Cd= - 0.402 V). If the cathode potential is made equal to 0.35 V, then only lead ions will be reduced, and cadmium ions will remain in solution.

When a current passes, the potential of the electrode changes compared to the equilibrium one (defined by the Nernst equation); this phenomenon is called polarization of the electrode. Reasons: 1) accumulation of reduction and oxidation products on the electrodes, which form, as it were, a new galvanic element, the emf of which is directed against an external source (chemical polarization), 2) change in the concentration of ions near the electrodes compared to the volume of the solution, that is, the occurrence of concentration galvanic element, the EMF of which is also directed against the voltage of the external current source (concentration polarization). A quantitative measure of polarization is overvoltage (the difference between the equilibrium EMF and the potential difference during the passage of current).

Coulometry is a highly sensitive and accurate method of analysis that allows you to determine up to 10-9 g of a substance. However, it is necessary to correctly select the electrolysis voltage (potential) in order to prevent side reactions from occurring.

and control automation.

VOLTAMPEROMETRY (POLAROGRAPHY).

The method is based on deciphering the current versus potential curves (polarization curves) measured in a cell with a polarizing indicator electrode and a non-polarizing reference electrode. The most common version of the method with a dropping mercury electrode is called polarography. This is a highly sensitive and fast method for determining inorganic and organic substances, one of the universal methods for determining trace amounts of substances, allowing the simultaneous

determination of several components in a mixture. A special feature of the polarography cell is the highly variable surface areas of the electrodes. The current density at the smaller electrode is several thousand times greater than at the reference electrode, due to which the current density is maximum near it and the cation reduction reaction occurs. The concentration of cations quickly decreases, dynamic equilibrium occurs when all cations approaching the drop due to diffusion are discharged and the current strength is constant (limiting, or diffusion current).

The cell structure is shown in Fig. The first electrode is mercury dripping from a capillary into the test solution. The second electrode is bottom mercury, there is a very low current density on it and near it the change in concentration is very small and does not affect the reaction. A constant potential is applied to the cell and it is slowly changed, thereby changing the current. The resulting graph of current versus potential is called a polarogram and is shown in the figure. It consists of three sections: A-B from the beginning of recording to the beginning of the reaction (slowly increasing according to Ohm's law); B-C is a sharp rise in current due to the reaction, B-D is the establishment of an almost constant diffusion current. When E1 (release potential) is reached, the reduction reaction begins, the cations take the electrons offered to them by the negatively charged electrode and turn into atoms. New cations approach due to diffusion, the current increases (called a wave). At a certain potential, the rate of reduction becomes equal to the rate of entry of cations due to diffusion. The potential at the point of maximum slope is called the half-wave potential, E1/2.

The limiting current at point B is limited by the rate of diffusion of ions to the surface of mercury and is called diffusion, Id. It is proportional to the concentration of ions (C) in solution (Ilkovich equation):

Id=607n(D)1/2m2/3t1/6C,

where n is the number of electrons participating in the reaction, D is the diffusion coefficient of ions, m is the flow rate of mercury, t is the dripping period, C is the ion concentration.

If several types of ions with different reduction potentials are present in a solution, they will produce a more complex curve, but the waves can be clearly separated. In Fig. An example of a polarogram of a solution containing cations of lead, zinc and cadmium. It has been proven that E1/2 does not depend on current and is a qualitative characteristic of the ion, therefore this value is used for qualitative analysis. For quantitative purposes, the value of the limiting diffusion current is used, since it is proportional to the ion concentration.

Polarography is applicable not only for the determination of cations, but also for organic substances that can be reduced. For example, aldehydes, ketones, peroxides, molecules with groups >C=N-, -NO2, -NHOH, -SS-.

CONDUCTOMETRY

Electrical conductivity measurements are used to determine water quality because conductivity is determined by the contributions of the electrical conductivities of all ions in the solution. Most often, conductometry is used for conductometric titration. Applicable to acid-base or precipitation reactions, which are accompanied by a noticeable change in electrical conductivity due to the formation of weakly dissociating electrolytes or poorly soluble compounds. Example: HCl+NaOH=NaCl+H2O. At the titration equivalence point, weakly dissociated water is formed and the electrical conductivity decreases. Further addition of NaOH leads to an increase in electrical conductivity.

Lecture No. 35
Electrogravimetric analysis

Electrolysisis a redox process associated with the decomposition of a substance under the influence of direct electric current.

The basic laws of electrolysis are Faraday's laws, established by him in the 30s. last century.

There are two Faraday laws:

Faraday's first law:The mass of a substance reduced at the cathode or oxidized at the anode is proportional to the amount of electricity passing through the solution or melt.

Faraday's second law:The same amount of electricity reduces or oxidizes masses of various substances on the electrodes, directly proportional to their chemical equivalents.

Both laws can be expressed by the formula:

$$m = \frac{Э \cdot I \cdot t}{F}$$

m – mass of oxidized or reduced substance[г]

E – electrochemical equivalent

F – Faraday's constant = 96500 C/mol – the amount of electricity consumed to release one equivalent.

I – current strength[A]

t – time[c]

$q = I \cdot t$- amount of electricity

$Э = {}^{A}/_{n}$

A – atomic mass of the element

n – metal valence

Faraday's laws are observed in all cases and under all conditions of electrolysis. If a substance is released in an amount less than that which can be found by calculation, this may mean that the expended amount of electricity is used unproductively, that is, along with the release of this substance, a side process takes place.

To assess the efficiency of using electricity to isolate the product for which electrolysis is carried out, the concept of current efficiency is used:

$$ВПТ = \frac{m_{практ.}}{m_{теор.}} \cdot 100\%$$

Chemical processes during electrolysis:

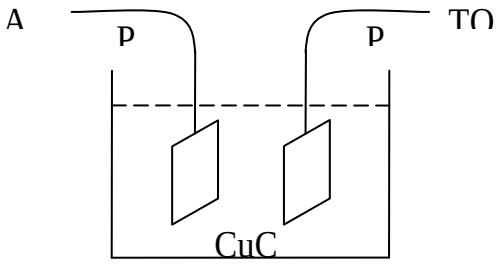
In electrolysis, a substance decomposes under the influence of a constant electric current.

Example:electrolysis of CuCl2 on an internal platinum electrode, pH = 7.

A (+) $Cl^-;\ H_2O$ $\quad 2Cl^- - 2\bar{e} = Cl_2$

TO (-) $Cu^{2+};\ H_2O$ $\quad Cu^{2+} + 2\bar{e} = Cu^0$

Total value:$Cu^{2+} + 2Cl^- = Cu^0 + Cl_2$



Processes at the cathode:

1. A metal cation will be discharged at the cathode if its standard electrode potential is significantly greater than that of hydrogen. Such metals are in the voltage series after hydrogen.

If the standard electrode potential is more negative than that of hydrogen, then hydrogen is released.

For pH = 7 or pH > 7:$2H_2O + 2\bar{e} = H_2 + 2OH^-$

For acidic solutions:$2H^+ + 2\bar{e} = H_2$

2. If the metal is in the voltage range from hydrogen to manganese inclusive, then both the metal and hydrogen are discharged. If it is higher than manganese, then it is not discharged from solutions at all.

3. If an aqueous solution contains a mixture of metal cations, then during electrolysis they are released at the cathode in the order of increasing negative or decreasing positive standard potentials.

So from the mixture: copper cations (, then cadmium (, and lastly zinc (.) are released first.$Cu^{2+}; Cd^{2+}; Zn^{2+} \varphi = 0{,}34$ В)$\varphi = -0{,}403$ В)$\varphi = -0{,}76$ В)

The value of the metal release potential changes with its concentration: an increase in concentration facilitates the discharge, a decrease makes it more difficult.

Processes at the anode:

1. If the anode is made of soluble metal, then the anode itself dissolves.

2. If the solution contains anions without oxygen acids (), then the acidic residue itself is discharged.$Cl^-;\ Br^-;\ Y^-;\ S^{2-}$)

3. If the solution contains anions of oxygen acids (), then water molecules are oxidized at the anode.$SO_4^{2-};\ NO_3^-;\ CO_3^{2-}$ и т.д.

In neutral and acidic environments:$2H_2O - 4\bar{e} = O_2 + 4H^+$

In an alkaline environment:$4OH^- - 4\bar{e} = O_2 + 2H_2O$

Examples:

Electrolysis of CuSO4 solution; pH>7

TO (-) $Cu^{2+};\ H_2O$ $Cu^{2+} + 2\bar{e} = Cu^0$

A (+)$SO_4^{2-};\ H_2O$ $4OH^- - 4\bar{e} = O_2 + 2H_2O$

Total value:$Cu^{2+} + 4OH^- = Cu^0 + O_2 + 2H_2O$

Electrolysis of Zn(NO3)2 solution; pH<7

TO (-) $Zn^{2+};\ H^+$ $Zn^{2+} + 2\bar{e} = Zn^0$

$2H^+ + 2\bar{e} = H_2$

A (+)$NO_3^-;\ H_2O$ $2H_2O - 4\bar{e} = O_2 + 4H^+$

Electrolysis of NaCl solution, pH=7

TO (-) $Na^+;\ H_2O$ $2H_2O + 2\bar{e} = H_2 + 2OH^-$

A (+)$Cl^-;\ H_2O$ $2Cl^- - 2\bar{e} = Cl_2$

Total value:$2H_2O + 2Cl^- = H_2 + 2OH^- + Cl_2$

Practical use:

- for analysis
- for corrosion protection of industrial structures
- manufacturing of household and industrial products

2. The electrogravimetric method of analysis is based on the separation of metals at the cathode (in rare cases at the anode) by electrolysis from aqueous solutions.

The mass of sediment deposited on the electrodes is determined by weighing before and after electrolysis.

Most metals are determined by isolating them in their pure form at the cathode.

Lead is determined in the form of oxide:

Pb2+ + 2OH- = H2PbO2 = 2H+ + PbO22-

TO (-) $2H^+ + 2\bar{e} = H_2$

A (+)$PbO_2^{2-} - 2\bar{e} = PbO_2$

The method is used to determine metals in ores and alloys of non-ferrous metals.

Advantages of the method:

- precision and simplicity of equipment

3.

In the absence of current, the equilibrium potential of the electrode is expressed by the Nernst formula:

$$\varphi = \varphi^0 + \frac{RT}{nF} ln\ a_{Me^{n+}}$$

When current passes, the electrode potential will not correspond to that calculated by the formula, the electrode will be polarized.

The phenomenon that causes the potential to deviate from equilibrium is called polarization.

Polarization can be caused by:

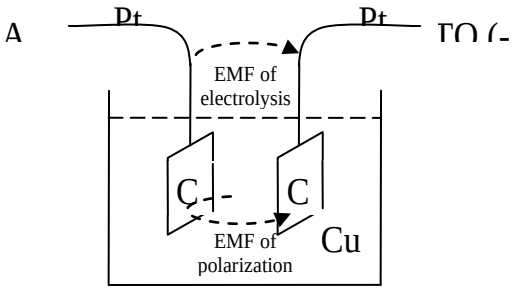
- ✓ chemical polarization
- ✓ concentration polarization
- ✓ overvoltage

Under the influence of current, the potential of the cathode changes - cathodic polarization; anode potential – anodic polarization.

The change in the potential of the cathode and anode under the influence of current causes the occurrence of polarization emf during electrolysis.

<u>Chemical polarization:</u>

Caused by changes in the surface of the electrodes due to the release of electrolysis products on them.



Let's consider the electrolysis of a CuCl2 solution with Pt│CuCl2│Pt platinum electrodes.

TO (-) $Cu^{2+}; H_2O$ $Cu^{2+} + 2\bar{e} = Cu^0$

A (+)$Cl^-; H_2O$ $2Cl^- - 2\bar{e} = Cl_2$

The cathode plate is coated with copper and becomes a copper electrode. The anode plate is saturated with chlorine and turns into a chlorine electrode.

A galvanic cell is formed:

Cu │ CuCl2 │ Cl2

The EMF of such an element is directed against the EMF of electrolysis and counteracts it.

The occurrence of reverse external emf during electrolysis, due to the release of electrolysis products on the electrodes, is called chemical polarization; and this emf is called polarization emf.

For electrolysis to occur with the required intensity, a voltage greater than the polarization emf must be applied to the electrodes.

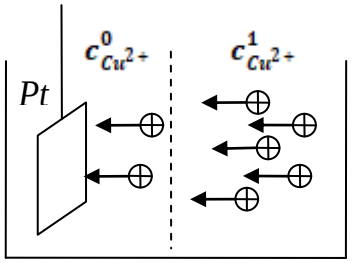
Chemical polarization can also be reduced by adding substances - depolarizers: to the cathode - oxidizing agents; to the anode - reducing agents.

<u>Concentration polarization:</u>

Caused by a change in the electrolyte concentration at the electrodes compared to the concentration in the depth of the solution.

During electrolysis, cations near the cathode are instantly discharged and their concentration is practically zero (). In the depth of the solution, the concentration of the cation is quite high ().$c^0_{Cu^{2+}} c^1_{Cu^{2+}}$

$c^0_{Cu^{2+}} \ll c^0_{Cu^{2+}}$



A potential difference arises;$\varphi = \varphi^0 + \frac{RT}{nF} ln\, c$

the potential near the cathode is more negative. $\varphi_1 < \varphi_2$

The potential shift caused by a change in the concentration of potential-determining ions under the influence of current is called concentration polarization.

The magnitude of concentration polarization depends on:

- current density (the higher the density, the greater the concentration polarization of the electrode).

Concentration polarization can be reduced by heating and stirring.

Decomposition voltage and overvoltage:

Decomposition voltage () E_p - this is the lowest voltage (lowest potential difference) at which electrolysis can continuously occur.

The decomposition voltage cannot be less than the polarization emf (). It should be greater than the polarization emf by the amount of overvoltage (). E_n η

$$E_p = E_n + \eta$$

$$E_p = (\varphi_a - \varphi_k) + \eta$$

Taking into account the overvoltage, the decomposition voltage is calculated using the formula:

$$E_p = (\varphi_a + \eta_a) - (\varphi_k + \eta_k)$$

Overvoltage- this is an additional voltage that must be applied to the electrodes in order for electrolysis to proceed unhindered.

At a low current density, the overvoltage at the electrode is equal to the difference between the release potential () of the ions and their equilibrium potential (). $\varphi_{выд.}$ $\varphi_{равн.}$

$$\eta = \varphi_{выд.} - \varphi_{равн.}$$

Release potential- this is the potential required to begin the release of the corresponding ions on the electrode, or the potential of the electrode at the moment when the decomposition voltage is reached and electrolysis begins.

The release potentials of metals practically coincide with the equilibrium potentials, that is, for many metals there is no overvoltage, with the exception of Fe, Co, Ni.

Gas release potentials differ significantly from their equilibrium potentials. Thus, for hydrogen the release potential shifts to the negative region, for oxygen – to the positive region of potentials.

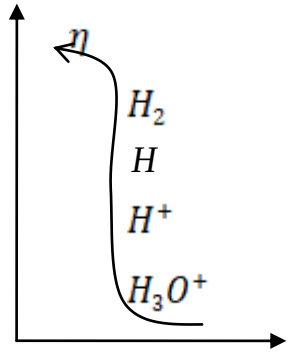
At room temperature and a current density of 0.01 A/cm2, the hydrogen overvoltage is:

Metal cathode	Pt	Fe	Cu	Zn	Hg	Pb
Hydrogen overvoltage, V	- 0.07	- 0.56	- 0.58	- 0.75	- 1.04	- 1.09

The hydrogen overvoltage can reach significant values, which makes it possible to isolate many metals in the voltage series up to hydrogen (for example: Zn, Cd, Ni).

The theory of hydrogen overvoltage was developed by Academician Frumkin and his school.

The hydrogen overvoltage is explained by the slowness of the discharges of hydrogen ions due to their hydration.



The slowest stage is the discharge stage of the hydrated hydrogen ion

$H_3O^+ + Q = H^+ + H_2O$. Hydration of a hydrogen ion is accompanied by the release of a large amount of energy:

$H^+ + H_2O = H_3O^+ + 280000\ {}^{ккал}/_{кг-экв.}$

The energy of this system is significantly higher than the energy of hydronium ions. The low energy level of these ions and the need to destroy the hydration shell of the ion during discharge determine the high activation energy of the discharge, and, consequently, the slowness of the electrode process.

Overvoltage depends on:

- the nature of the electrode (on a mercury electrode the overvoltage is very high, on a platinum electrode it is much lower)
- electrode surface (on a smooth surface the overvoltage is greater than on a rough surface - the electrodes are coated with platinum black)
- current density (the higher the current density, the greater the overvoltage)
- temperature (the higher the temperature, the lower the overvoltage)

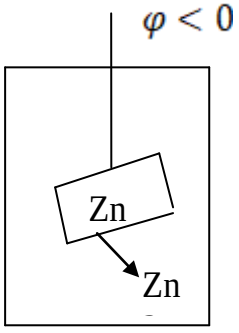
Lecture No. 36

Direct potentiometry

The potentiometric method of analysis is based on changing the value of the electrode potential depending on the physical or physicochemical processes occurring in the system.

When a metal plate is immersed in a solution, an electrode potential arises at the metal-solution interface. $\varphi_{Zn^{2+}/Zn^0} = \varphi^0_{Zn^{2+}/Zn^0} + \frac{0.059}{2} lg\, a_{Zn^{2+}}$

At t = 25°C



The magnitude and sign of the charge depend on the lattice energy of the metal at a given concentration of ions in the solution.

If the hydration energy is high, cations are formed and the metal becomes negatively charged due to excess electrons. The electrostatic field attracts cations from the solution. An electrical double layer appears. Neutralization of ions does not occur, because ions are held by water molecules. A certain potential difference is created inside the electrical double layer.

The magnitude and sign of the potential depend on:

- metal nature

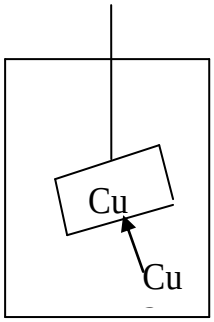
- solvent
- concentration of ions in solution

Andexpressed by the Nernst equation:

$$\varphi = \varphi^0 + \frac{RT}{nF} ln\ a_{Me^{n+}}$$

For dilute solutions at t = 25°C:

$$\varphi = \varphi^0 + \frac{0.059}{n} lg\ a_{Me^{n+}}$$



The hydration energy is low, copper settles on the plate, potential >0.φ

There are two types of metal plates:

1) Metal is a conductor in contact with a solution of its ions.

$Zn^0/ZnCl_2$ $Cu^0/CuCl_2$

$Zn^0 - 2e = Zn^{2+}$ $Cu^{2+} + 2e = Cu^0$

2) An inert metal (Pt) that is in contact with a solution of ions that make up the redox couple.

*For example:*platinum wire dipped in a solution with $Fe^{2+}$and Fe 3+.

In this case, a reduction half-reaction occurs at the electrode: Fe3+ + e = Fe2+

and oxidation half-reaction: Fe2+ - e = Fe3+.

A measure of redox ability is the electrode*redox potential*:

$$\varphi = \varphi^0 + \frac{0.059}{n}\ lg \frac{[\text{о-ля}]}{[\text{вос-ля}]}$$

$$\varphi_{Fe^{3+}/Fe^{2+}} = \varphi^0_{Fe^{3+}/Fe^{2+}} + \frac{0.059}{n}\ \text{lg}\frac{[Fe^{3+}]}{[Fe^{2+}]}$$

φ^0 - standard electrode potential– this is the potential measured relative to the hydrogen electrode at t=25 and the concentration of the determined ion = 1 mol/dm3.℃

It is impossible to measure the potential of one electrode, but it is possible to measure the EMF of a galvanic cell composed of two electrodes, the potential of one of which is a constant value, and the potential of the second changes with changes in the concentration of the ion being determined in the solution (such an electrode acts as an indicator).

If , then it will depend$\varphi_к = const$ only on the anode potential, which is an indicator.ЭДС $= \varphi_a - \varphi_к$

An electrode whose potential changes with changes in the concentration of the ion being detected is called an indicator electrode.

An electrode whose potential remains constant is called a standard or reference electrode.

Potentiometric analysis method is applied:

- to find the equivalence point in titrimetry
- to determine the concentration of ions in a solution
- for studying chemical reactions

Potentiometric analysis method is divided into direct potentiometry andpotentiometric titration.

Direct potentiometry- determines the value of the electrode potential, and calculates the concentration of the determined ion using the Nernst equation.

Potentiometric titration- the end of the reaction is determined by a sharp change in the electrode potential at the equivalent point of the indicator - electrode.

Methods of direct potentiometry (ionometry) are based on the direct application of the Nernst equation to find the activity or concentration of a participant in the electrode reaction from the experimentally measured EMF of the circuit or electrode potential.

Measuring pH using a glass electrode

Perhaps the most famous application of direct potentiometry involves measuring pH using a glass electrode. The glass electrode (Fig. 1) is a thin-walled glass ball 1 filled with an HCl solution or some kind of buffer solution 2. A silver chloride electrode 3 is placed inside the ball. This device is usually covered with a protective tube 4.

When in contact with a solution, the surface layer of glass acts as an ion exchanger, exchanging cations located in the voids of the silicate frame for hydrogen cations. In order for the electrode membrane to acquire this ability, it must first be soaked in an acidic solution.

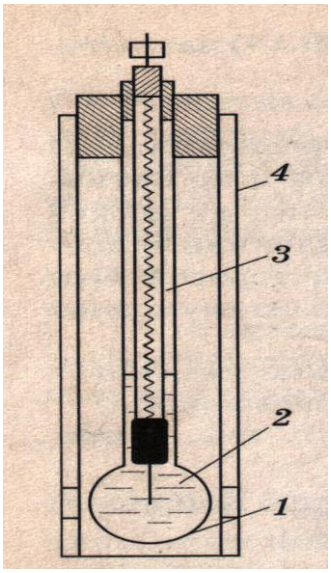


Fig.1. Glass electrode

The equilibrium value of the glass electrode potential depends on the activity of H+ ions in the analyzed solution (a1) and the internal solution of the electrode (a2). To a first approximation, this dependence has the form

$$E = \frac{RT}{F} \ln \frac{a_2}{a_1} \quad . (1.5)$$

Since the activity of H+ ions in the internal solution is constant, then

$$E = E_{const} + \frac{RT}{F} \ln a_1 . (1.6)$$

Substituting numerical values of parameters and moving from logarithms to decimal ones. At 25°C we have:

$E = Econst – 59.16pH$ (1.7)

The value of Econst depends on the pH value of the internal solution, as well as on the asymmetry potential of the glass membrane, which is the potential difference between the two sides of the glass membrane. It arises due to the mismatch in the properties of different sides of the membrane and can be measured experimentally. If the same solution is placed on both sides of the membrane, Econst will depend only on the equilibrium constant H^+ (solution) ↔ H^+ (glass), which characterizes the type of glass and some other properties of the glass electrode. The standard glass electrode potential is not usually determined. When using factory pH meters, this operation is replaced by setting up the devices using standard buffer solutions.

Currently, glass ion-selective electrodes have been designed that are sensitive to alkali metal ions Li^+, Na^+, K^+, Rb^+, Cs^+, as well as to Ag^+, Tl^+, NH_4^+ ions. Their structure and principle of operation are the same as those of a glass pH electrode.

Ion selective electrodes

The glass pH electrode is an example of a broad class of electrodes called ion-selective electrodes. Many ISEs used to determine various ions are designed in a completely similar way to glass ones. ISEs are classified by membrane type and are divided into solid and liquid.

Solid ISEs, in turn, are divided into electrodes with monocrystalline and polycrystalline membranes.

In an ISE with a single-crystal membrane, the ion-sensitive element is made of a poorly soluble crystalline substance with ionic conductivity. Charge transfer in such a crystal occurs due to defects in the crystal lattice. Vacancies can only be occupied by an ion of a certain size and charge, which determines the high selectivity of single-crystal membranes. Structurally, such electrodes are similar to glass ones: in both membranes, the test solution and the reference solution are separated, in which there is an internal reference electrode (usually silver chloride). Of the electrodes of this type, the fluoride electrode is widely used, in which the membrane is LaF_3, which has purely fluoride conductivity.

ISEs with polycrystalline membranes have an insufficiently stable potential and their selectivity is low. In such electrodes, the membrane is made by mixing the active substance with an inert matrix. Of practical importance is an ion-selective electrode with a silver sulfide membrane, suitable for measuring the activity of both Ag^+ and S^{2-} ions. Various halide and metal-sensitive electrodes are also constructed based on silver sulfide.

Liquid ISEs have a liquid membrane. In such electrodes, the reference solution is separated from the analyzed solution by a thin layer of organic liquid containing a liquid ion exchanger that is immiscible with water, but selectively reacts with the ion being determined. A layer of ion-sensitive organic liquid is obtained by impregnating a porous hydrophobic plastic membrane with this liquid. Electrodes of this type exist for Ca^{2+}, Na^+, K^+, NH_4^+.

Gas-sensitive membrane electrodes have been designed for the determination of NH_3, NO and some other gases. Recently, film electrodes have become widely used, in which a thin film is used instead of a liquid membrane. Film electrodes have the same mechanism of action as membrane electrodes, but they are more durable and more convenient to use.

ISE selectivity

ISE can be characterized quantitatively using the Nikolsky equation. It describes the dependence of the electrode potential on the concentration of foreign ions using the selectivity coefficient. In the case of one extraneous ion, Nikolsky's equation looks like this:

$$E = E^0 + \frac{RT}{z_i F} \ln[\, a_i + K_{ij}^{pot} a_j^{z_i / z_j} \,], \quad (1.8)$$

where ai is the activity of the determined ion with charge zi; aj is the activity of the determined ion with charge zj; Kpotij – potentiometric selectivity coefficient.

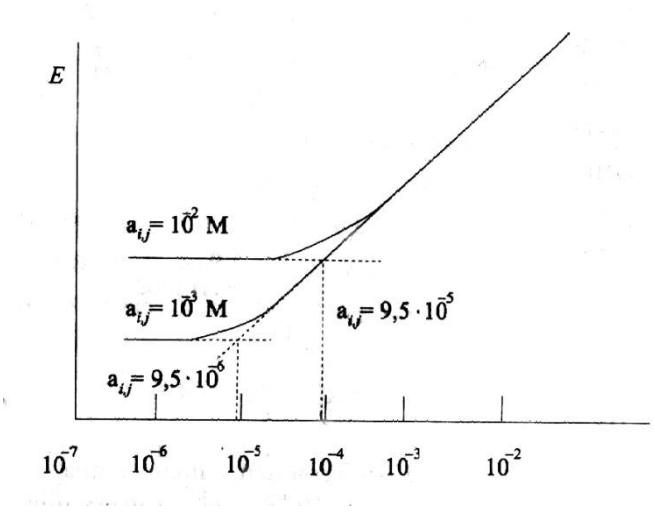
In general, in the presence of m interfering ions:

$$E = E^0 + \frac{RT}{z_i F} \ln[\, a_i + \sum_{j=1}^{m} K_{ij}^{pot} a_j^{z_i / z_j} \,]. \quad (1.9)$$

The selectivity coefficient shows at what ratio of concentrations of the determined and foreign ions the latter begins to have an interfering effect. The values of selectivity coefficients vary from very small values, close to zero, to one or more. The lower the selectivity coefficient, the higher the selectivity of the electrode. Thus, a selectivity coefficient equal to 1·10-3 means that the sensitivity of the electrode with respect to the detected and foreign ions is in the ratio of 1000: 1.

The most preferred method for determining the selectivity coefficient is a method based on the study of solutions containing mixtures of the analyte and foreign ions. To do this, a series of calibration dependences of the electrode potential on the concentration of the ion being determined are obtained, plotted in the presence of various concentrations of the foreign ion (Fig. 2).

At large excesses of foreign ions, the electrode potential is determined by the second term in the Nikolsky equation. It remains constant and does not depend on the concentration of the ion being determined (horizontal section on the calibration curve). From the abscissa of the intersection point of two sections of the calibration dependence (horizontal and inclined), equal to ai = Kijpot·ajz(i) / z(j), it is possible, knowing the constant value aj, to calculate the selectivity coefficient. The described method allows you to calculate the selectivity coefficient even from one calibration dependence, but for greater reliability it is necessary to use several.



Rice. 2. Determination of the ISE selectivity coefficient from calibration curves constructed in the presence of foreign ions with a concentration of 10-2 M (upper graph) and 10-3 M (lower graph). In this case, the selectivity coefficient is 9.5 · 10-3

Techniques used in direct potentiometry (ionometry)

*Calibration graph method.*The most commonly used technique is sequential dilution of the initial solution with distilled water. In this way, a series of 5–7 standard solutions with a known content of the analyte is prepared. The concentration of the analyte and the ionic strength in the standard solutions should not differ greatly from the concentration and ionic strength of the analyzed solution: under these conditions, determination errors are reduced. The ionic strength of all solutions is maintained constant by introducing an indifferent electrolyte (constant ionic strength method). Standard solutions are sequentially introduced into the electrochemical cell. Typically this cell is a glass beaker in which electrodes are placed.

The EMF of standard solutions is measured by thoroughly washing the electrodes and glass with distilled water before filling the cell with each standard solution. Based on the data obtained, a calibration graph is constructed in the coordinates E(EMF) – log c, where c is the concentration of the analyte in the standard solution. (The constant ionic strength method allows you to move from activities to concentrations.) Then the analyzed solution is added to the electrochemical cell (after washing the cell with distilled water) and the emf of the cell is measured. Using the calibration graph, log c(X) is found, where c(X) is the concentration of the analyte in the analyzed solution.

Based on the ISE calibration data, the following electrochemical characteristics are determined.

1. The Nernst region of the electrode function is the interval of the linear dependence of the potential on the activity (concentration) of potential-determining ions.

2. The slope of the electrode function is the angular coefficient of the calibration graph (E – pai, E – pci).

3. Detection limit of the potential-determining ion cmin. To do this, straight sections of the E – pci dependence are extrapolated; the resulting intersection point corresponds to the value cmit on the abscissa axis.

4. ISE response time – time to reach stationary potential.

5. Selectivity of the electrode relative to the ion being determined in the presence of foreign ions.

*Standard addition method.*A known volume V(X) of the analyzed solution with concentration c(X) is added to the electrochemical cell and the emf of the cell is measured. Then, an accurately measured small volume of a standard solution V(st) with a known (sufficiently large) concentration c(st) of the analyte is added to the same solution and the emf of the cell is determined again (it is necessary that $\Delta E \geq 30$ mV).

Calculate the concentration c(X) of the analyte in the analyzed solution using the formula

$$c(X) = c(cm)\frac{V(st)}{V(X)+V(st)}\left[\ 10^{\Delta E/S} - \frac{V(X)}{V(X)+V(st)}\ \right]^{-1}, \quad (1.10)$$

where ΔE is the observed change in potential in mV after adding the standard; S = 0.059/n – slope of the electrode function, V.

Lecture No. 37
Coulometry

Electrolysis is a chemical reaction of oxidation or reduction at an electrode under the influence of an electric current. To measure the amount of charge passed through the cell, coulometers or electronic integrators are used. A known reaction occurs in the coulometer with 100% current efficiency. Measuring the mass of the substance formed in the coulometer allows one to calculate the transferred charge.

The coulometric analysis method uses Faraday's laws of electrolysis:

1. The amount of substance reduced or oxidized as a result of electrolysis is directly proportional to the amount of electricity passed.

2. The masses of various substances released on the electrode during the passage of 1 Coulomb of electricity are equal to their electrochemical equivalents.

Electrolysis begins at a certain voltage between the electrodes, called the decomposition potential. In order for electrolysis to proceed quickly, the voltage in the circuit is maintained above the decomposition potential. If a solution contains several components with different decomposition potentials, they can be separated from the mixture in a certain sequence by adjusting the voltage. As the voltage increases, metals with a lower decomposition potential are first released at the cathode. For example, from a solution of Pb+2 and Cd+2 ions (with single activities), lead ions will first be reduced at the cathode (E0Pb= - 0126 V, E0Cd= - 0.402 V). If the cathode potential is made equal to 0.35 V, then only lead ions will be reduced, and cadmium ions will remain in solution.

When a current passes, the potential of the electrode changes compared to the equilibrium one (defined by the Nernst equation); this phenomenon is called polarization of the electrode. Reasons: 1) accumulation of reduction and oxidation products on the electrodes, which form, as it were, a new galvanic element, the emf of which is directed against an external source (chemical polarization), 2) change in the concentration of ions near the electrodes compared to the volume of the solution, that is, the occurrence of concentration galvanic element, the EMF of which is also directed against the voltage of the external current source (concentration polarization). A quantitative measure of polarization is overvoltage (the difference between the equilibrium EMF and the potential difference during the passage of current).

Coulometry is a highly sensitive and accurate method of analysis that allows you to determine up to 10-9 g of a substance. However, it is necessary to correctly select the electrolysis voltage (potential) in order to prevent side reactions from occurring.

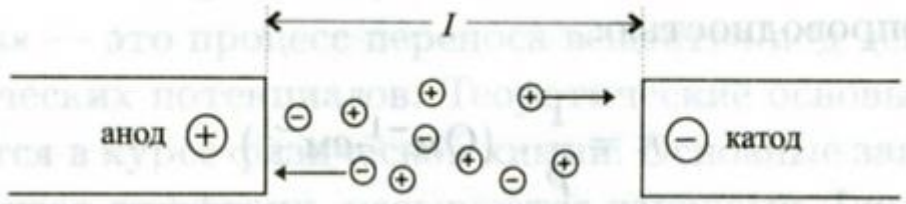
and control automation.

Lecture No. 38
Conductometry

The conductometric method of analysis or conductometry is an analysis method based on measuring the specific electrical conductivity of the analyzed solution.Electrical conductivity is

the ability of a substance to conduct electric current under the influence of an external electric field. Siemens electrical conductivity unit (cm).

Bodies or substances that conduct electric current are called conductors. Conductors contain a large number of current carriers. Depending on the nature of the current carriers, conductors of the first kind and conductors of the second kind are distinguished. Conductors of the first kind are metals. In them, the transfer of electricity is carried out by the movement of electrons along a conductor from the negative pole of the current source to the positive. The electrical conductivity of conductors of the first kind reaches 108 S/m. Conductors of the second type are solutions of electrolytes. Electrolytes are substances whose molecules or crystals, when dissolved, disintegrate into ions. In electrolyte solutions, electricity is transferred due to the movement of ions. Cations and anions move in opposite directions. Positively charged cations move towards the cathode, negatively charged anions move towards the anode (Fig. 26.1). The electrical conductivity of electrolyte solutions is in the range of 10-5 – 104 S/m.



Electrical conductivity

For electrolyte solutions, as well as for conductors of the first kind, Ohm's law is valid:

$E = IR$

where E is the potential difference between the electrodes, V (volts); I – current strength, A (ampere); R – resistance, Ohm (ohm).

The resistance of the electrolyte solution is

$$R=\frac{\rho l}{S}$$

Whereρ- resistivity, Ohm·cm; l – distance between electrodes, cm; S – cross-sectional area of the electrolyte solution between the electrodes, cm2.

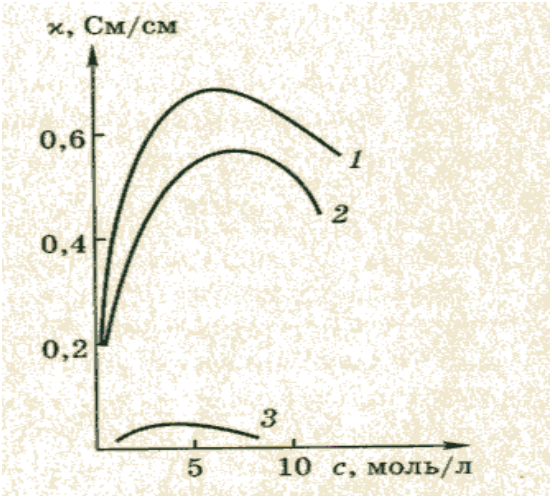
Electrical conductivityκ- the reciprocal of resistivity:

$$\kappa=\frac{1}{\rho}$$

Specific electrical conductivity is equal to the electrical conductivity of 1 cm3 of solution located between parallel electrodes with an area of 1 cm3 at a distance between them1 cm. The unit of measurement for electrical conductivity is S/cm.

In dilute solutions, the specific electrical conductivity increases with increasing concentration, at somereached exactly high concentrationreaches a maximum and then decreases. In Fig. 26.2 shows typicalmeasures of this dependence. Electricconductivity of a weak electrolyteta - acetic acid - significantly neitherthe same corresponding value for solutions of strong electrolytes: hydrochloric acid HC1 or potassium hydroxide KOH. The increase in specific electrical conductivity with increasing concentration in solutions of moderately high concentrations occurs due to an increase in the number of ions with

concentration. However, in concentrated solutions otherThese effects lead to a decrease in electrical conductivity. In concentrated solutionas the forces of interionic interaction increase, as a result of which the formation of interionic associates or ion pairs occurs, increasingThe viscosity of the solution decreases and other effects appear that reduce the speed of ion movement and cause a decrease in electrical conductivity. As a total result of the action of these factors, a maximum appears on the electrical conductivity curve. For analytical measurements, a section of the curve with increasing electrical conductivity is usually used, i.e., the region of dilute and moderately concentrated solutions.



Rice. 26.2. Dependence of specific electrical conductivity on the concentration of solutions: 1 – HCl; 2 – KOH; 3 – CH3COOH.

Equivalent electrical conductivity

The electrical conductivity of electrolyte solutions depends on their concentration, therefore in electrochemistry such quantities as molar and equivalent electrical conductivity are used.

Equivalent electrical conductivity is the conductivity of a solution containing 1 mole equivalent of a substance and located between two parallel electrodes, the distance between which is 1 cm. Its unit of measurement is cm • cm2/mol.

Equivalentλand specificκelectrical conductivity is related by the following equation:

κ= 1·10-3sλ

where c is the molar concentration of the equivalent, mol/l. (Coefficient 1·10-3 appears in this equation because 1 cm3 of solution contains 0.001 mol equivalent of electrolyte).

A characteristic of the movement of ions in an electric field is mobility u:

$$u = \frac{z_e e}{6 \pi r \eta}$$

where ze e is the charge of the ion; r – particle radius (cm);η- medium viscosity coefficient (kg/(m·With)).

The equivalent electrical conductivity is related to the ion mobilities by the following equation:

$\lambda = F(u^+ + u^-) = Fu^+ + Fu^-$

where F is Faraday's constant; u+ is the mobility of the cation; u- is the mobility of the anion.

Works$Fu^+$and Fu- are called the equivalent electrical conductivities of the corresponding ions:

$\lambda_+ = Fu^+$

$\lambda_- = Fu^-$

The sum of the equivalent electrical conductivities of the ions is equal to the equivalent electrical conductivity of the electrolyte:

$\lambda = \lambda_+ + \lambda_-$

Dependence of the electrical conductivity of a solution on its concentration

The electrical conductivity of a solution dependson the degree of electrolyte dissociation. Therefore, it should be expected that for strong and weak electrolytes the dependence of electrical conductivity on concentration will be different.

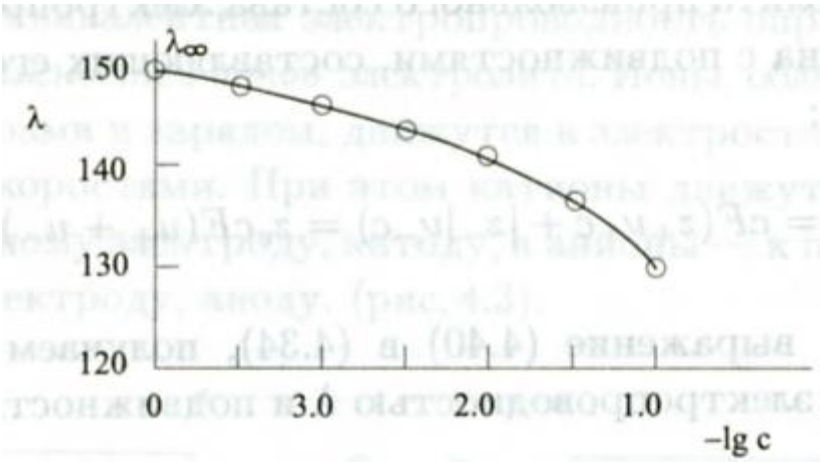
Strong electrolytes are completely dissociated even in fairly concentrated solutions. In this case, the electrical conductivity should be directly proportional to the concentration:

$\kappa = 1 \cdot 10^{-3} cF(u^+ + u^-)$

However, due to interionic interactions with increasing concentration, electrical conductivity increases more slowly than would be expected from this equation, and at very high concentrations (1-15 mol/l) it begins to fall. This phenomenon is associated with the formation of uncharged ion pairs of ionic associates, unable to conduct current .

The described phenomenon leads to the fact that the equivalent electricthe conductivity of strong electrolytes decreases with increasing concentrationcentration (Fig. 16.4).

At infinite dilution, there are no interionic interactions, and the ion mobilities reach their maximum values.ny. In Fig. 16.4 shows the value of the equivalent electrically conductivethe stability of the KCl solution at infinite dilution.



Rice. 16.4. Dependence of the equivalent electrical conductivity of a solution of a strong electrolyte (KCl) on concentration.

For any ion, the value of equivalent electrical conductivity at infinite dilution (Table 26.1) does not depend on the experimental conditions and can be used for an approximate estimate electrical conductivity of the electrolyte solution.

Table 26.1 Equivalent electrical conductivities of some ions at infinite dilution (18°WITH)

Катион	$\lambda_{+\infty}$, См·см^2/моль	Анион	$\lambda_{-\infty}$, См·см^2/моль
H^+	349,8	OH^-	197,6
Li^+	38,7	F^-	55,0
Na^+	50,1	Cl^-	76,3
K^+	73,5	Br^-	78,3
Ag^+	61,9	I^-	76,8
Mg^{2+}	53,1	ClO_4^-	67,3
Ca^{2+}	59,5	CH_3COO^-	40,9
NH_4^+	73,3	NO_3^-	71,5

As can be seen from this table, H+ and OH- ions are characterized by electrical conductivity that is many times higher than the electrical conductivity of other ions. This is explained by a special, so-called relay, mechanism of charge transfer by these ions in aqueous solutions, which consists of a series of successive acts of breaking and forming hydrogen bonds.

The dependence of the equivalent electrical conductivity of strong electrolytes on concentration (Fig. 26.4) in the region up to 0.01 M is well described by Kohlrausch's law ("square root law"):

$\lambda=\lambda_\infty-k\sqrt{c}$

The value of the constant k for each electrolyte has its own signreading.

For weak electrolytes with changing concentrationsThe degree of dissociation varies. As the concentration increases, the degree of dissociation decreases. Weak electrolytes include, in particular, organic acids and bases, as well as some salts - FeF3, HgCl2.

For dilute solutions of weak electrolytes, interionic interactions are negligible. The difference in electrical conductivity from the limiting one (at infinite dilution) is due in this case only with incomplete dissociation. Therefore, the degree of dissociationα equal to

$$\alpha=\frac{\lambda}{\lambda_\infty}$$

It is the ratio of the concentration of an electrolyte cation or anion to its total concentration:

$$\alpha = \frac{[K^+]}{c} = \frac{[A^-]}{c}$$

For weak electrolytes in very dilute solutions, an approximately linear relationship is observed between the equivalent electrical conductivity and concentration:

$$\lambda = \lambda_\infty - k'c$$

At higher concentrations, the degree of dissociation of weak electrolytes is significantly less than unity.

Currently, a large number of different measuring devices are used in conductometry. Each of them, in addition to common elements and metrological properties, also has individual characteristics: the type of signal conversion, the type of contact with the electrolyte under study, the type of operating current (voltage) used for measurement, the method that is used as the basis for the measuring device, etc. These features, which ultimately determine the metrological properties of the measuring device, and according toform the basis for the classification of conductometry methods (Fig. 26.9). All conductometry methods by typeweekend sign a l a are divided into two groups: analog and frequency (discretenye).

*Analog methods*are characterized by the fact that the electricalmask, most often the voltage arising in the measuring element - conductometric cell - measuring deviceAs a result of various transformations occurring under the influence of voltage from a source of operating voltage, at the output of the measuring device it turns into the same electrical quantity (current, voltage). In other words, in analog measurement methods, the operating voltage of the source is modulated in amplitude by the voltage from the conductometric cell and, after demodulation (detection), at the output of the measuring deviceAs a result, an electrical quantity appears that is proportional to the value of the parameter under study in the conductometric cell.

Analog methods are the most common and widely usedworked methods of conductometry.

*Frequency methods*characterized by the fact that tension, fusscurrent in the measuring element - conductometric cell, modulates the frequency of the operating voltage of the AC sourcecurrent. As a result, a discrete number of pulses per unit time appears at the output of the measuring device, by the number of which one can judge the value of the parameter under study.

Frequency methods arose in connection with the development of digital measurement systems. Application of frequency signalsMethods allows you to enter measurement results directly into digital measuring systems and electronic computers and obtain a digital record of the results. This creates great advantages when automating laboratory research.ideas and production processes.

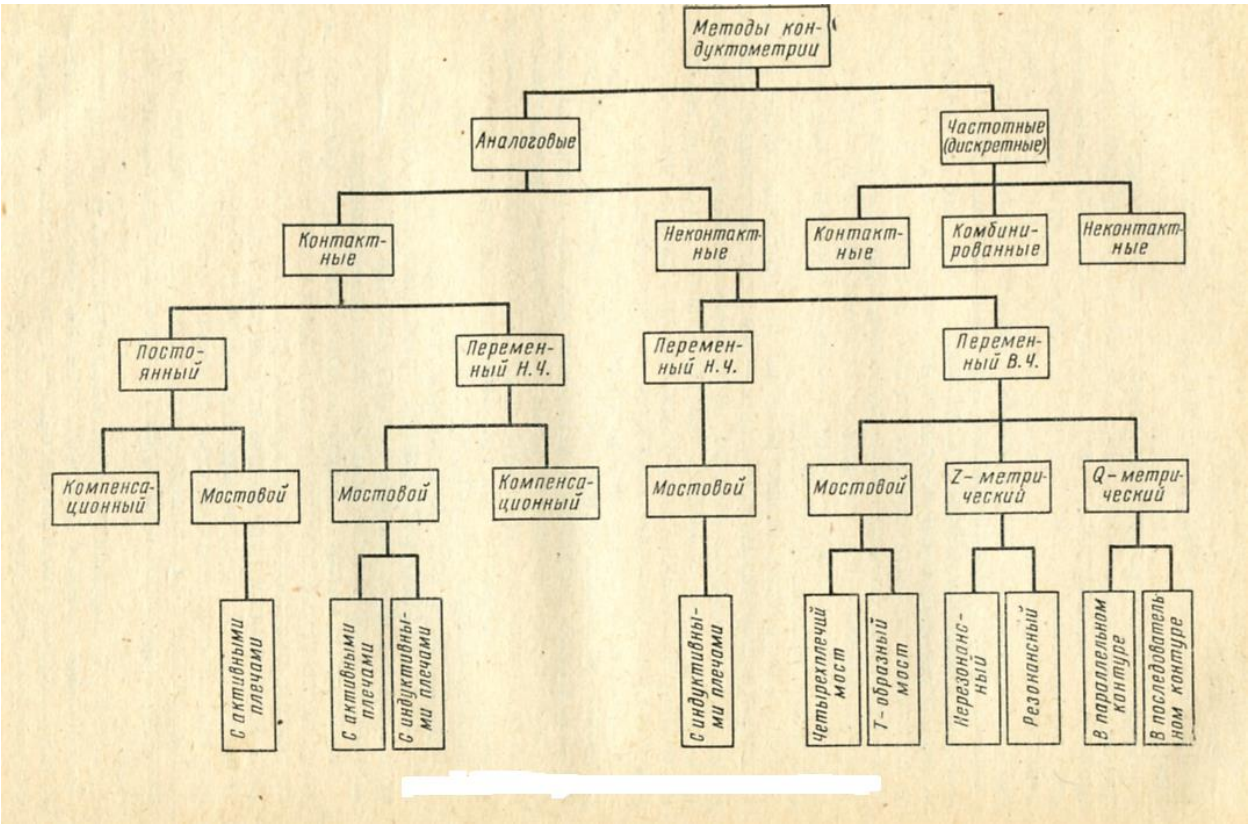
Analog and frequency conductometry methods by type of contactof the ionic conductor under study in conductometryEach cell is in turn divided into two groups: contact and non-contact (or non-contact) methods.

Contact methods are characterized by the fact that in the process of changerhenium electrolyte under study is in direct galvaniccontact with the electrodes of the conductometric

cell. Although they make it possible to make accurate measurements, they are not free from errors due, in particular, to a greater or lesser extentgreater degree of polarization phenomena on the electrodes.

Group of contactsanalog methods according to haThe nature of the voltage used for measurement is divided into two groups.

1. Low frequency alternating current methods. This group includesThese are the most thoroughly developed bridge and compensation methods. The advantage of these methods is the high accuracy of measurements andthe ability to obtain a direct reading of the measured value. Especially this



Rice. 26.9. Classification of conductometric methods of analysis.

refers to bridge measurement methods, which thanks to this have become the most widely used in conductometry.

Disadvantages of methods in this group: the presence of polarization phenomena, which are especially evident when measuring concentrated solutions and lead to errors in measurements; complex design and adjustment, especially when high precision is required.

2. Direct current methods, which are also divided into bridge and compensation methods.

The advantage of the methods of this group is the simplicity of the instruments and measurement methods compared to the first group. The disadvantages include the impossibility of accurately measuring the electrical conductivity of concentrated solutions due to the appearance of significant polarization effects and the need to have a cell of complex design for accurate measurements of the electrical conductivity of dilute solutions.

The group of contact frequency methods, due to the peculiarity of the measuring circuits, allows the use of the same instruments for measurements with alternating current of low (sound) frequency and high frequency. Currently, various types of RC and RL generators are almost exclusively used for this purpose. Active resistances in the oscillatory circuit of such generators are replaced by the resistance of the electrolyte under study, i.e. contact conductometric cell, and the resistance value determines the frequency at the generator output. The small amount of current flowing through the oscillatory circuit at relatively high frequencies creates minor polarization phenomena on the cell electrodes and allows the use of both large and miniature electrodes and cells. The latter are very convenient for physicochemical and analytical studies, especially with a limited volume of electrolyte.

With the appropriate choice of parameters of the oscillatory circuit of the generator, it is possible to measure resistances of various values in a wide range.

The disadvantage of the methods is the absence of a strictly linear relationship between changes in the resistance value of the electrolyte under study and the frequency at the output of the measuring device.

Non-contact methods differ from contact methods in that during the measurement process the electrolyte under study does not have direct contact with the electrodes of the conductometric cell and is connected to the measuring circuit inductively or through a capacitance.

Non-contact methods have been developed to eliminate polarization phenomena on the electrode that appear as a result of the flow of electric current through the electrode-solution interface, to measure the electrical conductivity of concentrated solutions, and for measurements in aggressive and volatile media.

The advantages of non-contact methods include the absence of interaction between the system under study and the electrode material and the impossibility of mechanical contamination of the electrodes; in addition, they make it possible to study the processes occurring in a system located in a sealed ampoule at high or low temperatures, study phase transitions, etc.

The great advantage of non-contact methods is the elimination of precious metals (platinum) from the conductometric cell, since in the absence of direct contact of the system under study with the electrodes, the latter can be made of any metal.

The disadvantage of non-contact methods is that they do not allow direct reading of the electrical conductivity value. Therefore, they are often used only to determine relative changes in electrical conductivity, for example, for high-frequency titration.

The group of non-contact analog methods is divided into two subgroups based on the nature of the voltage used for measurement.

1. Low frequency alternating current methods. These include inductive (transformer) and bridge methods.

2. High frequency alternating current methods. High-frequency measurement methods are carried out using bridge circuits and high-frequency generators. In the latter case, depending on the location of the conductometric cell in the HF generator circuit, the methods are called Q-

metric (by changing the value of the quality factor of the oscillating circuit of the generator) and Z-metric (by changing the impedance of any circuit).

Since Q- and Z-metric methods do not provide a direct reading of the measured value of conductivity or resistance, they have become widespread as methods for measuring the relative magnitude of changes in conductivity, for example for high-frequency titrations, which can be performed with great accuracy.

Non-contact frequency methods are also divided into two groups according to the type of operating current: low-frequency and high-frequency alternating current methods.

Currently known measuring devices that use low-frequency alternating current, modulated in frequency by changing the value of the active resistance of the electrolyte under study, have not yet become widespread. Frequency non-contact measuring devices for high-frequency alternating current are more developed and more widely used. Such devices are based on the principle of frequency modulation, carried out by changing the amount of losses in the inductance or capacitance of the oscillating circuit of LC, RC and RL generators.

In recent years, frequency combined methods have been developed based on the principle of frequency modulation in RC and RL generators. These methods use combined conductivity cells, which are a combination of contact and non-contact cells. Combined methods have very high sensitivity and can be used for conductometric titration.

Application of conductometric methods of analysis.

Direct measurement of electrical conductivity is the most effective method for monitoring the quality of distilled water in laboratories, process water in so-called fine chemical or pharmaceutical industries, in water treatment technology and assessment of wastewater contamination, heating engineering (boiler feeding), etc. Conductometric sensors are successfully used in automated production control schemes in some branches of the chemical, textile and food industries, hydroelectrometallurgy, etc. A method for the conductometric determination of small amounts of carbon (10~2-10~3%) in steels and metals has been developed. The technique involves burning a sample in a stream of oxygen, absorbing CO2 into a Ba(OH)2 solution, and measuring its electrical conductivity. The carbon content is found using a calibration curve.

Direct conductometry methods are used to control the quality of milk, various drinks and food products.

The simplicity and high accuracy of conductometric measurements, the possibility of using the obtained data in automated monitoring and control circuits and other advantages of the electrical conductivity method arouse great interest in this method at the present time. However, direct conductometric measurements are very sensitive to the influence of impurities, especially acid-base impurities due to the sharp difference in the mobilities of H+ and OH- ions compared to the mobilities of other ions.

Conductometric titration has a wide range of applications. Strong mineral acids in an aqueous solution are titrated with alkali at high and fairly low concentrations (up to 10-4 mol/l). Strong bases are also titrated with strong acids. Formic, acetic and other acids of medium strength are easily titrated. Conductometric titration curves for a number of organic acids

(succinic, adipic, etc.) when titrated with a weak base have a more pronounced break at the equivalence point than titration curves with a strong base. These acids are titrated with an ammonia solution, and both protons react. Weak bases can be titrated with strong and weak acids. For example, ethanolamines are easily titrated with acetic acid solutions. Of practical importance is the conductometric titration of ammonium salts and other weak bases with alkali solutions and the titration of salts of weak acids (acetates, phenolates, etc.) with strong acids. Amino acids (glycine, alanine, valine, etc.) are titrated with strong bases. Mixtures of weak acids, mixtures of weak bases, as well as mixtures of acids or bases with salts of weak acids or weak bases can be titrated conductometrically.

Particularly wide possibilities for titrating various electrolytes and their mixtures are opened by the use of organic and aqueous-organic solvents: aqueous-dioxane, aqueous-acetone, aqueous-alcohol, glacial acetic acid, etc. Three-, four- and five-component mixtures are analyzed in these solutions.

Many cations and anions are determined by conductometric titration. Silver nitrate is used to titrate chloride, bromide, iodide, cyanide, thiocyanate, oxalate, vanadate, tartrate, salicylate and some other anions. Titration in 90% alcohol is used to determine C1- in natural waters at a content of about 10 μg. The content of I- and C1- in a mixture can be determined without prior separation. Titration with acetate or barium chloride is used to determine sulfate, chromate, carbonate, oxalate, citrate and other anions, usually when alcohol is added to the analyzed solution. Sulfates are determined using this method in natural waters and similar objects.

The high-frequency titration method can use almost any chemical reaction: acid-base interaction, precipitation, etc. in aqueous and non-aqueous solutions. High-frequency titration curves have the same appearance as conventional conductometric titration curves. The concentration range of titration of weak acids and bases by the high-frequency method remains approximately the same as in conventional conductometric titration.

Lecture No. 39
Voltammetry

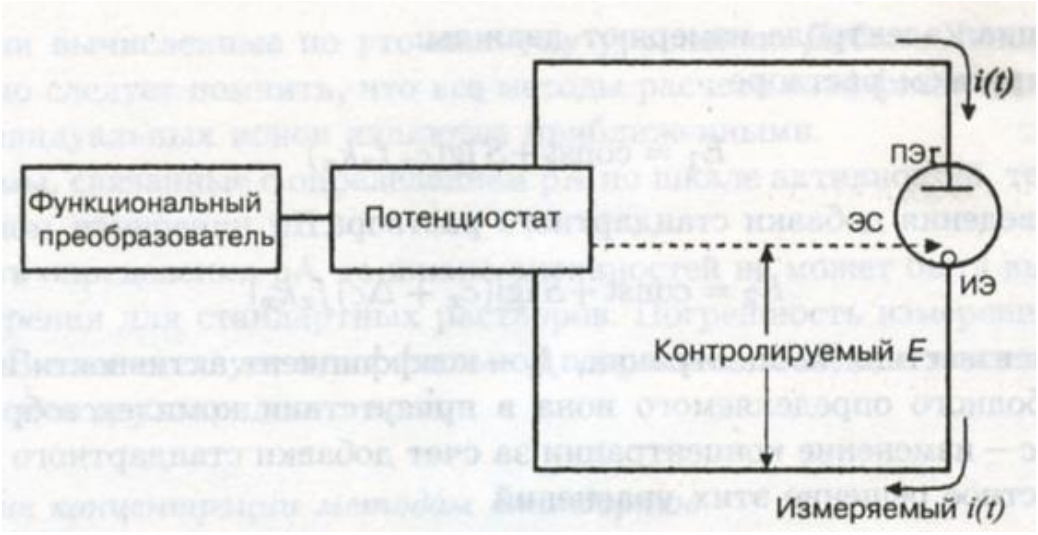
Voltammetry includes microelectrolysis methods in which the potential of the indicator electrode is created by an external source and is knownas a function of time, and the resulting current-potential and current-time dependencies serve as a source of information about the composition of the solution. Depending on the type of potential sweep and the mechanism of mass transfer, there are voltammetry with linear potential sweep (voltammetry at constant current), methods with stepwise change in potential, guideRodynamic methods and stripping voltammetry.

Voltammetric methods are precise methods for the determination of many organic and inorganic substances (mainly metal ions) that can be electrochemically oxidized or reduced (electroactive substances) in trace quantities. Using voltammetry, it is possible to simultaneously determine several substances. If the working electrode is a microelectrode, the volume of the analyzed solution is relatively large, and the timeThe analysis time is small, the concentration of the analyte in the solution volume changes insignificantly during the analysis. Voltam-perometric methods

are moderately selective, but selectivity can be significantly increased, for example by combining liquid chromatography with electrochemical detection.

The development of voltammetry dates back to the first work (1922.) Jaroslav Heyrovsky (DC voltammetry on a dropping mercury electrode), who was awarded the Nobel Prize in 1959.

The voltammetric cell consists of the analyzed solution, two electrodes of different sizes and a reference electrode. The microelectrode is the indicator electrode, while the other conductive electrode serves as the auxiliary or counter electrode. The potentiostat controls the voltage between the indicator electrode and the auxiliary electrode, maintaining the potential difference between the indicator electrode and the reference electrode according to a preselected voltage sweep provided by the programmer (or microcomputer). DifferenceThe potential between the indicator electrode and the reference electrode is measured by a high-resistance feedback loop (there is no current in it). A potentiostat is considered an "active instrument" that externally controls the potential of the indicator electrode. In Fig. Figure 7.8 shows a diagram of an installation for operation at a controlled potential. For voltammetric analysis of aqueous solutions, a simpler two-electrode circuit (indicator electrode and reference electrode) can be used.



Rice. 7.8. Scheme of the experimental setup for operation at a controlled potential: IE – indicator electrode;. PE – counter electrode; ES – reference electrode.

An indicator electrode is an ideally polarizable electrode, i.e., an electrode characterized by a large potential shift during an infinite cycle.but low current. The polarization of the electrode corresponds to the horizontal portion of the i-E curve of the electrode and determines the potential range suitable for analytical purposes, since it can be used to study the processes of electrochemical oxidation or reduction of the analyte. In contrast, an ideally non-polarizable electrode is an electrode with a fixed potential that does not change when relatively small currents flow. Non-polarizable electrodes, such as electrodes of the second type or an electrode made of bottom mercury with a large surface, are used in voltammetry as reference electrodes. An auxiliary electrode (conducting counter electrode) can be, for example, a platinum wire.

Voltammograms are usually recorded in an unstirred solution containing a large excess of an inert electrolyte, called the supporting electrolyte.

7.3.2. Indicator electrodes

In voltammetry, various indicator electrodes are used; the most commonly used electrodes are discussed below.

Mercury dripping electrode. In classical polarography, the indicator electrode is mercurydripping microelectrode. A mercury drop is formed at the end of a glass capillary (10-20 cm long, internal diameter 0.05 mm), connected by a flexible tube to a reservoir of mercury. Mercury drops have a reproducibledimmable diameter and lifetime from 2 to 6s. The lifetime of a drop depends on the height of the mercury column above the capillary, i.e., the hydrostatic pressure of mercury. Sometimes a mechanical hammer is used to control the lifetime of the droplets. Mercury dripping electrode has the following advantages:

1) constant renewal of the electrode surface prevents contamination of the electrode surface, which is reflected in the high reproducibility of the current-potential relationships;

2) the overvoltage of hydrogen on mercury in aqueous solutions is large, therefore it is possible to study the processes of reduction of electroactive substances with more negative potentials than the reversible potential of the discharge of hydrogen ions. In an acidic solution, for example,0.1 MHC1, the release of hydrogen gas is observed at potentials more negative - 1.2 V;

3) mercury forms amalgams with many metals, reducing their reduction potential.

The polarization range of the mercury electrode (rel. NCE) in an aqueous solution in the absence of O2 is from +0.3 to approximately -2.7 V. In the cathode region, it is limited by the reduction potentials of the cations of the background electrolyte (the background electrolyte is added to ensure diffusion mass transfer). The most negative potentials can be achieved by using tetra-alkylammonium salts. Mercury oxidation

$2Hg \rightleftarrows Hg_2^{2+} + 2e$

limits the polarization range in the anodic potential region. From this we can conclude that it is mainly possible to determine reducing electroactive substances using a mercury microelectrode.

Static mercury drop electrode.The static electrode design, like the mercury dripping electrode, has a reservoir of mercury and a glass capillary, but the repeatability of the droplet size and the dripping period are more precisely controlled. This is achieved using a solenoid located between the mercury reservoir and the capillary, and a mechanical hammer at the capillary. Thus, by correctly setting the on and off times of the solenoid, the drop separation time can be adjusted, and the device can be used as a static electrode (hanging drop) or a dripping electrode with a controlled dripping period.

The static mercury electrode has all the characteristics of a dropping mercury electrode, which is especially convenient for routine analysis. An additional feature associated with the constancy of the surface of a mercury droplet will be discussed in connection with highly sensitive pulsed current measurement methods.

Solid electrodes. To determine oxidizing substances, solid electrolytes are usually used.yes. Of the solid electrodes (for example, Pt, Au, C) used in electrolysis, various types of graphite electrodes have found wide use in analytical voltammetry. This is due to a wide range of anodic potentials, low electrical resistance and ease of renewal of the electrode surface. Carbon paste electrodes and glassy carbon electrodes are used for electrooxidation monitoring.tion both in an unstirred solution and in a flow of electrolyte, for example, in HPLC. In the latter case, electrochemical detection using a thin-layer cell allows the determination of nano- and pico-gram quantities of biogenic amines.

In the anodic region, the polarization range of graphite electrodes is limitedhigh O2 release potential (+1.5V).

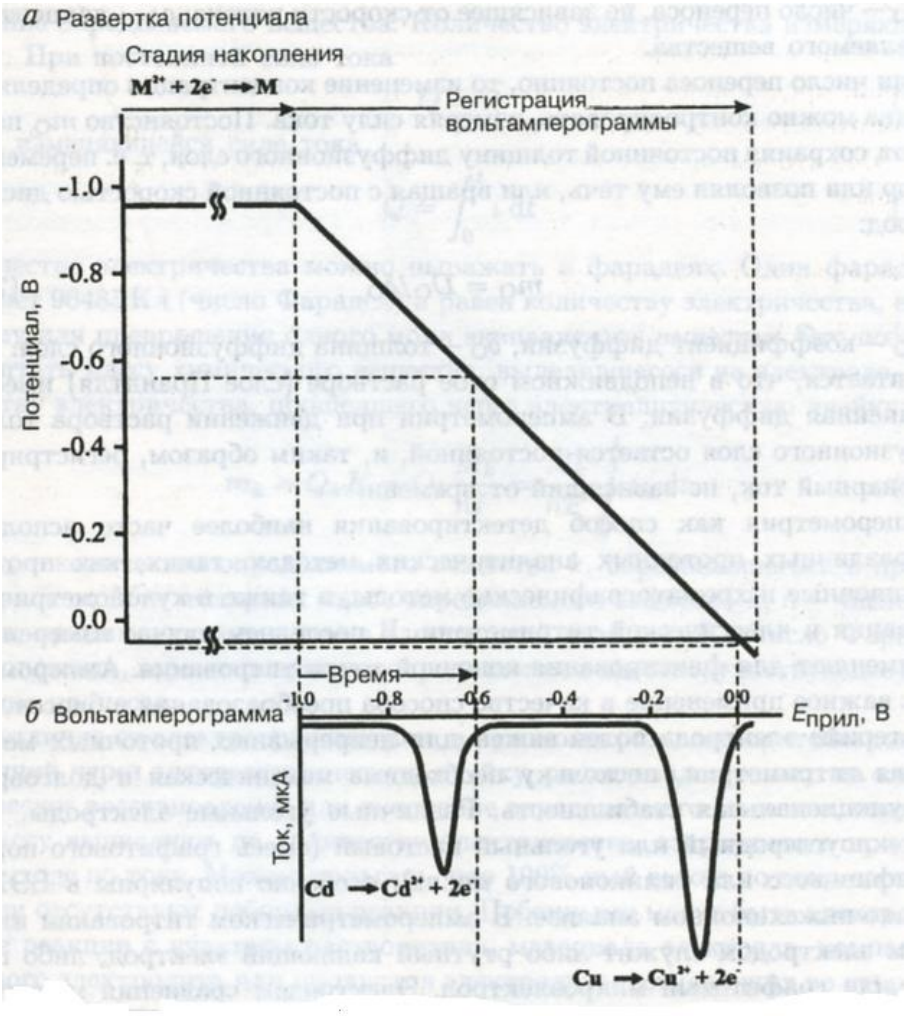
7.3.3. Stripping voltammetry

The main stages of inversion electrochemical methods are

1) preliminary accumulation of the analyte on an electrode with a constant surface area using electrolysis at a controlled potential;

2) removal or dissolution of the analyte from the electrode as a result of a voltammetric or chemical reaction.

Common to all inversion methods is the stage of preliminary accumulation (sedimentation), but the techniques used at the final stage of analysis may vary. If dissolution is carried out electrochemically, the method is called stripping voltammetry (SVA) (Fig. 7.9); in inversion potentiometry based on the stage of removal of the accumulation productlies a chemical reaction.



Rice. 7.9. Anodic stripping voltammetry: a – potential scan at the stage of accumulation and recording of the voltammogram, b – anodic stripping voltammogram with linear potential scan.

Since inversion methods are based on the preliminary accumulation of the component being determined, they are suitable for the concentration range of 10-6 -10-^{8}M, i.e. for determining trace amounts of metals.

*Anodic stripping voltammetry*is used mainly to determine metals capable of forming amalgams, while cathodic stripping voltammetry is used to determine substances that form

insoluble mercury salts on the electrode surface. In the latter method, at the stage of anodic preelectrolysis, Hg(I) ions are formed and the substances being determined (anions) are deposited on the electrode surface in the form of poorly soluble Hg(I) salts. During a cathodic potential sweep, the deposit is reduced to the Hg(I) ion and cathodic peaks of the anions are observed. In addition to mercury, a silver electrode can also be used in cathodic stripping voltammetry. The method of cathodic stripping voltammetry is convenient for determining halide, sulfate, oxalate and mercaptan ions.

Lecture No. 41
Chromatographic analysis methods

IN1903M.S. Tsvet was the first to set out the principles of chromatography (Greek “chromo” - color, “grapho” - write) and created a method for separating the pigments of green plants.

The chromatographic method allows the separation and analysis of complex mixtures. The separation of substances occurs due to the different adsorbability of the components of the mixture.

Chromatography is a dynamic process that occurs in a system of two immiscible phases, one of which is mobile and the other immobile. The mobile phase can be either a gas or a liquid, and the stationary phase can be a solid or a thin film of liquid adsorbed on a solid.

Classification of chromatographic methods

1) according to the state of aggregation of the mobile phase
- gas chromatography (GC)
- liquid chromatography (LC)

2) according to the geometry of the stationary phase layer
- columnar
- flat-layer (sometimes paper and thin-layer)

The chromatographic process can be represented as follows:

Column filled
solid sorbent

A stream of liquid flows through it. Substance X, dissolved in a liquid, moves with it, but at the same time tends to remain on the surface of the solid sorbent due to adsorption, ion exchange, etc. Each molecule X moves part of the time, and part of the time is held by the stationary phase.

The possibility of separating two solutes X and Y is due to the difference in their affinity for both phases, i.e. one of them is in the mobile phase most of the time, so it reaches the end of the column faster.

$$k' = \frac{n_S}{n_m},$$

where k' is the recovery factor

$\frac{n_S}{n_m}$ —the ratio of the number of moles of a substance in the stationary phase to the number of moles of a substance in the mobile phase

The extraction coefficient characterizes the degree of retention of a substance.

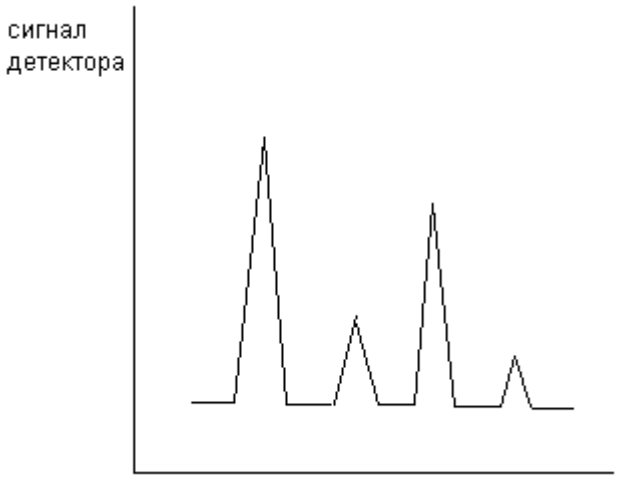
The degree of separation of two substances can be expressed through the separation coefficient (α):

$$\alpha = \frac{k_2'}{k_1'},$$

Where k_1' —extraction coefficient of the second substance,

k_1' —extraction coefficient of the first substance.

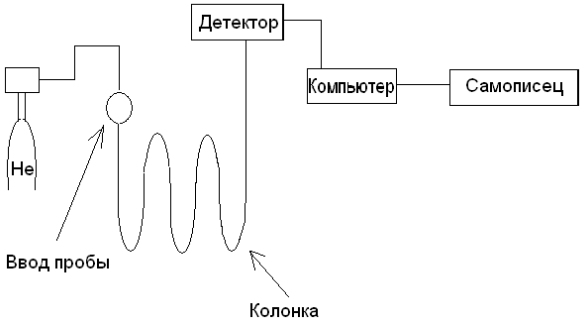
A detector placed at the outlet of the column registers, and a recorder records the detector signals.



Rice. 10. Detector signals.

Figure 10 shows a chromatogram of a four-component mixture. The area of each peak is proportional to the mass fraction of the component in the mixture.

Gas chromatograph diagram



Lecture No. 42

Methods of chromatographic qualitative analysis

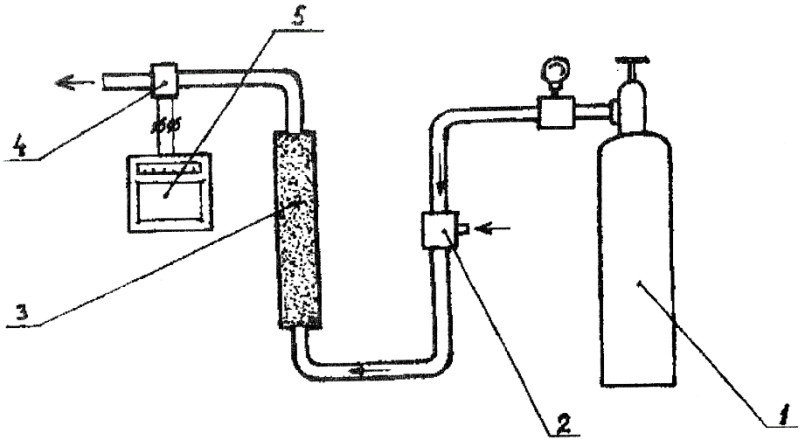
Chromatographic methodsin environmental monitoring systems have also received quite wide practical application. The most commonly used methods are gas and liquid chromatography, with the former being more common. In addition to the above, there are also methods of thin layer chromatography and others.

Gas chromatographicThe method is based on the separation of compounds between two immiscible phases, one of which is stationary (liquid or solid) and the other is mobile (inert carrier gas). The method under consideration makes it possible to determine negligible amounts of substances, incl. not possessing specific reactivity, analyzing mixtures consisting of tens and hundreds of components with similar properties.

There are two main types of gas chromatography (GC): gas adsorption and gas liquid chromatography (GLC). In gas adsorption chromatography, the stationary phase is a solid sorbent, and in gas-liquid chromatography, it is a liquid applied in a thin layer to an inert solid carrier.

The gas chromatography method allows in one analysis to determine the qualitative and quantitative composition of a complex mixture containing up to 100-200 volatile components. Highly sensitive selective detectors allow the determination of microimpurities with a concentration of 10-4% (μg/ml) and sometimes less.

The schematic diagram of a gas chromatograph is shown in Fig. 1.



1 – cylinder with inert gas; 2 – sample injection device; 3 – column; 4 – detector; 5 – recorder

Rice. 1. Schematic diagram of a gas chromatograph

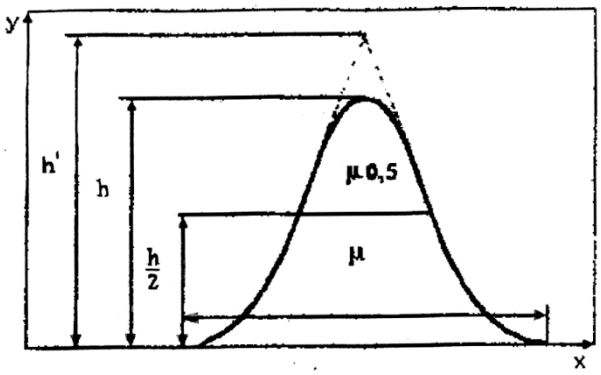
The main part of the chromatograph is the column in which the analyzed mixture is separated into its constituent components. Separation is based on the distribution of molecules of various components between the mobile gas phase and the stationary phase of the sorbent. Well-sorbed components move along the sorbent layer more slowly than poorly sorbed components. The separated components exit together

with the carrier gas and are detected by the detector. The detector signal is recorded on the tape of a recording (self-recording) device. In the chromatogram, each component has its own peak. The time from the moment of sample injection to the release of the maximum peak is called the retention time. To identify components, the relative retention index of the component is determined and compared with the indices in the lookup tables. This is how substances are identified.

Gas chromatography (like other types of chromatography) refers to hybrid methods that combine a separation method (on a chromatographic column) and a method for determining the separated components (using a detector). Due to the separation, the method is selective, and due to the properties of the detector, it is sensitive.

The graphical time dependence of the detector signal responding to changes in the concentration of substances separated on a chromatographic column is called a chromatogram. With sufficiently complete separation, the chromatogram is a collection of peaks, each of which corresponds to one of the components of the analyzed mixture. The position of the peaks on the chromatogram serves to identify the components of the sample, and the area under the peaks or peak height characterizes the concentration of the analyte in the sample.

The most important peak parameters are (Fig. 2): h – peak height; □r – base width; □0.5 – peak width at half height; h' – reduced peak height.



Rice. 2. Symmetrical chromatographic peak

If it is advisable to measure the peak width in units of time □, s or gas volume V, cm3, then the following relations are used:

$$\tau = \frac{\mu}{B} \text{ или } V = \tau \cdot \frac{V_a}{60},$$

where □ – peak width, mm; B – speed of the device chart tape, mm/s; Va – carrier gas flow rate at the outlet of the column, cm3/min.

The areas of chromatographic peaks are automatically measured using integrators included in modern chromatographs. Along with this, other methods are used, in particular:

a) graphically find the height (h) and width of the peak at the middle of the height (□□□□); if the peak shape is close to the normal distribution curve, then the peak area Q can be calculated from the relationship: Q = 1.065□□□□□□h;

b) construct a triangle by drawing tangents to both sides of the peak and connecting them with a third line parallel to the zero line (the area of the resulting triangle is approximately equal to:

0.96Q : Q = 0.516□□r□h').

Quantitative analysis in chromatography is based on the relationship between the area or height of the chromatographic peak on the content of the component being determined. Quantitative analysis of peak heights is less reliable, since this value depends on the experimental conditions. The following methods of quantitative chromatographic analysis are most often used.

Absolute calibration method.In this method the concentration

i-component in the sample is determined as

$$C_i = K_Q \frac{Q}{V_{пр}} \cdot 100\left[\%(об)\right],$$

where Q is the peak area in the chromatogram; Vpr – sample volume at a fixed temperature; kq is the calibration coefficient determined on the basis of calibration mixtures of known composition, and

$$K_Q = \frac{C_K V_K}{Q_K \cdot 100},$$

where Sk is the concentration of the component in the calibration mixture, % (vol.); VK – volume of mixture; QK is the peak area of the component in the chromatogram.

If the determining parameter is height, then instead of the peak area QK its height is substituted.

Internal normalization method.The concentration of the i-th component is determined by the formula:

$$C_i = \frac{K_i Q_i}{\sum_{i=1}^{n} Q_i} \cdot 100\left[\%(об)\right],$$

where n is the number of components in the mixture; Ki and Qi are correction factors and peak areas of the mixture components.

If the analyzed mixture consists of substances of a similar nature, and the sensitivity of chromatographic detectors to these substances is almost the same, then Ci is determined without taking into account correction factors:

$$C_i = \frac{Q_i}{\sum_{i=1}^{n} Q_i} \cdot 100\left[\%(об)\right]$$

Internal standard method.It is used in cases where the peaks of some components of the mixture are absent or completely not recorded in the chromatogram. The concentration of the i-th component is calculated using the equation:

$$C_i = \frac{K_i Q_i}{K_{st} Q_{st}} \cdot 100 \cdot r$$

where r is the ratio of the mass of the standard to the mass of the analyzed sample; Qi and QST are the peak areas of the i-th component and the standard added to the sample; Ki and KST are correction factors that take into account the sensitivity of the detector to the corresponding substances.

The detector is the most important element of a gas (and any) chromatograph, in which changes in the composition of the gas mixture passing through it are converted into a change in the output signal. There are flow and concentration detectors.

The signal of the flow detector is proportional to the instantaneous value of the mass velocity of the analyte entering it. The signal of the concentration detector is proportional to the instantaneous concentration of the analyte in the volume of the detector chamber. Of the large number of gas chromatographic detectors, the most often used in practice are a concentration detector for thermal conductivity (katarometer) and a flow detector - flame ionization detector (FID).

Detectors are also divided into non-selective (catarometer, FID, electrical conductivity, etc.) and selective (TID, ECD, FPD, etc.). the former are used more often in practice.

The sensitivity of the detector for thermal conductivity Sc is determined by the equation:

$$S_c = \frac{Q \cdot V_a}{B_1 B_2 g_{пр}} (\text{мВсм}^3/\text{мг}),$$

where Q is the area of the recorded peak, cm2; Va – volume of carrier gas, cm3/min; B1 – sensitivity of the recorder recorder, cm/mV; B2 – speed of movement of the chart tape, cm/min; gpr – mass of the injected sample, mg.

Typically, the sensitivity of thermal conductivity detectors is about 103 mV·cm3/mg; the minimum detectable concentration of the substance is about 10–3% (vol.).

The sensitivity of the flame ionization detector (FID) Sj is determined by the equation:

$$S_j = \frac{Q \cdot 60}{B_1 B_2 g} (\text{Кл}/\text{мг}),$$

where Q is the area of the recorded peak, cm2; B1 – recorder sensitivity, cm/A; B2 – speed of movement of the chart tape, cm/min; g – mass of the analyzed component, mg; 60 – coefficient.

Typically, the sensitivity of a flame ionization detector is on the order of 4·10–6 C/mg for propane; minimum detectable flow of matter of order 2·10–8 mg/s.

There are other detectors: electron capture (ECD), flame photometric (FPD), photoionization (PID) and others. Each of the detectors has its own group of substances to which it is specific, and it is used for them.

In Fig. Figure 3 shows a general view of the hardware and software complex commercially produced in Russia based on the gas-liquid chromatograph “Crystal-2000”, equipped with a set of detectors.

Liquid chromatography represents the separation over time of the components of a mixture in accordance with the difference in their physicochemical properties and subsequent detection in the flow of the mobile liquid phase. Liquid chromatography (LC) is based on the distribution of substances between two immiscible phases: a stationary phase and a mobile liquid phase, which passes through a layer of stationary phase. There are “solid-liquid” and “liquid-liquid” chromatography.

*Solid-liquid*chromatography is adsorption. Silica gel, carbon, aluminum oxide and other sorbents are used as adsorbents. Liquid-liquid chromatography is partitioning. The liquid used as the stationary phase is applied to an inert carrier and a flow of mobile phase liquid is passed

through it. Liquids must be immiscible. This method is generally used at high pressures to separate non-volatile compounds. This method is called “high pressure chromatography”. Special mixtures are used as a stationary phase, for example, polyethylene glycol PEG-600 or PEG-4000. Non-polar solvents or their mixtures, for example, hexane with diethyl ether or hexane with ethanol, are used as the mobile phase.

This method uses columns with an internal diameter of several millimeters and sample volumes of the order of tens of microliters, so the volumes of solutions used are extremely small, and for good separation of the components of mixtures it is necessary to use detectors with a fairly small internal volume.

In LC, both universal and specific detectors are used. The latter record substances according to their specific parameters. Variable wavelength photometric, fluorescent, and electrochemical detectors are commonly used.

In continuous flow analyzers, samples are drawn in and injected into a fluid stream that transports them to the detector. During the transfer of substances, they are often specially chemically modified in various ways. A type of liquid chromatography is ion chromatography (IC), which selectively analyzes various cations and anions.

Continuous titration in flow-through liquid systems combines the ease of estimating the concentration of the analyte, characteristic of direct methods, with the high accuracy of titrimetric methods. All these methods are based on achieving equivalent ratios of the analyte and titrant during continuous mixing of the reagent with the sample solution and differ in the choice of variable parameters, as well as the equipment used. In such systems, electrochemical and, in particular, potentiometric detectors are widely used. It is important that in this case, not too strict requirements are allowed for the response speed of the detector and (with certain exceptions) for the reproducibility of its results.

In Fig. Figure 4 shows a general view of the liquid chromatograph "Milichrome-6".

"Milichrome-6" Efficient Fluid System:

- automatic sample input device for 30 samples;
- high-precision dosing in the range from 1 to 99 µl;
- two microsyringe pumps, each with a volume of 2500 µl;
- maximum pressure 8+1.0 MPa;
- flow rate – 2-999 µl/mm;
- flow instability, no more than 0.8%;
- a cuvette made of a chemically inert material with an adjustable backpressure valve eliminates the formation of air in the lines;
- hydrodynamic mixer ensures reproducibility of mixed liquids at flow rates up to 200 µl/min;
- corrosion resistance of materials allows working with concentrated acids;
- isocratic and gradient (any form) mode of operation;

- microcolumns with an efficiency of at least 5000-6000 t.t. volume 250-300 µl with eluent consumption 1300-1600 µl per analysis;

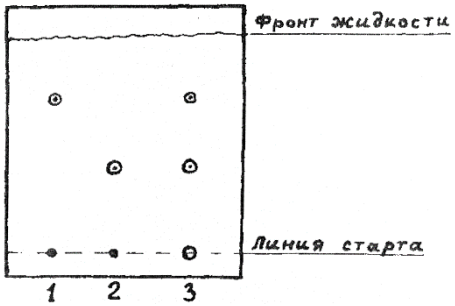
- column thermostat with a set temperature range of 35÷850C, with a temperature control error of 10C.

Small-sized electronic unit made of imported components of high reliability.

A system for controlling the device and processing chromatographic information based on a modern computer and a user-friendly UniChrom program operating in a Windows environment.

The superiority of the Milichrome-6 chromatograph lies in the unique set of its functionality and allows you to cost-effectively carry out analysis of any complexity simultaneously for several compounds with high accuracy and reproducibility, using previously generated libraries of spectra and spectral ratios of substances.

Thin layer chromatography- This is chromatography on a glass or metal plate on which a layer of sorbent is applied. Samples of the "witness" substances and the test mixture are applied to the starting line. The edge of the plate is immersed in the solvent. As the liquid moves across the plate, the mixture separates. The plate is dried and developed, and the substances are identified by the position of the spots of the separated components and witness substances, as shown in Fig. 5.

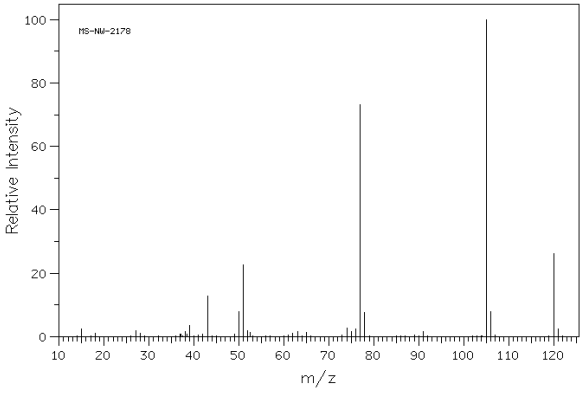


1, 2 – "witness" substances; 3 – analyzed mixture

Rice. 5. Chromatography on a plate in a current layer

Lecture No. 44

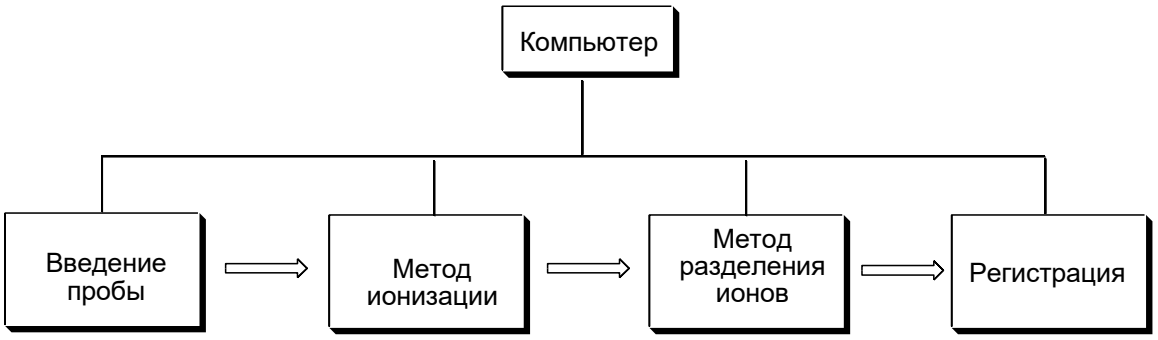
Mass spectrometry method



This method is fundamentally different from the spectroscopic methods discussed above. Structural mass spectrometry is based on the destruction of an organic molecule as a result of ionization in one way or another.

The resulting ions are sorted by their mass/charge ratio (m/z), then the number of ions

for each value of this ratio is recorded as a spectrum. In Fig. 5.1. The general diagram of a typical mass spectrometer is presented.



Rice. 5.1. Block diagram of a typical mass spectrometer

Some form of chromatography is usually used to introduce a sample into a mass spectrometer, although many instruments have the ability to directly introduce the sample into an ionization chamber. All mass spectrometers have devices for ionizing the sample and separating ions by m/z value. After separation, the ions must be detected and their quantity measured. A typical ion collector consists of collimating slits that direct only ions of one type into the collector at a time, where they are detected and the detection signal is amplified by an electron multiplier. Modern mass spectrometers are equipped with specialized software: computers control the accumulation, storage and visualization of data.

It has now become common practice to combine a mass spectrometer with a gas (GC-MS) or liquid (LC-MS) chromatograph.

All mass spectrometers are divided into two classes: low (single) and high resolution (R) devices. Low resolution spectrometers are instruments that can separate whole masses up to m/z 3000 (R = 3000/(3000-2990) = 3000). On such a device, the compounds C16H26O2 and C15H24NO2 are indistinguishable, since the device will record a mass of 250 in both the first and second cases.

High resolution instruments (R = 20000) will be able to distinguish between the compounds C16H26O2 (250.1933) and C15H24NO2 (250.1807), in this case R = 250.1933/(250.1933 – 250.1807) = 19857.

Thus, using low-resolution instruments, it is possible to determine the structural formula of a substance, but often for this purpose it is additionally necessary to involve data from other methods of analysis (IR, NMR spectroscopy).

High-resolution instruments can measure the mass of an ion with an accuracy sufficient to determine the atomic composition, i.e. determine the molecular formula of the substance under study.

The last decade has seen rapid development and improvement of mass spectrometers. Without discussing their structure, we note that they are divided into types depending on 1) the method of ionization, 2) the method of ion separation. In general, the method of ionization is independent of the method of ion separation and vice versa, although there are exceptions. This tutorial will discuss mass spectra obtained by electron impact ionization.

Electron impact ionization mass spectra

Electron impact (EI) is the most common ionization method in mass spectrometry. The advantage of this method is the ability to use search engines and databases (the EI method was historically the first ionization method; the main experimental data bases were obtained on devices with EI).

A sample molecule in the gas phase is bombarded with high energy electrons (usually 70 eV) and ejects an electron, forming a radical cation called a molecular ion:

$$M + e \rightarrow M^{+\bullet} \text{ (molecular ion)} + 2e$$

The lowest energy of bombarding (ionizing) electrons at which the formation of an ion from a given molecule is possible is called the ionization energy (or, less successfully, "potential") of the substance (Ue).

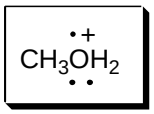
Ionization energy is a measure of the strength with which a molecule holds the least strongly bound electron.

As a rule, for organic molecules the ionization energy is 9-12 eV, so bombardment by electrons with an energy of 50 eV and above imparts excess internal energy to the resulting molecular ion. This energy is partially dissipated by breaking covalent bonds.

As a result of such a rupture, the molecular ion disintegrates into particles of smaller mass (fragments). This process is called fragmentation.

Fragmentation occurs selectively, is highly reproducible and characteristic of a given compound. Moreover, fragmentation processes are predictable, and it is they that provide the broad capabilities of mass spectrometry for structural analysis. In essence, structural analysis by mass spectrometry consists of identifying fragment ions and retrospectively reconstructing the structure of the original molecule based on the directions of fragmentation of the molecular ion. For example, methanol forms a molecular ion according to the following scheme:

$$CH_3OH + e^- \longrightarrow \left[CH_3OH\right]^{\bullet +} \text{ (m/z 32)} + 2e^-$$



молекулярный ион

One dot is the remaining odd electron; when a charge is localized on an individual atom, the sign of the charge is indicated on that atom.

Many of these molecular ions decay within 10-10 - 10-3 s and give a series of fragment ions (primary fragmentation):

$$CH_3\overset{\bullet +}{O}H \longrightarrow CH_2OH^+ \text{ (m/z 31)} + \dot{H}$$

$$CH_3\overset{\bullet +}{O}H \longrightarrow CH_3^+ \text{ (m/z 15)} + \dot{O}H$$

$$CH_3\overset{\bullet +}{O}H \longrightarrow CHO^+ \text{ (m/z 29)} + H_2$$

Each of the resulting fragments can then itself disintegrate into even smaller fragments (secondary fragmentation).

If some of the molecular ions have a sufficiently long lifetime, they reach the detector and are recorded as a molecular ion peak. Since the charge of the parent ion is unity, the m/z ratio for this peak gives the molecular mass of the substance being tested.

Thus, the mass spectrum is a representation of the relative concentrations of positively charged fragments (including the molecular ion) depending on their masses.

Special literature provides tables of the most frequently occurring fragment ions, which indicate the structural formula of the ion and its m/z value.

The height of the most intense peak in the spectrum is taken as 100%, and the intensities of other peaks, including the molecular ion peak, are expressed as a percentage of the maximum peak.

In certain cases, the peak of the molecular ion may also be the most intense. In general: the intensity of the peak depends on the stability of the resulting ion.

Mass spectra often contain a series of fragment ion peaks that differ by homologous difference (CH2), i.e. 14 amu Homologous series of ions are characteristic of each class of organic substances, and therefore they carry important information about the structure of the substance under study.

Table 5.1

Homologous series of ions of some classes of organic compounds

Connection class	Formula	m/z
Alkanes	CnH2n+1	15, 29, 43, 57, 71, 85…
alkenes, naphthenes	CnH2n-1	27, 41, 55, 69, 83…
alkynes, dienes	CnH2n-3	25, 39, 53, 67, 81…
alcohols, ethers	CnH2n+1O	31, 45, 59, 73, 87…
aldehydes, ketones	CnH2n-1O	29. 43, 57, 71, 85…
acids, esters	CnH2n-1O2	45, 59, 73, 87, 101…
Amines	CnH2n+2N	30, 44, 58, 72, 86, 100…
nitriles	CnH2n-2N	40, 54, 68, 82, 96…
alkylbenzenes		38, 39, 50-52, 63-65, 75-78, 91, 105, 119…

Typically, peaks with masses M+1 and M+2 appear in the mass spectrum of any organic compound, which is associated with the isotopic composition of the elements included in the organic compound. For convenience, elements are called A, A+1, A+2 depending on what isotope they have in addition to the main one. Below are data on the isotopic composition of the most commonly found elements.

Table 5.2

Isotopic composition of some elements

Element	Isotope (natural content, %)			Item type
N	^{1}N (99.99)	^{2}N (0.01)	-	A
WITH	^{12}C (98.9)	^{13}C (1.1)	-	A+1
N	^{14}N (99/64)	^{15}N (0.36)	-	A+1
O	^{16}O (99/8)	-	^{18}O(0.04)	A+2
F	^{19}F(100)	-	-	A

Si	^{28}Si (92/18)	^{29}Si (4.71)	^{thirty}Si (3.12)	A+2*
P	^{31}P (100)	-	-	A
S	^{32}S (95.0)	^{33}S (0.76)	^{34}S (4.2)	A+2*
Cl	^{35}Cl (75.8)	-	^{37}Cl (24.2)	A+2
Br	^{79}Br (50.5)	-	^{81}Br (49.5)	A+2
I	^{127}I (1000	-	-	A

*The content of 30Si and 34S isotopes is low, therefore silicon and sulfur belong to A+2 elements

The ratio of the intensities of the peaks M, M+1 and M+2 depends on the elemental composition, on the number of atoms of a given element in the molecule and on the natural content of the heavier isotope of this element. Thus, for hydrocarbons, the most significant contribution to isotope peaks is made by the isotope ^{13}C. For methane, the intensity of the M+1 peak will be 1.1% of the molecular ion peak; for a hydrocarbon with fourteen carbon atoms, the probability of including the 13C isotope increases, so the intensity of M+1 = 14 • 1.1 = 15.4% of the molecular peak.

To determine the number of carbon atoms in a molecule from the mass spectrum, it is necessary to divide the intensity of the M+1 peak as a percentage of M by 1.1. For example, a molecular ion is observed in the spectrum, the intensity of the M peak is 66.5%, the intensity of M+1 is 2.29%. We find the intensity of the peak M+1 relative to M in percent:

66.5 – 100%

2.29 – x%

x = 3.44%

We find the maximum number of carbon atoms: 3.44 : 1.11 = 3.

It must be taken into account that in the case of the presence of several atoms of (A+2) elements in the molecule, intense peaks M+4 and M+6, etc., may appear in the spectrum. This issue is presented in more detail in [Lebedev. Silversein].

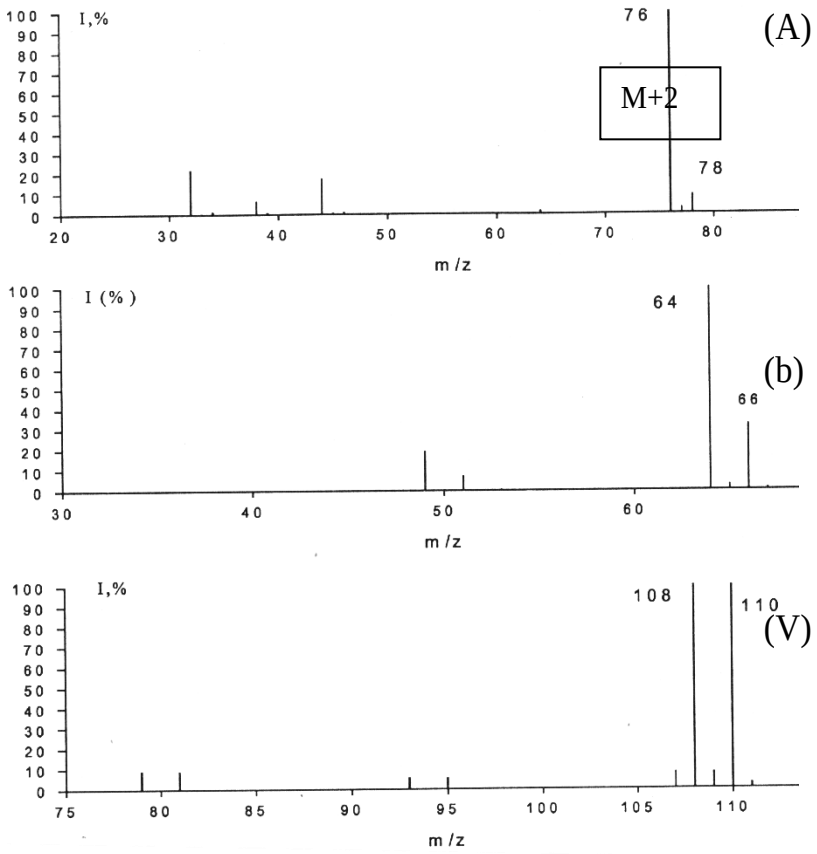
There is a simple rule: “If the intensity of the M+2 peak is less than 3% of the intensity of the M peak, the compound does not contain chlorine, bromine, sulfur and silicon atoms.”

Chlorine, bromine, sulfur and silicon are well identified by mass spectrometry due to the signal multiplicity characteristic of each element (Fig. 5.1).

It is important to remember that mass spectra obtained on a single-resolution instrument do not always allow an adequate assessment of the multiplicity of the signal (essentially, the elemental composition).

Reliable interpretation of signal multiplicity is only possible when obtaining a mass spectrum on a high-resolution instrument. Actually, this is the basis for the method of determining the elemental composition by mass spectrometry. The use of mass spectrometry to determine the elemental composition of a substance is well covered in the literature

M



Rice. 5.2. Mass spectra of carbon disulfide (a), ethyl chloride (b), ethyl bromide (c).

Mass spectrometry– one of the most effective and widely used analytical methods today. It is distinguished by high selectivity, sensitivity and accuracy.

The principle of the method is that the substance being determined is transferred to a gaseous state, ionized, and the resulting ions (charged fragments of the original molecules) are separated in a magnetic field according to the mass-to-charge ratio. Gaseous ions are separated in a magnetic field depending on the ratio m/z (m/e), where m is the mass, z (e) is the charge of the ion. Most often, the ionization of molecules in the gaseous state occurs under the influence of a flow of electrons. Electrons collide with a molecule, and in conditions of deep vacuum, the result of collisions is affected by the energy of the incident electrons. As soon as the electron energy is above the ionization threshold (10-12 eV), the molecule is ionized and the valence electron is removed to form a positively charged ion. The most probable processes are the formation of singly charged positive ions:

$M + e = M^+ + 2\ e$

The formation of two or more highly charged ions, as well as the capture of an electron with the formation of negative ions, are less likely processes. The essence of the method can be briefly described as follows: a substance entering an ionization chamber is ionized (disintegrates into ions), a beam of ions is formed, followed by their separation in electric or magnetic fields according to the magnitude of the mass-to-charge ratio, trapping ions with the same values of this ratio and recording by the device. The mass number of the ion is determined by the m/z (m/e) value, and the ion concentration is judged by the intensity of the corresponding signal.

Therefore, mass spectrometric analysis usually includes several stages: 1) Injection of gas or production and introduction of vapor of the test substance into the ion source; 2) Obtaining ions from atoms or molecules and forming them into a beam; 3) Separation of ions based on mass to charge ratio; 4) Detection of ions with subsequent measurement of their number or ion current. Schematic diagram of the mass spectrometer:

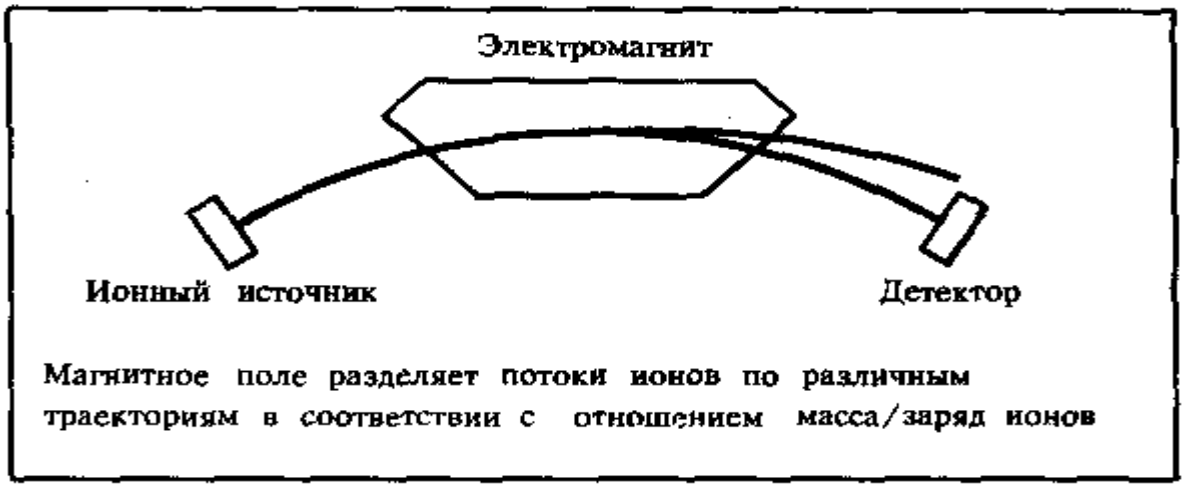


Рис. 2. Блок-схема масс-спектрометра.

1 – sample input system (inlet system) – gas input (steam from liquid);

2 - ion source is intended for the formation of gaseousionsthe substance under study and the formation of an ion beam, which is sent further to a mass analyzer (the most universal method of ionizing a substance is electron impact);

3 – mass analyzer (cathode, anode, accelerating plates, permanent magnet)

4 – detector;

5– pumping system

1. Sample injection (inlet) system

In the sample inlet (input) system, which is a chamber, the analyzed substance, when heated, is converted into a gaseous state at a residual pressure P = 10-2 --10-3 Pa (mm Hg). If the analyzed sample is a gaseous substance, then the evaporation stage is eliminated. Liquid substances that are not volatile at room temperature are heated to T = +300°C. Modern instruments provide direct injection of the sample into the ionization

chamber. Next, the molecular beam of the substance is ionized. In the ionization chamber there is a high vacuum P = 10-6 Pa. At this pressure, most substances go into a gaseous state (become volatile) without undergoing destruction.

2. Ion source, ionization chamber.

Ionization is the transformation of molecules into ions, which requires the expenditure of certain energy. Ionization methods. The choice of ionization method depends on the properties of the substance being determined, the matrix in which it is included, and the desired degree of ionization. Using standard equipment, it is possible to ionize substances with molecular mass up to 20,000, but there are devices for ionizing compounds whose molecular mass reaches 150,000–200,000.

A) In electron impact ionization, the molecules of a gaseous substance are bombarded by a stream of electrons, resulting in the formation of many fragment ions. Mass spectra in this case are very complex, and special spectra catalogs are used to interpret them.

B) One of the most common methods of soft ionization of volatile substances is chemical ionization. In this method, a high concentration of methane (ammonia) is maintained in the ionization chamber, which is ionized first when bombarded by electrons. Then methane ions collide with molecules of the substance under study, and as a result of ion-molecular reactions, (M + 1)+ and (M – 1)+ ions are formed.

C) Bombardment with fast atoms is used for soft ionization of liquid samples. Inductively coupled argon plasma is used for elemental and isotopic analysis. With its help, a sample is selected and ionized, and ions are separated in a mass spectrometer. For elemental analysis of surfaces, the method of secondary ion mass spectrometry is used. A stream of Ar+ or Xe+ ions bombards the surface of the sample, and the released molecular secondary ions are sent to a mass analyzer. Another method of soft ionization is the so-called field desorption; in this case, ions are formed under the influence of a strong electric field. It is more often used for the ionization of non-polar, thermally unstable substances, as well as compounds with large molecular weights. mass (of polymers), i.e. in cases where bombardment with fast atoms cannot be used.

If the ionization energy increases, the molecular ion breaks up into smaller fragment ions, which can then participate in rearrangement reactions to form other ions. Consequently, the mass spectrum is a kind of “fingerprint” of a substance. Ionization that results in significant fragmentation is called hard ionization. In contrast, with soft ionization, significantly less fragmentation is observed, but the height of the molecular ion peak increases.

D) Spray ionization (electrospray, thermal spray, etc.) is becoming increasingly widespread. In this method, the introduction of a solute and its ionization are carried out in one stage.

Electron impact ionization uses a stabilized beam of electrons perpendicular to the flow of the sample substance. The electron energy is usually 10-100 eV. When bombarded by

electrons, several processes occur simultaneously: the formation of positive molecular ions (at low energies 10-15 eV) and fragmentation of molecules with the formation of fragment ions (at high energies 50-70 eV).

Processes occurring under the influence of electron impact:

A) E = J, energy e is equal (close) to the ionization potential, i.e. energy required to produce an ion, a molecular ion is obtained;

B) E > J, the energy e is greater than the ionization potential, and fragment ions are formed;

B) E>>>J, the energy e is much greater than the ionization potential, and rearrangement ions are formed.

For example. Molecule A-B-C-D is exposed to a beam of electrons:

E=J

A–B–C–D --e→[A–B – C – E]+ + 2 e molecular ions

E > J -- e→[A – B]+ + C – D* fragment ions (bonds are not broken)

E > J -- e→[A – B – C]+ + D* fragment ions

E>>>J -- e→[A – B – E]+ + C* rearrangement ions

The processes of formation of positively charged molecular and fragment ions can be considered using the example of ethane CH3 – CH3. As a result of the interaction of an ethane molecule with ionizing electrons, a molecular ion is formed, which characterizes the molecular weight and empirical formula of the compound: CH3 – CH3 -- e→[CH3– CH3]+ + 2e m/z =30

Only 11-12% of the formed ions do not dissociate, the rest disintegrate with the rupture of C-C and C-H bonds into fragment ions:

[CH3 – CH3]+ -- e→[CH3 – CH2]+ + H* m/z =29

--e→[CH3]+ + CH3* m/z =15

--e→ [CH2]+ + [CH3]+ + H* m/z =14

--e→[CH]+

--e→ [C]+

The resulting positively charged ions and fragments pass through the accelerating plates, the potential difference between which is quite high (several thousand volts). Here they acquire energy eV, (where V = 5-100 V, the potential that accelerates the movement of electrons e - charge) and their speed increases to v. The energy eV will be equal to the kinetic energy of the ions mv2/2 (m is the mass of the ion, v is the speed of the ion):

eV = mv2/2

Ionization potentials J (eV):

organic compounds - 8 – 13

alkanes - 10 – 13

unsaturated compounds - 9 – 10

aromatic - 8.5 – 9

polycyclic aroma. connections - less than 8.5

The directions of ion decay for each class of compounds are strictly defined and these directions are called “fragmentation paths.”

3. Separation of ions by mass in a mass analyzer (magnet and analyzer)

Mass analyzers come in various types. The analyzer has a shape curved at a right angle and is placed in a magnetic field. In the analyzer, the ions formed in the ionization chamber travel a curved path, are separated and recorded. After acceleration in an electric field, the ions cross a magnetic field of strength H at right angles, thus being subjected to the action of a force Hev directed perpendicular to the movement of the ion (e = +1 is the charge of the ion, v is the speed of movement of positively charged ions). The trajectory of the ions will be a circle of radius r. Equating the forces Hev= mv2/r, we find:

r = m*v/ H*ev = r * He/m

substitute the value of v into the equation e *V =mv2/2 e *V = m*r2 *H2 *e2/2m2 hence r2=2V*m/ H2 *e

basic MS equation: m/e = r2H2 /2V

where: r – radius of the circle of motion of the ion;

H – magnetic field strength;

V is the potential accelerating the movement of electrons.

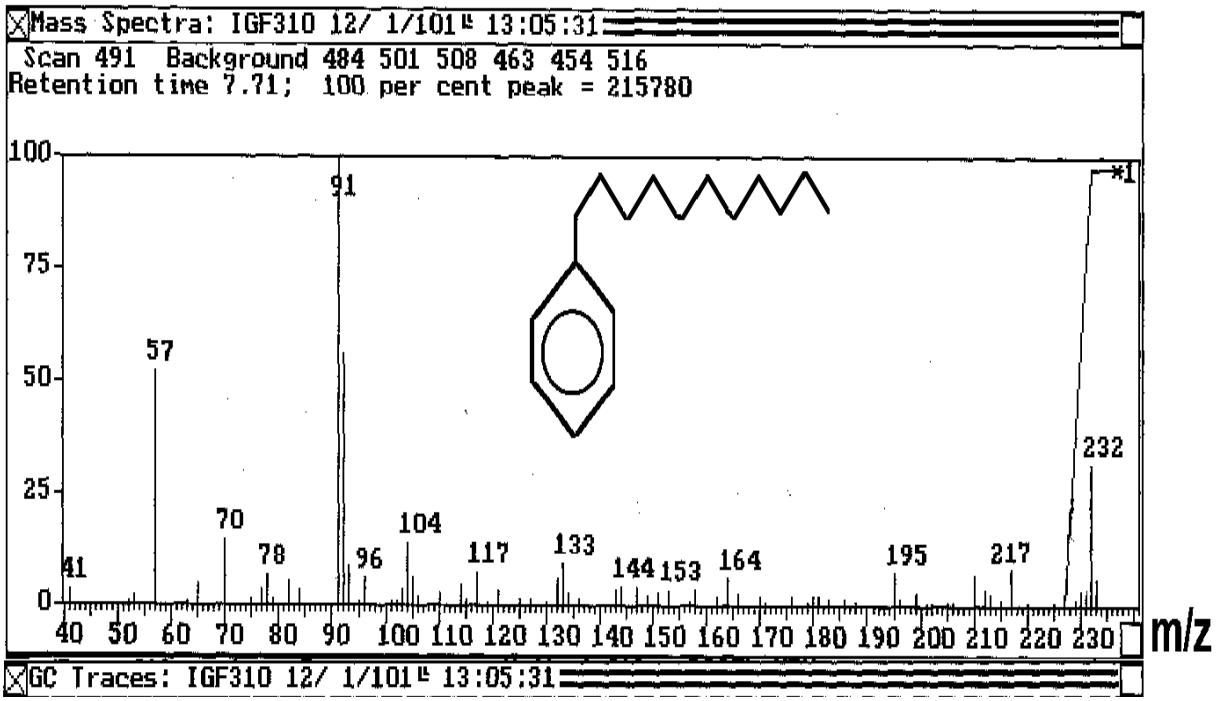
The greater the mass m of the ion, the greater the r, the longer the trajectory that this ion travels, thus the separation of ions by mass occurs. If by mass m1<m2<m3, then the ion with mass m1 will come out first, then m2 and then m3. This directional movement creates a total ion current, it is fed to the recording device and a spectrum is obtained.

4. Detector. Ion detection is carried out electrically. Currently, instruments contain devices that transmit information from the detector to a computer, which significantly speeds up data processing.

The mass spectrum is represented by a dependence in the form of a spectrogram or table containing m/e values and the corresponding intensities. In mass spectra, the molecular ion is the heaviest than fragment and other ions, so the molecular ion often appears last in the mass spectrum.

Most often, the mass spectrogram is given in a normalized form - the intensity of the highest peak is taken as 100%, and the content of the rest is recalculated to it.

Rice. Mass spectrum of n-undecylbenzene C6H5–C11H23 (C17H28)



Qualitative analysis. Based on the measurement of ion mass. Identification of masses is carried out by the position of the line in the mass spectrum, which is fixed by measuring the distance between lines with a known mass and the analyzed line. There are special atlases.

Quantitative analysis.Quantitative measurements are carried out using the current recorded by the detector. Calculations are based on the fact that the peak ion current J is proportional to the content of the component.

Considering the energetics and mechanism of these reactions, it is possible to reconstruct the structure of the original compound from the mass spectra

Lecture No. 45

Applications of mass spectrometry

The table presents the results of determining the group composition of hydrocarbons in transformer oils using the MS method for adsorption purification of oils of various origins.The data presented in the table showed that saturated hydrocarbons of oils from Baku oils (Oil Rocks, Siazan fields) contain relatively few isoparaffin hydrocarbons and relatively many naphthenic hydrocarbons, including tri-, tetra- and pentacyclic, compared to saturated hydrocarbons oils obtained from eastern sulfur oils (Tuymazinskaya and Romashkinskaya).

Table.

Composition of paraffin and naphthenic hydrocarbons in transformer oils of adsorption purification of various origins (mass spectrometry data)

Type of hydrocarbons	Hydrocarbon content in oil from petroleum, %			
	"Oil Rocks"	Siazan	Tuymazinsky	Romashkinsky
Paraffin				
With direct connection	1.6	1.2	Footprints	Footprints
Branched structure	11.9	13.7	21.0	26.4
Naphthenic				
Monocyclic	12.3	10.8	11.9	15.8
Bicyclic	14.3	12.5	11.0	12.6
Tricyclic	12.9	10.8	7.4	7.8
Tetracyclic	12.0	12.5	5.0	4.5
Pentacyclic	7.2	5.2	1.8	0.5
Total	72.2	66.7	58.1	67.6

Mass spectrometry allows you to solve the following problems:

1) Establishment of the structure of individual compounds isolated from oil

2) Determination of group or structural-group composition in the analysis of complex mixtures.

Modern M-S devices are classified according to 2 criteria:

1. By excitation energy:

a) low-voltage MS, electron impact energy Eud reaches values of 10-15 eV, with molecular ions most often observed (molecular mass spectrometry);

b) high-voltage M-S Eud = 50 -70 eV, in which fragment ions are formed, fragment or fragmentation M-S

2. According to the resolution of the device. Resolution is the measure of a device's ability to separate 2 peaks with a certain mass difference:

m/ □m=102 III class; m / □m=103 -104 II class; m / □m=104 -105 I class

Example: m1=180; m2=180.3; □m =0.3 180:0.3 = 1800:3=600, i.e. The resolution of the device is class III

The registration methods are so well developed that they make it easy to count individual ions. The advantage of mass spectrometry is that a small amount of substance is required for filming, 0.1-1.0 mg. Disadvantage: the substance decomposes.

Nowadays, various applications of mass spectrometry have gone far beyond the scope of unique projects, and an entire journal issue would not be enough to describe the numerous designs of mass analyzers and ionization methods. Portable chromatomass spectrometers are in service with the US Army in Iraq. They can detect small traces of chemical weapons reagents and are used for preliminary analysis of the environment. High-precision instruments for mass spectral analysis are purchased by customs services - this is a way to carefully control the composition of petroleum products and determine the origin of oil literally down to the well, since the isotopic composition is unique for each field.

A modern mass spectrometer can occupy an experimental room or be placed in a small box on a table, contain a superconducting magnet, or do without a magnetic field at all. The sensitivity of these devices is amazing. 1 mg of organic pollutant per 1 ton of water is enough for a mass spectrometer to doubt its quality, and even less for an inorganic impurity. Paradoxically, high sensitivity can itself become a source of problems: for example, when checking passengers, insignificant traces of drugs accidentally found on banknotes can be found on the hands of a completely respectable citizen.

1.2 Laboratory work

Laboratory work No. 1.
General rules for laboratory work. Safety precautions. Chemical glassware, their preparation for work

When working in a chemical laboratory, due attention should be paid to safety precautions.

The best precaution is to work with small quantities of reagents. This is one of the advantages of the semi-micromethod.

Careful and careful work will protect your hands from cuts from glass, burns from hot objects and concentrated acids or alkalis. When heating, you cannot hold test tubes and flasks with the opening facing you or someone working nearby, and you cannot lean over the opening of the vessel in which the reaction is taking place.

If concentrated acid gets on your skin, it should be washed off immediately.a large amount of water, then rinse the affected area with a solution of soda or a diluted ammonia solution; If alkali comes into contact with the skin, rinse thoroughly with water and then with a diluted solution of a weak acid.

In case of burns received from touching hot equipment, the burned area must be covered with gauze soaked in a 2% solution of potassium permanganate or a 3% solution of tannin.

If your hands are cut by glass, you should first remove glass fragments from the wound, then wash off the blood with a 2% solution of potassium permanganate and, after smearing the wound with iodine tincture, bandage it. The necessary medications are always available in the laboratory first aid kit.

You need to be careful when smelling gases: hold the test tube in your half-extended left hand so that the hole is below the level of your nose, and direct a weak stream of air towards you with your right hand. In case of poisoning with hydrogen sulfide, chlorine, bromine, it is necessary to remove the victim to air.

Flammable substances such as hydrogen, lamp gas, gasoline, ether and others must be kept away from fire. Every student should know where the simplest fire extinguishing means are located in the laboratory: water, sand, felt (blanket), fire extinguisher, and also be able to use them.

We must remember well that in a chemical laboratory special care, conscientiousness and accuracy are required when performing laboratory work. This will ensure the success of the work.

When performing laboratory work on electrochemical and optical methods of analysis, it is prohibited to leave switched on instruments in the laboratory unattended.

Table 1
Acid-base classification of cations

Index	Analytical group					
	I	**II**	**III**	**IV**	**V**	**VI**
	K+ Na+ NH4+	Ba2+ Sr2+ Ca2+	Al3+ Cr3+ Zn2+ Sn2+ Sn4+ As5+ As3+	Mg2+ Mn2+ Fe2+ Fe3+ Bi3+ Sb3+ Sb5+	Cu2+ Hg2+ Cd2+ Co2+ Ni2+	Ag+, Pb2+, Hg2+
Characteristics of the Group	Chlorides, sulfates and hydroxides are soluble in water	Sulfates are insoluble in water and acids	Hydroxides are amphoteric, soluble in excess alkali	Hydroxides are insoluble in excess alkali	Hydroxides form soluble ammonia	Chlorides are insoluble in water and dilute acids
Group reagent	Doesn't have	2n H2SO4 solution	Excess 4N solution NaOH or KOH	Excess 25% solution NH4OH	Excess 25% solution NH4OH	*2n* HCl solution
The nature of the compounds obtained	Solution K+, Na+, NH4+	Sediment BaSO4, SrSO4 CaSO4 (PbSO4)	Solution AlO2-, CrO2-, ZnO22-, SnO32 -, AsO32-	Sediment Mg(OH)2 Mn(OH)2, Fe(OH)2, Fe(OH)3, Bi(OH)3 HSbO2 HSbO3	Solution [Cu(NH3)4]2+ [Hg(NH3)4]2+ [Cd(NH3)4]2+ [Co(NH3)4]2+ [Ni(NH3)4]2+	Sediment AgCl PbCl2 HgCl2

table 2
Classification of anions

Group	Anions	Group reagent	Group characteristics	Specific reactions
1	SO42-, SO32-, CO32-, PO43-, BO2-, B4O72-, AsO33-, CrO42- AsO43-	BaCl2 in a neutral or slightly alkaline solution	Barium salts are practically insoluble in water	Na2SO3+HCl=SO2↑+H2O+2NaCl Na2HPO4+BaCl2=↓BaHPO4+2NaCl K2CrO4+BaCl2=↓BaCrO4+2KCl Na2B4O7+AgNO3+3H2O= 2AgBO2+2H2BO3+2NaNO3
2	Cl -, J-, Br-	AgN03 in the presence of HN03	Silver salts are practically insoluble in water and dilute nitric acid	AgCl↓+2NH4OH(k)=[Ag(NH3)2]Cl+2H2O [Ag(NH3)2]Cl+2HNO3= AgCl↓+2NH4NO3 4KJ + 2CuSO4 = J2 + 2K2SO4 + 2CuJ2 2KBr+MnO2+2H2SO4= Br2+MnSO4+ K2SO4 + 2H2O
3	NO3-, NO2-, CH3COO-	No group reagent	Barium and silver salts are soluble in water	CH3COONa+H2SO4= 2CH3COOH+ Na2SO4 Cu+8HNO3+H2SO4= 3Cu(NO3)2+4Na2SO4+4H2O+2NO2↑

Laboratory work No. 2
Reactions of cations of the first analytical group

The first analytical group of cations: K+, Na+, NH4+. It contains alkali metal cations, the salts of which are mostly highly soluble. There is no group reagent. All cations are monovalent and have no color.

K+ ion discovery reaction

Sodium acid tartarate (sodium hydrogen tartrate) gives a white crystalline precipitate:

KC1 + NaHC4H4O6 = NaC1 + KHC4H4O6↓,

Reaction conditions:

1) strictly neutral solution environment;
2) a sufficiently high concentration of potassium ions in the solution;
3) cold (to facilitate precipitation);
4) rubbing a glass rod against the walls of the test tube accelerates the process of sediment formation, as crystallization centers are created;

absence of interfering ions (all ions except Na+ interfere with the opening of K+).

Na+ ion opening reaction

Acidic potassium orthoantimonate (potassium dihydroantimonate) forms a white crystalline precipitate:

NaC1+ KH2SbO4= KCl+ NaH2SbO4↓

Reaction conditions:

1) neutral or slightly alkaline solution;
2) concentrated solution, since Na+ ion may not be detected from dilute solutions due to low sensitivity;
3) cold;
4) rubbing a glass rod against the walls of the test tube accelerates the process of sediment formation, as crystallization centers are created;

absence of interfering ions (the opening of Na+ is interfered with by all ions except K+).

NH4+ ion discovery reactions

1. Specific reaction. Caustic alkalis KOH and NaOH displace ammonia from the solution, which can be detected:

A) by smell;

b) by the blueness of wet red litmus paper. The reaction is mutualThe action of ammonium salts with alkalis, for example with ^OH, proceeds according to the equation:

NH4Cl + NaOH = NaC1 + NH3↑+ H2O

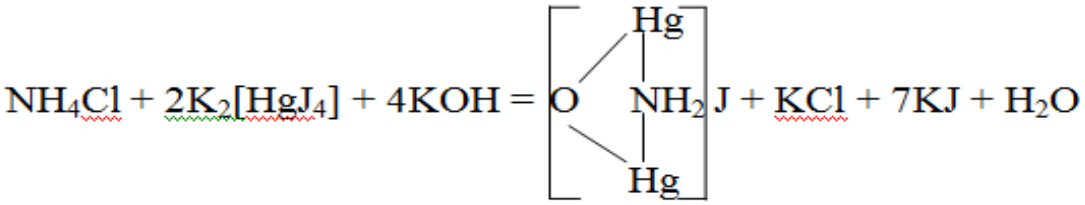
Reaction conditions:

1) the reaction should be carried out at pH>9;
2) the solution must be heated;

The wet indicator paper must be held so that it does not touch the walls of the test tube and the liquid;

3) V wet litmus paper is used as an indicator,which turns blue in the presence of the NH4+ cation

2. Nessler's reagent (an alkaline solution of a complex salt) gives a red-brown precipitate of mercurammonium iodide:



The reaction is carried out in a test tube or on a glass plate, onto which a drop of a dilute NH4+ salt solution is placed and 2-3 drops of Nessler's reagent are added.

Reaction conditions:

- When performing the experiment, it is necessary to take an excess of Nessler's reagent, since the precipitate is soluble in ammonium salts.

Laboratory work No. 3

Reactions of cations of the second analytical group

The second analytical group consists of the cations Ba2+, Ca2+, etc. This group of cations is characterized by the insolubility of their sulphate salts (sulfates) in water. Group reagent - 2N solution of sulfuric acid (or its soluble salts).

Ba2+ reactions

1. With the group reagent it forms a white, fine-crystalline precipitate, insoluble in acids and alkalis:

BaC12 + H2SO4 = BaSO4↓+ 2HC1

The reaction is very sensitive: the solubility of the precipitate in water is 1: 400,000.

2. Potassium chromate and dichromate form a yellow precipitate, insoluble in acetic acid, but soluble in strong acids:

BaCl2 + K2CrO4 = BaCrO4↓+ 2KS1

2BaC12 + K2Cr2O7 + H2O = 2BaCrO4↓+ 2KS1 + 2NS1

The last reaction is reversible. To completely precipitate Ba2+, sodium acetate CH3COONa is introduced into the solution, which neutralizes HC1 according to the equation

CH3COONa + HC1 = CH3COON + NaC1

Ca2+ reactions

1. With a group reagent at sufficient concentration, a white crystalline precipitate is isolated:

CaC12 + H2SO4 = CaSO4↓ +2HC1

The precipitate is significantly soluble in water. Complete release of Ca2+ is achieved by introducing ethanol into the solution. It should be noted that CaSO4 is soluble in hot HC1 and (NH4)2SO4 according to the equation:

2CaSO4 +2HC1=Ca(HSO4)2 +CaCl2

CaSO4+ (NH4)2SO4= (NH4)2[Ca(SO4)2]

The dissolution of CaSO4 in a solution of ammonium sulfate is used in the analysis to separate it.

2. Oxalic acid ammonium (ammonium oxalate) gives a white crystalline precipitate, soluble in strong acids:

CaC12 + (NH4)2C2O4 = CaC2O4↓+2NH4Cl

Note: The Ba2+ ion interferes with the detection of the Ca2+ ion; in the case of their simultaneous presence in the solution, before detecting Ca2+, it is necessary to remove Ba2+ ions from this solution by the action of K2Cr2O7 in the presence of CH3COONa.

Laboratory work No. 4
Reactions of cations of the third analytical group

(Ag+, Pb2+, [Hg2]2+) is characterized by the insolubility of their chlorides in water. The group reagent here is a solution of HC1 (or any of its salts), with which each of the ions gives a white precipitate.

Identification of ions is based on the various properties of their chloride precipitates:

PBC12 - dissolves in hot water;

AgC1 - dissolves in a concentrated solution of NH4OH;

HgCl2- does not dissolve either in hot water or in a concentrated solution of NH4OH, but under the action of NH4OH the white precipitate of mercuric chloride turns black.

Discovery reactions of silver ion Ag+

All three reactions are carried out in one test tube sequentially:

1. AgNO3+ HC1 = HNO3+AgCl

The nitric acid solution formed during the reaction above the precipitate must be carefully poured off, otherwise the remaining two reactions may not work.

2. White cheesy sediment*AgC1 dissolves in concentrated ammonia (NH4OH) to form a complex - silver ammonia:*

AgC1↓+ 2NH4OH(conc) = [Ag(NH3)2]+Cl- + 2H2O

3. The ammonia complex is stable only in an alkaline environment and is destroyed in an acidic environment:

[Ag (NH3)2]C1 + 2HNO3 = 2NH4NO3 + AgCl↓

Reaction conditions:

1) excess HC1 is undesirable,
2) to dissolve the AgCl precipitate, use a concentrated solution of NH4OH (until the precipitate completely disappears);
3) Add HNO3 to the complex solution until the solution becomes acidic (check with an indicator).

Discovery reactions of lead ions Pb 2+

Forms a slightly soluble precipitate with the group reagent*PBC12, soluble in hot water (virtually verify):*

Pb(NO3)2 + 2HC1 = PbCl2 + 2HNO3

Note: PBC12, partially soluble in cold water. To remove Pb2+ from solution, carbonates are used:

2Pb(NO3)2+(NH4)2CO3+ 2NH4OH = (PbOH)2CO3↓+ 4HNO3 + 4NH3↑

Specific reaction "golden shower" with KJ:

Pb(NO3)2 + 2KJ=PbJ2+2KNO3

The yellow precipitate of PbJ2 dissolves in a hot solution of acetic acid. When cooled, it precipitates again in the form of golden crystals.

Note: the yellow color of the PbJ2 precipitate is due to iodine, not lead (the AgJ precipitate is also yellow, but with a different tint).

Reaction conditions:

1) obtain a PbI2 precipitate, take a small amount of it, add hot water and a few drops of CH3COOH;
2) Cool the solution with running water until "golden rain" appears throughout the entire volume of the solution. Observe the precipitate in reflected light.

Discovery reactions of mercury ion [Hg2]2+

Both reactions are carried out in one test tube sequentially.

A white precipitate of mercuric chloride is formed with the group reagent:

Hg2SO4+2HCl = Hg2Cl2 + H2SO4

Note: the Hg2+ ion (unlike [Hg2]2+) does not form a precipitate with HC1; it is a cation of the sixth analytical group (see Table 1).

Specific reaction: white precipitateHg2C12 turns black when exposed to a concentrated solution of NH4OH:

Hg2Cl2+ NH4OH(conc) = [KH2Hg]C1 + Hg+ NH4C1+ 2H2O

Note: the white precipitate of Hg2C12 turns black due to the release of fine metallic mercury on its surface (see reaction equation).

Laboratory work No. 5
Analytical task: analysis of a mixture of cations first, second and third analytical groups

During the analytical task, each student needs to find out which cations are in the solution offered to him.

Analysis procedure

Mix the analyzed solution thoroughly and determine the reaction of the medium using an indicator.

Laboratory work No. 6
Reactions of cations of the fourth analytical group

The fourth analytical group consists of ions Al3+, Zn2+, Cr3+, etc. Cations of the fourth group form hydroxides with alkalis, which have amphoteric properties. When there is an excess of alkali, the hydroxides of these cations form water-soluble compounds: aluminates, zincates, chromites.

Group reagent - 2N NaOH or KOH solution.

ReactionsAl3+

1. With a group reagent, i.e. upon interaction with NaOH or KOH, a white amorphous precipitate of A1(OH)3 is formed, soluble both in excess of alkali to form an aluminate, and in acid to form the corresponding salt:

AlCl3+ 3KOH= 3KCl+ Al(OH)3↓

Al(OH)3↓+ KOH= KAlO2+ 2H2O

Al(OH)3↓+ 3HCl= AlCl3+3H2O

It should be noted that when aluminate is heated in the presence of crystalline NH4C1, it again transforms into precipitate A1(OH)3:

KAlO2 + NH4C1 + H2O = Al(OH)3↓+KCl + NH3

Specific reaction. Alizarin (an alcohol solution containing acetic acid) forms pink or red colored compounds with freshly precipitated aluminum hydroxide. Since alizarin is capable of producing colored compounds with other cations, to eliminate their influence the reaction is carried out in the presence of

K4 [Fe(CN)6] by drop method.

A drop of K4 [Fe(CN)6] is applied to a strip of filter paper, dried, and a drop of the test solution is placed in the same place. As a result, all interfering cations remain in the center of the spot in the form of ferrocyanides, and aluminum, due to capillary forces, moves to the periphery in the form of a colorless watery ring.

To convert aluminum into hydroxide, the spot is kept above a slag in concentrated ammonia vapor. The appearance of a pink or red color after wetting with alizarin and drying the ring indicates the presence of aluminum.

Reactions Zn2+

1. With a group reagent (i.e. with alkali solutions NaOH, KOH), a precipitate is formed, soluble in acids and in excess alkali with the formation of zincate:

ZnSO4 + 2KOH = K2SO4 + Zn(OH)2↓

Zn(OH)2↓+2HCl = ZnC12 + 2H2O Zn(OH)2↓+2KOH = K2ZnO2 + 2H2O

2. Characteristic of zinc is its ability to form soluble complexes - ammonia, which must be taken into account when identifying it:
   Zn(OH)2 + 4NH3, = [Zn(NH3)4](OH)
3. Yellow blood salt K4[Fe(CN)6] in reaction with Zn2+ gives a white precipitate, soluble in alkalis:
   3ZnC12 + 2K4[Fe(CN)6] = Zn3K2[Fe(CN)6]2↓+6KS1

Reactions Cr 3+

1. With a group reagent (i.e. with alkali solutions NaOH, KOH), a precipitate is formed, soluble in acids and in excess alkali with the formation of chromite:
   Cr2(SO4)3 + 6KOH = 3K2S04 + 2Cr(OH)3↓
   Cr(OH)3↓+ 3HCl = CrCl3 + 3H2O
   Cr(OH)3↓+ KOH = KCrO2 + 2H2O

When boiled, potassium chromite KSrO2, due to complete hydrolysis, turns into Cr(OH)3:

KSrO2 + 2H2O = Cr(OH)3↓+ CON

Summary equation:

Cr(OH)3↓+ KOH $\underset{\text{нагрев t0 холод}}{\longleftrightarrow}$ KCrO2+2H2O

Specific reaction. Hydrogen peroxide H2O2 in an alkaline medium converts the Cr3+ ion into the Cr6+ ion (in this case, the green color of the solution turns into yellow or orange). Further, in an acidic environment, the Cr6+ ion under the influence of H2O2 turns into blue Cr2O5 peroxide. The reactions proceed according to the equations:

Cr2(SO4)3 + 3H2O +10NaOH = 2Na2CrO4 + 3Na2SO4 + 8H2O
2Na2CrO4+H2SO4= Na2Cr2O7+Na2SO4, + H2O
Na2Cr2O7+4H2O2+H2SO4= 2CrO5+Na2SO4+5H2O

Reaction procedure

To 2-3 drops of a solution of salt Cr2 (SO4)3 add 4-6 drops of a 2N NaOH solution (until the precipitate of Cr(OH)3 dissolves and chromite NaCrO2 forms), then add 2-3 drops of a 3% solution of H2O2 and boil the contents test tubes for 3-4 minutes (until the solution turns yellow). The cooled solution is acidified with H2SO4, add 5 drops of a mixture of ether and isoamyl alcohol, 2-3 drops of H2O2 solution and shake vigorously. The appearance of an intense blue color in the upper ether layer indicates the formation of Cr05.

Various chromium perocomplexes are formed, for example, in an acidic environment - blue CrO(O2)2S, where S means molecules of water or an oxygen-containing organic solvent. It is purple in a neutral environment. Its composition is CrO(O2)2OH.

Laboratory work No. 7
Reactions of cations of the fifth analytical groupsMg2+, Mn2+, Fe2+, Fe3+, Bi3+, Sb3+, Mn2+, etc.

This group includes cations whose hydroxides are insoluble in excess caustic alkalis and ammonia. The latter is used as a group reagent.

ReactionsFe2^{+}

1. The group reagent forms a gray-green precipitate, which over time, oxidizing, turns brown:

FeSO4+ 2KOH=K2SO4+ Fe(OH)2↓

4Fe(OH)2↓+2H2O+O2= 4Fe(OH)3

2. *Specific reaction. When interacting with the red blood salt K3[Fe(CN)6], a blue precipitate "Turnboole blue" is formed:*

3FeSO4+2K3[Fe(CN)6]= Fe3[Fe(CN)6]2↓ +3K2SO4

Fe3+ reactions

1. Caustic alkalis and ammonia form a red-brown precipitate:
   FeCl3+3KOH = Fe(0H)3↓ +ZKS1
2. Yellow blood salt*K4[Fe(CN)6] gives a blue precipitate called "Prussian blue":*
   4FeCl3+3K4[Fe(CN)6]= Fe4[Fe(CN)6]↓ +12KCl
3. Rodanide potassium*KCNS or ammonium NH4CNS gives an intense red color:*
   FeCl3 +3KCNS↔Fe(CNS)3 + ZKS1

ReactionsMn2+

1. With the group reagent it forms a white precipitate of manganese hydroxide, which quickly darkens due to its oxidation to permanganous acid:
   MnSO4 + 2KOH = K2SO4 + Mn(OH)2↓
   Mn(OH)2↓|+ 2O2 =2H2MnO3
2. *Specific reaction. Oxidizing agents in an acidic environment, for example PbO2 in nitric acid, convert divalent manganese into heptavalent manganese, which has a crimson color:*
   2Mn(NO3)2 + 5PbO2 + 6HNO3 = 2HMnO4+ 5Pb(NO3)2+2H20
   Reaction conditions:

A) the reaction is carried out with only a small amount*Mn2+, large concentrations of formed HMnO4 are immediately decomposed by HNO3 to MnO2;*

b) there should be no chlorine ions in the solution, because they are reduced again

pour in NMPO4 untilMn2+:

2HMn04 +14HC1 = 2MnC12 + 5C12 + 8H20

Carrying out the reaction. Approximately 10 mg of PbO2 is added to the test tube, and

0.3-0.5 mg of concentrated HNO3 and heat to boiling. After making sure that there is no manganese in PbO2, add 1-2 drops of the test solution to the test tube and boil again, then allow the excess PbO2 to settle and observe the crimson color that appears.

3. Oxalic acid from precipitated Mn(0H)2 and browned sediment forms a bright pink complex compound:

   2Mn(OH)2 + 2O2 = 2H2MnO3

   2H2MnO3 + 7H2C2O4 = 2H3[Mn(C2O4)3] + 2CO2 + 6H2O

Carrying out the reaction. Place 3-4 drops of salt in a test tubeMn2+ and 1-2 drops of alkali and shake until the sediment turns brown, then add 3-4 drops of the reagent, i.e. oxalic acid and a pink color is observed.

ReactionsMg2+

1. With alkalis it forms a white gelatinous precipitate, soluble in acids and ammonium salts:

   MgC12 + 2KOH = 2KC1+Mg(OH)2↓

   Mg(0H)2↓+2HC1 = MgC12 + 2H2O

Solubility in ammonium salts is explained by the fact that Mg(OH)2 enters into an exchange reaction, which results in the formation of a well-dissociating magnesium salt and a poorly dissociating NH4OH:

Mg(OH)2+2NH4Cl =MgCl2+ 2NH4OH

2. Sodium hydrogen phosphate in the presence of NH4Cl and NH4OH gives a white crystalline precipitate, soluble in acids:

   MgCl2+Na2HPO4+NH4OH=MgNH4PO4+2NaCl + H2O

   NH4C1 is added to prevent the formation of Mg(OH)2.

Carrying out the reaction. To 2-3 drops of a solution of magnesium salt, add 2-3 drops of a solution of NH4OH and drop by drop of NH4C1 until the precipitate Mg(OH)2 dissolves, then add the reagent drop by drop. If an amorphous precipitate forms, it is dissolved in acid, after which, adding NH4OH solution drop by drop, a crystalline precipitate is achieved.

Laboratory work No. 8
Reactions of cations of the sixth analytical group

The sixth analytical group includes the cations Cu2+, Co2+, Hg2+, etc. The group reagent is a concentrated ammonia solution, in excess of which the cations of the sixth group form water-soluble complex compounds - ammonia.

Cu2+ reactions

1. With the group reagent it gives a precipitate that is soluble in an excess of the precipitant, forming a complex - copper ammonia, colored dark blue:

   2CuSO4 + 2NH4OH(conc) = (CuOH)2SO4↓+ (NH4)2SO4

   (CuOH)2SO4↓+ NH4SO4 + 6NH4OH(conc) = 2[Cu(NH3)4]SO4 + 8H2O

2. Yellow blood salt K4 [Fe(CN)6] forms a red-brown precipitate:

2CuSO4 + K4Fe(CN)6] = Cu2[Fe(CN)6] + 2K2SO4

Co2+ reaction

1. WITH group reagent forms a precipitate that dissolves inexcess NH4OH and NH4C1 with the formation of ammonia of a dirty green color:
   CoC12 + 2NH4OH(conc) = CoOHCl↓ + NH4Cl
   CoOHCl↓ +5NH4OH(conc) + NH4Cl = [Co(NH3)6]Cl2 + 6H2O
2. *Specific reaction: with ammonium or potassium thiocyanate gives a soluble blue complex salt:*
   CoC12 + 4KCNS = K2[Co(CNS)4] + 2KS1
   Reaction conditions:
   a) the environment is neutral;
   b) high concentration of the reagent.

The reaction is carried out using the drop method: a drop of KCNS (or NH4CNS) and the test solution are applied to a strip of filter paper, then another drop of KCNS (or NH4CNS). For 20-30 seconds, filter paper is placed over the opening of a bottle with a concentrated ammonia solution. After drying the stain in the presence of cobalt, a blue color appears.

Hg reactions^{2+}

1. With the group reagent it forms a white precipitate, which dissolves in an excess of precipitant and NH4Cl:
   HgCl2+NH40H(conc) = [NH2Hg]Cl↓ +NH4Cl + H2O
   [NH2Hg]Cl↓+2NH4ON(conc) + NH4C1 = [Hg(NH3)4]Cl2 + 2H2O
   2.C KJ gives a red precipitate that is soluble in excess KJ to form a complex:
   HgCl2 + 2KJ = HgJ2↓ +2KC1
   HgJ2+2KJ=K2[HgJ4]
   Note: the alkaline solution K2 [HgJ4] is called Nessler's reagent.

Laboratory work No. 9
Analytical task: analysis of a mixture of cations
IV, V and VI analytical groups

During the analytical task, each student needs to find out which cations are in the solution offered to him.

Analysis procedureMix the analyzed solution thoroughly and determine the reaction of the medium using an indicator.

Laboratory work No. 10
Analytical reactions of group I anions
(SO42-, SO32-, S2O32-, CO32-, HPO42-, B4O72-, SiO32-)

Reactions SO42-

Barium chloride BaCl2 forms with the SO42 anion a white crystalline precipitate of BaSO4, which is insoluble in acids and alkalis:

H2SO4 + BaC12 = BaSO4↓ +2HC1

Carrying out the reaction. Add 2-3 drops of the reagent to 4-5 drops of H2SO4 solution. Divide the resulting precipitate into 2 parts. Add acid to the first test tube and alkali to the second.

Reactions CO32-

K2CO3 + BaCl2 = BaCO3↓+2KS1

Barium carbonate BaCO3 easily dissolves in acids, releasing carbon dioxide, which causes cloudiness in the water.

BaCO3 + 2HCl = BaCl2 + CO2↑+H2O

Ca(OH)2+CO2 = CaCO3+H2O

Reactions PO43-

1. Molybdenum liquid (a solution of ammonium molybdate in nitric acid) with phosphate ion gives a yellow crystalline precipitate when heated:

Na2HPO4+12(NH4)2MoO4+23HNO3=
(NH4)3PO4*12MoO3↓+21NH4NO3+2NaNO3+12H2O

Laboratory work No. 11
Analytical reactions II (Cl-, Br-, J-) and III (NO3-, NO2-, CH3COO-) group of anions

Cl reactions^{-}

Silver nitrate AgN03 forms with the Cl- anion a white curdled precipitate AgCl, insoluble in water and acids. The precipitate dissolves in ammonia, and a complex silver salt [Ag(NH3)2]Cl is formed. Under the action of nitric acid, the complex ion is destroyed and AgCl precipitates again.

The reactions occur in the following sequence:

KCl+ AgNO3= AgCl↓+ HNO3

AgCl↓+ 2NH4OH(conc)= [Ag(NH3)2]Cl+2H2O

[Ag(NH3)2]Cl +2HNO3=AgCl↓+ 2NH4NO3

Reactions Г

1 . Silver nitrate AgN03 forms a yellow precipitate with iodine ion, insoluble in nitric acid and concentrated NH4OH solution (unlike AgCl and AgBr):

KJ + AgNO3 = AgJ↓ +KNO3

2. Iodine ions are easily oxidized to free iodine by various oxidizing agents, for example:

2KJ + PbO2 + 2H2SO4 = J2 + PbSO4 + K2SO4 + 2H2O

4KJ + 2CuSO4 = J2 + 2K2SO4 + 2CuJ2

Detection of iodine by this method is similar to detection of bromine. The organic solvent layer turns purple.

3. Specific reaction. Lead cations form a golden precipitate with iodine ions.

Reactions Br^-

1. Silver nitrate with bromine ions forms a yellowish precipitate:

KBr + AgNO3 = AgBr↓ + KNO3

The precipitate does not dissolve in HNO3 and (NH4)2CO3, but does dissolve in excess NH4OH.

AgBr↓ + 2NH4OH = [Ag(NH3)2]Br + 2H2O

2. In an acidic environment, bromine ions are oxidized and become free bromine:

2KBr + MnO2 + 2H2SO4 = Br2 + MnSO4 + K2SO4 + 2H2O

Carrying out the reaction. Add an oxidizing agent, 4-6 drops of an organic solvent (benzene, gasoline, toluene) to the test solution and acidify with sulfuric acid. After thoroughly shaking the mixture, a layer of organic solvent, colored yellow or brown, appears on the surface.

NO_3^- reactions

1. Ferrous sulfate reduces the NO3- ion in an acidic environment to NO:

2NaNO3 + 6FeSO4 + 4H2SO4 = 3Fe2(SO4)3 + 2NO↑ + Na2SO4 + 4H2O

A brown ring appears around the FeSO4 salt crystals, since NO and FeSO4 form an unstable complex compound:

NO+ FeSO4 = [Fe(NO)]SO4

Carrying out the reaction. Place several crystals of FeSO4 salt in a test tube, 2-4 drops of HNO3 solution, and carefully add 1-2 drops of H2SO4 solution (conc.) along the walls of the test tube.

Reactions CH3COO'

Sulfuric acid (1:1) releases acetic acid from a solution of acetates, which has a specific odor:

CH3COONa+H2SO4 = 2CH3COOH + Na2SO4

Carrying out the reaction. Place 5-6 drops of sodium acetate solution into a test tube and add 2 drops of concentrated sulfuric acid. Heat carefully.

Ferric chloride FeCl3, when interacting with solutions of acetates, forms iron acetate Fe(CH3COO)3 of a red-brown color, which, when diluted and heated, easily undergoes hydrolysis with the formation of a precipitate of the basic salt of iron (III) acetate:

3CH3COONa+FeC13 = Fe(CH3COO)3 + 3NaCl

Fe(CH3COO)3 + 2H2O = Fe(OH)2 CH3COO↓+2CH3COOH

Carrying out the reaction. The same amount of ferric chloride is added to 6 drops of the test solution. This produces red-brown iron acetate. When it is diluted with water 2-3 times and heated, a precipitate of Fe(OH)2CH3COO appears.

Laboratory work No. 12.
Analytical task:Analysis of a mixture of group I, II, III anions

During the analytical task, each student needs to find out which cations are in the solution offered to him.

Analysis procedureMix the analyzed solution thoroughly and determine the reaction of the medium using an indicator.

Laboratory work No. 13.
Analytical task:Analysis of dry salt mixture

All studied compounds can belong either to one class of inorganic compounds (acids, bases, oxides, salts), or to a mixture of salts or acids. In the first case, with an individualized connection, the analysis usually does not present any difficulties and boils down to the fact that after some preliminary tests, the ions are determined by qualitative reactions.

The analysis of a mixture of salts requires more complex research techniques. The study of this test substance can be reduced to the following operations:

- preliminary test;
- sample dissolution;
- discovery of cations;
- discovery of anions.

Laboratory work No. 14
Gravimetry. Taking dishes and preparing them for work. Bringing the crucible to constant mass. Studying the work with technical and analytical balances

Gravimetry (from Latin gravis - heavy and Greek metreo - measure) is a set of quantitative analysis methods based on measuring the mass of the component being determined, isolated from the analyzed sample either in a free state or in the form of a compound of known composition. The analytical signal in gravimetry is mass. Gravimetry can be used to determine almost any component of the analyzed object, if their content in the sample exceeds 0.1%. Gravimetry is a standard-free method. The main advantage of gravimetry is the high reliability of the results. The error of

determination does not exceed 0.1-0.2%. Disadvantages are associated with the high labor intensity and duration of analytical operations, difficulties in determining very small quantities of substances, and low selectivity. Therefore, in mass laboratory analyzes it is replaced, if possible, by other methods. In gravimetric analysis, two groups of methods are usually distinguished: precipitation and distillation. Precipitation methods are of greatest practical importance. From a part of the test substance of known mass (sample), the component to be determined is isolated in one way or another in the form of some compound. Direct separation is possible only in a few cases, for example, removal of hygroscopic or crystallization water by heating. Usually, a sample of a solid substance is transferred into a solution, from which, using a suitable reagent, the component being determined is isolated in the form of a practically insoluble substance (precipitated form). The precipitate is separated by filtration, decantation or other methods, washed from traces of sorbed components, and often reprecipitated. Then it is dried or calcined until a stable compound of a strictly defined composition (weight, gravimetric form) is formed, the mass of which is measured. For example, when determining Ca2+, the precipitated form is CaC2O4, the weight form is CaO or CaCO3. Knowing the mass of the sample (a) and the weight form (b), calculate the content x (% by mass) of the component being determined:

x =(bF/a) . 100 (2)

The factor F, called the gravimetric factor, is equal to the content of the component being determined in 1 g of its weight form:

F= mM1/nM2 (3),

where m and n are stoichiometric coefficients in the equation of the chemical transformation of the isolated component into its weight form, M1 is the molar mass of the determined component, M2 is the molar mass of the gravimetric form. For example, when determining iron by mass of Fe2O3 m = 2, n = 1. In cases where the components being determined form volatile compounds, distillation methods can be used. Decomposition of samples with the release of gaseous products is achieved by calcination or the action of reagents (acids, alkalis, etc.) when heated. The volatile component is passed through an absorbent solution, and the amount of gaseous product released from the sample is calculated from the increase in the mass of the solution (direct methods). The mass of the substance residue can be determined after removing the volatile product from it. The content of the component in such cases is determined by the difference in mass before and after distillation (indirect methods).

The main analytical instrument used in chemical analysis is a scale, which allows one to compare the mass of a body with the mass of weights or determine the mass of a body using another standard, for example, by compression (extension) of a spring. In laboratory practice, laboratory technical and laboratory analytical balances are used. The

accuracy of scales (error, reproducibility) is characterized by the spread of instrument readings when repeatedly weighing the same item. Laboratory technical scales are designed for weighing samples that do not require high precision. The accuracy of the VLKT-500 laboratory quadrant technical scales used in the workshop is 0.02 g (±0.01 g). Weighing limit 500 g. Laboratory analytical balances (VLA-200) are used for high-precision measurements. Provides measurement accuracy of 0.00002 g (±0.00001 g). The weighing limit is 200 g. The sensitivity of the scale is determined by the mass of the load that causes a shift by one scale division, that is, the price of the scale division. In the VLA-200 analytical balance it is equal to 0.00001 g, in the VLKT-500 technical balance it is 0.01 g. When weighing on an analytical balance, it is not recommended to take samples smaller than 0.10000 g, otherwise the error will greatly increase. Using an analytical chemistry textbook, study the structure of analytical balances, outline the rules of weighing and the rules for taking readings. The implementation of all analytical operations and the corresponding measurements is inevitably accompanied by various types of errors. Systematic errors are associated with the characteristics of the analysis method used, the accuracy of the instruments, the purity of the reagents, etc. Each of the systematic errors in the analysis is constant in value during repeated analyzes. Systematic errors can be detected when performing analysis under other conditions (with other instruments, reagents, etc.) and taken into account. Random errors (for example, caused by fluctuations in temperature, air humidity, inaccuracy in setting the level of the solution in the burette, etc.) are possible for each analysis, have various causes, and are not constant either in absolute value or in sign. The presence of random errors affects the results of parallel determinations that differ from each other. As the number of parallel determinations increases, the influence of random errors on the analysis result decreases. Random errors are assessed based on the theory of mathematical statistics. Gross errors or blunders (spilling part of the solution, incorrect selection of an aliquot sample, incorrect calculation of weights, etc.), made due to the negligence or incompetence of the analyst, are detected by a sharp distortion of the analysis result. Thus, analytical measurements of the same quantity have different values for different reasons. Therefore, the analysis uses not the result of a single determination, but the average (arithmetic) value of several parallel determinations. There are the concepts of “measured value”, “result of a single determination”, “result of analysis”. Measured value – the observed value of mass, volume, reading of a measuring device or other quantitative characteristic found during analysis. The result of a single determination is the final measured value of the quantity being determined, obtained in the process of measurements and all auxiliary operations and calculations. The result of the analysis is the average value of the results of parallel determinations. The science of measurements, methods and means of ensuring their unity and ways to achieve the required accuracy is called metrology. The main metrological characteristics of the analysis are the accuracy and reproducibility of the analysis results. The absence (or close to zero) of systematic errors in chemical analysis ensures its correctness. A quantitative assessment of correctness is the difference between the analysis result (average) X and the true value of the value being determined

- μ. In relation to the correctness of the analysis, the result is expressed as an error (absolute error) and a percentage error (relative error). The error is the difference between the arithmetic mean experimental value X and the true value μ (without taking into account the sign) and is expressed in the same units as the value being determined: grams, milliliters, etc. Percentage error is an error expressed as a percentage of the true value. For example, the error in determining 0.2030 g of hydrogen peroxide was 0.0030 g, then the percentage error is (0.0030 / 0.2030) •100 = 1.47%. Sometimes the percentage measure of correctness is calculated - the result expressed as a percentage of the true meanings. Reproducibility (accuracy, error) is a characteristic of random errors in chemical analysis. The reproducibility of the analysis is assessed by the closeness to each other ("scattering") of the results of parallel determinations. A quantitative assessment of reproducibility is the standard deviation: absolute S or relative Sr, calculated based on several parallel determinations using mathematical statistics methods. With respect to reproducibility, the reported data should contain the mean value X, standard deviation S, number of parallel determinations n. When presenting the results of the analysis, an assessment of the reliability of the obtained result is reported using a statistical criterion - a confidence interval, for a given reliability (confidence probability). Eα – confidence interval (boundaries, upper and lower, of possible variations of the desired value) at a given reliability (degree of probability). methods and means of ensuring their unity and ways to achieve the required accuracy is called metrology. The main metrological characteristics of the analysis are the accuracy and reproducibility of the analysis results. The absence (or close to zero) of systematic errors in chemical analysis ensures its correctness. A quantitative assessment of correctness is the difference between the analysis result (average) X and the true value of the value being determined - μ. In relation to the correctness of the analysis, the result is expressed as an error (absolute error) and a percentage error (relative error). The error is the difference between the arithmetic mean experimental value X and the true value μ (without taking into account the sign) and is expressed in the same units as the value being determined: grams, milliliters, etc. Percentage error is an error expressed as a percentage of the true value. For example, the error in determining 0.2030 g of hydrogen peroxide was 0.0030 g, then the percentage error is (0.0030 / 0.2030) •100 = 1.47%. Sometimes the percentage measure of correctness is calculated - the result expressed as a percentage of the true meanings. Reproducibility (accuracy, error) is a characteristic of random errors in chemical analysis. The reproducibility of the analysis is assessed by the closeness to each other ("scattering") of the results of parallel determinations. A quantitative assessment of reproducibility is the standard deviation: absolute S or relative Sr, calculated based on several parallel determinations using mathematical statistics methods. With respect to reproducibility, the reported data should contain the mean value X, standard deviation S, number of parallel determinations n. When presenting the results of the analysis, an assessment of the reliability of the obtained result is reported using a statistical criterion - a confidence interval, for a given reliability (confidence probability). Eα – confidence interval (boundaries, upper and lower, of possible variations of the desired value) at a

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Questions for self-control

1. What is weighing accuracy on analytical balances type VLA-200?

2. Why can't you weigh objects (substances) that have a different temperature? temperature than the scales?

3. Weight porcelain crucible turned out to be equal to 8.5 g. In what form should this mass be recorded in the journal if weighing was carried out on:

- technical scales;
- analytical balances.

4. Analytical balances failed after three separate weighings. ny tablets. The laboratory assistant had to weigh the remaining three tablets on technical scales. How many digits should a laboratory assistant save when calculating the sum of the masses of tablets during mathematical processing of weighing results?

5. What is the sensitivity of the scale? How many times is the sensitivity Are analytical balances more sensitive than technical quadrant balances?

Laboratory work No. 15
Determination of the amount of sulfate ions in solution

The determination of barium by the gravimetric method is based on the precipitation of barium in the form of sulfate, calcination of the sediment to a constant mass, weighing it and calculating the barium content. BaSO4 is a sparingly soluble compound (PR = 1.1*10-10). The weight form corresponds to the deposited one. 2N is used as a precipitant. H2SO4 solution.

Progress

1) The volume of the initial barium salt solution is diluted to 70-80 ml with distilled water and heated to 80-90°C.

2) A pre-calculated volume of sulfuric acid (precipitant) is placed in a glass, diluted to 70-80 ml and heated to 80-90oC.

3) Barium precipitation.The precipitant is added dropwise from a burette to the barium salt solution with constant stirring, allowed to stand until the solution above the precipitate becomes clear, checked for completeness of precipitation, and left until a crystalline precipitate forms for several hours.

4) Filtration of sediment.Place the ring on a tripod and place a funnel in it (the beveled end of the funnel should touch the glass). Fold the paper filter and place it in a funnel. Wet the filter with water so that there are no air bubbles left between the glass and the paper. Carefully pour the settled liquid over the sediment through a funnel (always over a glass rod to avoid splashing of the liquid). The filter must not be filled to the brim! When removing the glass, move the spout upward along the stick. The stick is left in the glass after decanting!

5) Washing the sediment.To avoid losses, as well as to remove impurities, use diluted

precipitant solution (5 cm3 of sulfuric acid per 100 cm3 of water). The precipitate is washed by decantation: 15-20 cm3 of washing liquid is added to a glass, mixed, the precipitate is allowed to settle and the liquid is again poured onto the filter. Repeat the operation 3-4 times.

6) The precipitate is transferred quantitatively to the filter (to do this, pour a small amount of washing liquid into a glass, stir up the precipitate and transfer the suspension onto a stick onto the filter). Traces of sediment are removed from the glass and stick with a piece of filter paper and placed in a funnel.

7) Washing the sediment on the filter. The sediment is washed with a large number of small portions of liquid, which is allowed to drain completely each time (the washing liquid is distilled water). After repeating the operation 4-5 times, a test is made to determine the completeness of removal of impurities (a sample of 1-2 cm3 is acidified with nitric acid, silver nitrate is added. If the AgCl turbidity does not appear, the washing is stopped).

8) Drying the sediment.The funnel with the sediment is covered with a sheet of damp filter paper, and the edges are pressed against the outer surface of the funnel. After this, the funnel is placed in a drying cabinet (for no more than 20 minutes)

9) Weigh the clean, calcined crucible. Remove the filter with sediment from the funnel, and, holding it over the crucible, carefully roll it up and place it in the crucible. The filter is ashed and calcined in a muffle furnace at 600-800°C to constant weight (the last weighing result should not differ from the previous one by more than 0.0002 g).

10) Data from all weighings are recorded in a table

Crucible no.	**Crucible mass, g**	**Mass of the crucible with sediment after drying, g**	**Sediment mass, g**

11) Based on the result obtained, the mass of barium is calculated in the original solution and report the result to the teacher. Calculate the relative error in determining the mass of barium based on the true value reported by the teacher

Questions for control

1. The essence and types of gravimetric analysis method.
2. Precipitable and weight forms; requirements placed on them.
3. Conditions for analytical isolation and properties of crystalline precipitates. What goals are pursued by creating certain conditions during the deposition of crystalline sediments?
4. Requirements for precipitators. Calculation of the amount of precipitant.
5. Why is a solution of a precipitant added to a solution of the substance being precipitated, and not vice versa?
6. Explain the purpose of diluting and heating solutions of the precipitant and the precipitated substance, and constant stirring during precipitation.
7. What processes occur with crystalline sediments during their aging? Why is sediment aging beneficial for analysis?
8. What volume of a) water and b) 0.01 M sulfuric acid solution can be washed with 0.2 g of barium sulfate so that the losses do not exceed the accuracy of the gravimetric method of analysis? PR(BaSO4) = 1.1*10-10.

Laboratory work No. 16
Taking dishes and preparing them for work.
Learning how to use a burette and pipette

For precise volume measurementsIn quantitative chemical analysis, volumetric flasks, pipettes and burettes are used. Volumetric flasks. Volumetric flasks are used for preparing standard solutions and for diluting test solutions to a certain volume. These are flat-bottomed flasks with a long narrow neck, on which a circular mark is applied. The volume indicated on the wall of the flask corresponds to the volume of liquid (at the calibration temperature), if the flask is filled so that the lower part of the liquid meniscus touches the mark, and bringing the volume of liquid to the mark must be carried out so that the eyes of the observer and the mark are at the same level (mark merges into a straight line). There should be no drops of liquid on the neck of the flask above the mark, the inner walls of the flask should be clean, and the liquid should wet them in an even layer. The flasks are closed with special ground stoppers. Volumetric flasks must not be heated, otherwise the glass may deform, which will result in a change in their capacity.

*Pipettes.*Used for precise selection of a certain volumesolution and transferring it from one vessel to another. Before use, the pipette is thoroughly washed, then rinsed several times, first with tap water and then with distilled water. After making sure that the water wets the inner walls in an even layer, without leaving drops (otherwise the washing is repeated), the entire inner surface of the pipette is rinsed 2-3 times with the solution that is supposed to be taken. To do this, the solution is poured into a dry, clean glass and used exclusively for rinsing the pipette. Do not immerse an unwashed pipette into a flask with a test or standard solution. Next, immerse the lower end of the pipette deep into the

solution, fill it with the solution so that the liquid level in it is approximately 2 cm above the mark. After this, quickly clamp the upper hole of the pipette with your index finger and, lifting the pipette, remove drops of the solution from the outside of the pipette with a piece of filter paper paper. Then the hole is slightly opened so that the excess liquid drains out and the lower edge of the meniscus touches the mark (the mark should be at eye level). Close the hole tightly again and transfer the pipette to a previously prepared vessel. Holding the pipette vertically, remove your finger from its hole and allow the liquid to flow freely; when all the liquid has flowed out, touch the tip of the pipette to the wall of the vessel and wait a few seconds until the remainder flows out. Then remove the pipette, not paying attention to the small amount of solution remaining in its nose - the calibration of pipettes is designed specifically for this method of pouring.

There are measuring pipettes (with divisions marked on them)and Mohr pipettes (with an extension in the middle), allowing you to measure a strictly defined volume.

*Burettes.*Burettes allow you to measure the required volumes of liquidand calibrated for pouring. Conventional laboratory macroburettes are graduated cylindrical tubes with a tapered end, which is equipped with a special stopcock or connected by a rubber tube to an extended glass tube. A small glass ball is inserted into the rubber tube; If you lightly press the rubber band in the place where the ball is placed, narrow channels are formed between it and the ball through which liquid flows out of the burette. The zero division is located at the top of the burette.

Before use, burettes should be thoroughly washed with detergent mixtures.and water so that the liquid drains from the inner walls in an even layer, leaving no drops. Before use, the burette must be rinsed 2-3 times with the solution that will be poured into it, so that when the burette is subsequently filled with the solution, it does not change its concentration due to dilution with water that wets the walls of the burette. After rinsing the burette, it is fixed strictly vertically in a stand and filled, using a funnel, with the solution to a level exceeding the zero mark by 2 - 3 cm. It is necessary to ensure that the entire burette, to the very tip, is filled with the solution. There should be no air bubbles in the burette (especially often they appear in its narrowed part). To remove air bubbles from the burettes, bend the glass tube upward and release some of the liquid. After this, the solution is again poured above the zero mark, the funnel is removed and the initial zero level of the solution is set.

During the titration process, you do not need to pour the liquid out of the burette very quickly; After the end of the titration, you must wait 30 s before counting the volume of solution poured from the burette. This is done so that the liquid remaining on the walls of the burette has time to drain. The reading on the burette is always carried out with an accuracy of 0.01 ml; before each titration, the level of the solution must be brought to the zero position, i.e. Always use the same part of the burette.

Laboratory work No. 17

Checking the capacity of a 250 ml measuring flask. Preparation of 500 ml of 0.1 N NaOH solution

Sodium hydroxide NaOH is a white, opaque, highly hygroscopic crystalline substance that diffuses in air and reacts easily with CO2 in the air. Therefore, the composition of NaOH is not constant and this compound is not suitable as a setting substance for the preparation of titrated solutions. Typically, titrated solutions of sodium hydroxide are prepared by diluting a calculated amount of a concentrated NaOH solution of known concentration with distilled water. First, prepare approximately 0.1 N solution, then check its normality. To prepare 1 liter of 0.1 N NaOH solution, 100% NaOH is required a=E(NaOH)· 0.1· 1=4 g. Let us assume that the density (ρ) of the initial NaOH solution is 1.285 g/cm3 (26% solution) . To prepare 1 liter of 0.1 N NaOH solution, you need to take a 26% solution g(NaOH)=4· 100/26 g, the volume occupied by g g of a 26% solution at ρ=1.285 is V=g/ρ= 4· 100/26· 1.285 =11.97 ≈ 12 ml. Thus, to prepare 1 liter of 0.1 N NaOH solution, measure 12 ml of the original concentrated NaOH solution and dilute it with distilled water to a volume of 1 liter. The resulting solution is thoroughly mixed and protected from absorbing CO2 from the air. The following are used as setting substances: oxalic acid, benzoic acid, potassium biphthalate and HCl solution, the characteristics of which are established by sodium tetraborate.

Laboratory work No. 18
Preparation of a 0.1 N standard solution of oxalic acid and standardization with it of a 0.1 N NaOH solution

Determination of the amount of acid in a solution.

***Equipment*:**stand, 100 ml volumetric flask, conical flasks, measured and graduated pipettes, burette, funnel, watch glass, technical and analytical balances.

***Reagents*:**oxalic acid, hydrogen chloride solution, sodium hydroxide solution, phenolphthalein.

Preparation of a primary standard solution of oxalic acid

The weight of oxalic acid is calculated according to formula 1, assuming that it is necessary to prepare 100 ml of a 0.1 N solution, since the prepared solution will also be used to standardize a 0.1 N solution of sodium hydroxide.

Procedure for preparing the solution

Determine the mass of the watch glass on a quadrant balance and clarify it on an analytical balance. Apply a calculated portion of oxalic acid to a watch glass and weigh it first on a technical and then on an analytical balance. Add oxalic acid through a wide-neck funnel into a 100 ml volumetric flask. Calculate the mass of the acid added to the flask from the difference between the mass of the watch glass with the substance and the mass of the watch glass. In accordance with clause 1.3. prepare a solution of oxalic acid and calculate its concentration using formula 2.

Preparation of a secondary standard solution of sodium hydroxide and its standardization

The concentration of the sodium hydroxide solution is determined by titration with a primary standard solution of oxalic acid. The interaction of the reagents proceeds according to the following scheme:

$H_2C_2O_4 + 2NaOH = Na_2C_2O_4 + 2H_2O$

Based on the stoichiometry of the total reaction, a molecule of oxalic acid is neutralized by two molecules of alkali. This means that the equivalent of an acid in this reaction is equal to 1/2 of a molecule of H2□2□4, and the molar mass of the equivalent is equal to 1/2 of the molar mass of the acid.

- Hence:

M (z*$H_2C_2O_4$*2H_2O) = z*M($H_2C_2O_4$*2H_2O)= 2*126.0680=63.0340 g/mol

Procedure for conducting the experiment

Calculate the volume of sodium hydroxide solution (density 1.400 g/ml, mass fraction 36.99%) required to prepare 500 ml of 0.1 N solution. Add the calculated volume of sodium hydroxide solution to the bottle, adding distilled water to 500 ml. Fill the burette with the prepared sodium hydroxide solution, after rinsing with the first portion of the solution. Add 10 ml of a primary standard solution of oxalic acid into a conical flask using a volumetric pipette (after rinsing the pipette). Add 2 drops of indicator - phenolphthalein. Titrate the oxalic acid solution with sodium hydroxide solution. Change in color of the solution - from colorless to pink.

Processing the experiment results

The results of calculations and experimental determinations are included in the table.

Volume H2C2O4 solution, ml	**Volume NaOH solution, ml**	**Conc. NaOH solution, mol/l**	**Average conc. NaOH solution, mol/l**	**Std. deviation S**	**t**	**Confidence interval Eα**	**Result Ana Lisa X±$E_α$**

Laboratory work No. 19
Determination of the amount of ammonia in ammonium salts

Since it is impossible to directly titrate an ammonium salt with an alkali due to the absence of a jump in the titration curve, indirect titration methods are used, for example, the reverse titration method (titration by excess). Progress

1) Obtain from a laboratory assistant a sample containing ammonium salt, and

take a sample weighing 0.5-0.6 g.

2) The sample is quantitatively transferred to a 100 ml volumetric flask, dissolved and adjusted to the mark with water, and mixed thoroughly.

3) Place 10 ml of the prepared solution into three titration flasks and add 20 ml of sodium hydroxide solution (0.1 N).

When alkali is added to a solution of ammonium salt, the following reaction occurs:

$$NH4Cl + NaOH = NaCl + H2O + NH3\uparrow$$

To completely remove ammonia, the flasks are heated on a hotplate. The complete removal of ammonia is checked by adding wet indicator paper to the released vapors. (No bluing of the paper indicates complete removal of ammonia).

4) The flasks with the solution are cooled, methyl orange is added and the excess alkali is titrated to 0.1 N. HCl (color transition: from yellow to red-orange). The burette for titration is prepared as described above. Titration is carried out three times, the results are averaged.

Questions for control

1. Essence and classification of titrimetric methods.
2. Requirements for reactions used in titrimetric analysis.
3. Define the concepts: titration, titer, titrant, standard and standardized solution, equivalence point.
4. What is the accuracy of titrimetric methods, and how can it be improved?

Laboratory work No. 20
Prepare 500 ml hydrochloric acid and 0.1 N standard borax solution.
Standardization of hydrochloric acid using borax

Equipment:burette, 10 ml pipettes, graduated cylinder, graduated pipettes, titration flasks, funnels.

Reagents:standard solutions of Na2B4O7, working solution of HC1, NaOH, test solutions of HC1, acetic acid, indicators.

When dissolved in water, borax is strongly hydrolyzed at the anion to form weak boric acid:

$$Na2B4O7 + 7\ H2O \leftrightarrow 2\ NaOH + H3BO3.$$

When titrated with hydrochloric acid, the hydrolysis equilibrium shifts almost completely to the right, because the alkali released during hydrolysis is neutralized by acid:

$$NaOH+HCl = NaOH + H2O.$$

Summing these two equations, we get:

Na2B4O7 + 2 HCl + 5H2O = 2 NaCI + 4 H3BO3.

2)Selection of indicator: the solution at the equivalence point contains NaCl and free H3BO3, which causes a weakly acidic reaction of the medium. Therefore, titration must be performed in the presence of methyl orange (see table).

3)Titration procedure:

a) pour distilled water out of the burette, rinse it from the inside with the prepared HC1 solution and fill it to the zero mark. Make sure that there are no air bubbles in the burette nose. The burette is installed in a stand strictly vertically;

b) prepare samples of sodium tetraborate solution for titration. About 50 ml of solution is transferred from a common laboratory flask to a clean, dry flask. To rinse the analytical pipette, it is filled with a solution, which is then drained. Using a pipette prepared in this way, transfer 10 ml of the solution into each of three conical titration flasks. Add 1-2 drops of methyl orange to each flask;

c) titrate the sodium tetraborate solution with HC1 solution from a burette. The first titration is indicative. Adding titrant in small portions from a burette, constantly stir the contents of the flask. The titration is completed when 1 drop of titrant causes a color change from yellow to orange. The second and subsequent titrations are carried out more accurately. First, the titrant is quickly added to the titration flask in a volume that is 0.5 ml less than the volume determined during the approximate titration. The titrant is then added dropwise, carefully observing the color change of the solution. The titration is stopped when a noticeable change in color occurs with the addition of just one drop.

The titration is repeated until three convergent ones are obtained, i.e. results differing from each other by no more than 0.1 ml. All results are entered into a table.

Volume of Na2B4O7 solution,	**Volume of HCl solution, ml**	**CH HC1, mol/l**	**T (HCl), g/ml**
10.0 10.0 10.0			

d) The volume of HC1 solution used for titration is found as the arithmetic mean of 3 results:

$$V(HCl) = \frac{V(1)+V(2)+V(3)}{3}$$

Calculations of normality and titer are made using the law of equivalents:

Cn(HCl)xV(HCl)=Cn(Na2B4O7)xV(Na2B4O7);

$$Cn(HCl) = \frac{CH(Na_2B_4O_7) \times V(Na_2B_4O_7)}{\text{---}};$$

$$T(HCl) = \frac{V(HCl) \times CH(HCl) \times Me(HCl)}{1000}$$

Laboratory work No. 21
Determination of the amount of soda in technical caustic soda

Alkali solutions almost always contain carbonates as impurities. These substances can be determined separately in one solution by titration with acid. The carbonate ion is a weak diacid base and therefore attaches two hydrogen ions in series:

$$CO_3^{2-} + H^+ = HCO_3^-$$
$$HCO_3^- + H^+ = H_2CO_3$$

The equivalence point of the first reaction corresponds to pH 8.34. This produces a solution of hydrocarbonate. If an alkali was simultaneously present in the solution, then at a given pH value it also almost completely reacts. Thus, by titrating the initial solution with an acid to pH 8.34, the alkali is simultaneously neutralized and the carbonate is converted into bicarbonate. Phenolphthalein can serve as an indicator in this titration. Further addition of acid converts the bicarbonate to carbonic acid. The equivalence point corresponds to pH 4. In this case, titration should be carried out with methyl orange indicator.

Based on the foregoing, we can conclude that the analysis of a mixture of alkali and carbonate comes down to sequential titration of the test solution with acid until phenolphthalein becomes discolored, and then until the yellow color of methyl orange changes to pink.

Obtain from the laboratory technician the test solution in a 50 ml volumetric flask and adjust the volume to the mark with distilled water. Using an analytical pipette, withdraw 10 ml of the solution into titration flasks. Add 1-2 drops of phenolphthalein to each flask and titrate the test solution with a working solution of hydrochloric acid until the color disappears (pink color should not appear again within 30 seconds). Record the first reading of burette V1 in Table 8. Add 1-2 drops of methyl orange to the flask and continue titrating until the solution turns yellow to pink. Record the second reading of burette V2. Then refill the burette with acid and titrate further samples until reproducible results are obtained. Record the results of all titrations in a table.

Volume subject solution, ml	**HCL titrant volume, ml**		**Weight NaOH, G**	**Weight Na2CO3, G**
	with phenolphthalein	**with methyl orange**		

10.0 10.0 10.0				

The volume of acid solution spent on the first titration (V1) is equivalent to that contained in the alkali solution and half of the total amount of carbonate, since the CO_3^{2-} ion attaches only one hydrogen ion. The volume of acid spent on the second titration (V2 - V1) is equivalent to half the amount of carbonate available, because at this stage, the HCO_3^- ion adds a second proton. The reaction with carbonate requires equal volumes of acid at each stage. Therefore, a total volume of acid V3 = 2(V2 – V1) ml is used for the titration of carbonate. The neutralization of alkali affects the volume of acid V4 = V2 – V3. Calculate V3 and V4 based on the found volumes of consumed acid, calculate the concentration of the analyzed solution for each substance.

Questions for self-study:

1What factors determine the choice of indicator in acid-base titration?

2 Acid-base titration curves.

3 What standard solutions are used in acid-base titrations?

Calculation tasks:

1.What mass of oxalic acid dihydrate $H_2C_2O_2$ needs to be sculpted so that 20 ml are spent on its titration0.1 MNaOH solution? (M($H_2C_2O_4 \cdot 2H_2O$) = 126 g/mol). Answer:*0.1260 g*

2.9.7770Gconcentrated solution of HNO_3 was diluted with water to1 lin a measuring flask. To titrate 25.00 ml of the resulting solution, 3.40 ml was consumed0.1040 MNaOH solution. Determine the mass fraction of nitric acid in its concentrated solution. Answer:*62.73 g*

3.To titrate 20.00 ml of HC1 solution with a titer of 0.001825 g/ml, 23.04 ml of NaOH solution was consumed. Calculate the molar concentration of the equivalent and the titer of the NaOH solution. Answer: 0.04 mol/l; 0.001600 g/ml

4.For titration0.2860 g$Na_2CO_3 \cdot 10H_2O$ in the presence of methyl orange, 24.10 ml of HC1 solution was consumed. Calculate the molar concentration and titer of the HC1 solution. Answer: 0.08299 mol/l, 0.003029 g/ml.

Laboratory work No. 22
Oxidometry preparation of 0.05 N $KMnO_4$ solution and determining its exact normality using a standard solution of oxalic acid

The starting solution for establishing the concentration of potassium permanganate is oxalic acid dihydrate $H_2C_2O_4 * 2H_2O$. The reaction proceeds according to the equation: $5H_2C_2O_4^{2-} + 2MnO_4^- + 6H^+ = 10CO_2 + 2Mn^{2+} + 8H_2O$

Progress

1) $_4$ $_2$ Calculate the mass of oxalic acid crystal hydrate($H_2C_2O*2H_2O$) required to prepare 100 ml of 0.1 N. solution. Take the calculated portion of oxalic acid and transfer it to a 1000 ml volumetric flask. Dissolve in a small amount of distilled water.

The solution is thoroughly mixed.

2) Prepare three conical heat-resistant titration flasks. Add 15 ml of sulfuric acid solution (2N) to each, heat to 80-90°C, add 10 ml of the prepared oxalic acid solution. (The oxalic acid solution is added to the flask immediately before titration, since oxalic acid is destroyed at elevated temperatures.) The solution is quickly titrated with a solution of potassium permanganate, first adding 1-2 drops of the titrant and waiting, stirring, until the solution becomes colorless. Subsequent portions of the titrant can be added more quickly. The end of the titration is determined by the persistent pink color of the solution that appears when an excess drop of titrant is added. The burette is prepared for titration as described above. Titration is carried out 3 times. The arithmetic mean is taken as the measurement result. The molar concentration of potassium permanganate equivalent is calculated using the formula:

N KMnO4 = NH2C2O4 .VH2C2O4 / V KMnO4

Laboratory work No. 23
Iodometry. Preparation of 0.05 N sodium thiosulfate solution and standardization with potassium dichromate

*Iodometric titration*is called a titrimetric method of analysis, based on determining the amount of iodine spent to complete the reaction with a substance with reducing properties, or released as a result of the reaction of KI with a substance with oxidizing properties.

The basis of equilibrium: iodometric definitions is the following

[I3]- + 2ē « 3I-;*E0* = +0.545 V

Iodine and sodium thiosulfate are used as titrants in iodometric titration.

Task 1. Standardization of sodium thiosulfate solution

Potassium dichromate is used to standardize sodium thiosulfate solutions. The reactions of Na2S2O3 with K2Cr2O7 and other strong oxidizing agents proceed non-stoichiometrically, therefore, standardization of a sodium thiosulfate solution is carried out by substitution titration: when K2Cr2O7 reacts with excess KI, an amount of iodine equivalent to the first substance is formed, which is then titrated with the Na2S2O3 solution being standardized.

The end point of titration in iodometry is most often detected by the disappearance or appearance of color of the iodine-starch complex.

Progress

Add 15 ml of 10% KI solution into three titration flasks. Add 5 ml of H2SO4 solution (1:4) and 10 ml of 0.05 N solution to each flask. K2Cr2O7 solution. There is no need to measure solutions of potassium iodide and sulfuric acid with a pipette (you can use a cylinder), but a solution of K2Cr2O7 is necessary. (Why?)

The titration flasks are covered with a watch glass and placed in a dark place for approximately 5 minutes. (Why?) The burette is prepared for titration as usual by filling it with the sodium thiosulfate solution to be standardized. Begin the titration without an indicator, which is added at the end of the titration, when the color of the titrated solution turns pale yellow. (Why?) Starch is used as an indicator, after the addition of which the solution turns blue. The end point of titration is considered to be the moment the color of the analyzed solution changes from blue to pale green. Titration is carried out 3 times. Based on the average volume of sodium thiosulfate, its concentration is calculated

N (Na2S2O3) = N (K2Cr2O7) .V (K2Cr2O7) / V(Na2S2O3)

When performing subsequent iodometric determinations, the resulting value of sodium thiosulfate concentration is used in calculations.

Laboratory work No. 24
Complexometry. Preparation of a 0.05 N EDTA solution and standardization using a standard zinc solution

Target: To study the theoretical foundations of the complexometry method, which is widely used in analytical studies.

Tasks: Acquiring skills in complexometric titration and performing quantitative calculations. Develop skills and abilities in drawing up equations for complexation reactions.

Main questions of the topic:

1. Theoretical foundations of complexometry.
2. Classification of complexometry methods.
3. Standardization of titrants in complexometry.
4. Complexometry indicators, their principle of operation.
5. Calculations in complexometry.

Task 1.A sample of metallic magnesium was dissolved in hydrochloric acid and the resulting solution was titrated with 15.00 ml of EDTA solution with a molar concentration of 0.1500 mol/l. Calculate the mass of a sample of magnesium. Answer:*0.05468 g*

Task 2.A sample of magnesium bicarbonate weighing 3.500 g was dissolved in water and titrated with 12.05 ml of EDTA solution with a molar concentration of 0.05000 mol/l. Calculate the mass fraction of magnesium bicarbonate in the sample as a percentage. Answer: 2.518%

Task 3.A sample of mercury (II) nitrate monohydrate weighing2,900 gdissolved in water to obtain 50.00 ml of solution. An aliquot of 5.00 ml was titrated with 11.06 ml of EDTA

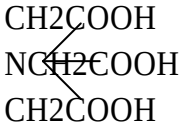
solution with a molar concentration of 0.07500 mol/L. Calculate the mass fraction of mercury (II) nitrate in the sample as a percentage. Answer: 93.33%

Task 4. Sample of manganese (II) nitrate hexahydrate weighing4,500 gdissolved in water and prepared 200.0 ml of solution. To titrate 10.00 ml of the resulting solution, 13.50 ml of EDTA solution with a molar concentration of 0.05000 mol/l was consumed. Calculate the mass fraction of manganese in the sample as a percentage. Answer: 16.48%

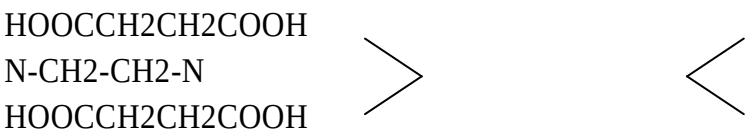
Theoretical foundations of the method. Analytical laboratories widely use analytical methods based on the use of reactions accompanied by the formation of complex compounds of cations with organic reagents - complexones. The resulting compounds are called intracomplex (claw-shaped, chelate) salts.

Complexons are usually called organic compounds that are derivatives of aminopolycarboxylic acids.

The simplest complexone is nitrilotriacetic acid (NTA, complexone I, abbreviated H2U):

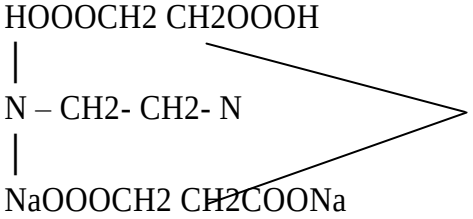


The most important is tetrabasic ethidenediaminetetraacetic acid (EDTA, complex II, abbreviated H4U):



Complexons, along with carboxyl groups (-COOH), contain amine nitrogen (-N). Due to this structure, these compounds are distinguished by multi(poly)dentity, i.e. the ability to form several coordination bonds with complexing metal ions at once.

In practice, the disodium salt of ethylenediamine-tetraacetic acid (EDTA, Na-EDTA, complexon III or Trilon B, abbreviated as Na2H2U) is usually used:



The ethylenediaminetetraacetic acid ion forms up to six bonds with the metal ion through the oxygen atoms of carboxyl groups and nitrogen atoms. One complexone ion replaces several monodentate ligands. When titrating metal complexing salts with EDTA, the following reactions occur:

$Na_2H_2У \rightarrow 2\ Na^+ + H_2У^{2-}$

$Me^{2+} + H_2У^{2-} \leftrightarrow MeУ^{2-} + 2\ H^+$

$Me^{3+} + H_2U^{2-} \leftrightarrow MeU^- + 2\ H^+$

$Me^{4+} + H_2U^{2-} \leftrightarrow MeU + 2\ H^+$

According to the above equations, 1 mole of cations reacting with NaEDTA, regardless of their oxidation state, binds 1 mole of Na-EDTA. The equilibria of these transformations are shifted to the right, because the resulting complex compounds are very strong. In addition, in accordance with the Le Chatelier-Brown principle, the completeness of these reactions increases with increasing pH of the solution, i.e. when binding hydrogen ions with alkali. However, it should be borne in mind that when the pH of the solution increases, metal hydroxide may precipitate. Therefore, when using complexones for analytical purposes, it is necessary to create an optimal pH value of the solution, depending on the strength of the complex and the solubility of the corresponding hydroxide. For example, iron (III) ion forms both a strong complex with Na-EDTA and a very poorly soluble hydroxide. Therefore, the complexation reaction can occur at a pH no higher than 3.

The Ca^{2+} cation forms a less stable complex and a relatively highly soluble hydroxide. It reacts most fully with Na-EDTA at pH 9-10. A certain pH value of the solution is achieved using buffer solutions.

The equivalence point in complexometry is established using indicators, which are organic dyes that form colored complex compounds with cations (metal indicators). The resulting complex compounds are less stable than intracomplex salts formed by the cations being determined with complexones. Therefore, during the titration with a complexon of a solution containing a colored complex compound formed by cations with an indicator, a change in the color of the solution is observed at the equivalence point. This is explained by the fact that the complex compound of the indicator is destroyed and the indicator is released in a free form. Since the color of the complex compound of the indicator differs from the color of the free indicator, a change in the color of the titrated solution occurs. This can be represented schematically as follows:

$Me^{2+} + Hind^- \leftrightarrow Meind^- + H^+$

colorless colored colored different color

$Meind^- + H_2E^{2-} \leftrightarrow VtE^{2-} + Hind^- + H^+$

colored colorless colored

Thus, the indicator metal reacts to changes in the concentration of the cation in the same way as an acid-base indicator behaves when the pH of the titrated solution changes.

The indicator for ions of magnesium, copper, zinc, manganese, aluminum, etc. is eriochrome black T. The indicator itself is blue, and its complexes with metals are red. The reaction equation can be represented as follows:

$Me^{2+} + Hind^{2-} \leftrightarrow Meind^{-} + H^{+}$
blue red
$Meind^{-} + Na_2H_2Y + OH^{-} \leftrightarrow Na_2MeY + Hind^{2-} + H_2O$

Another widely used indicator metal is murexide (ammonium purpurate), which forms stable complex compounds with cations of calcium, nickel, cobalt, copper, etc.

Murexide is a dark red powder, the aqueous solution of which is colored violet, varying depending on the environment: pH < 9 - red-violet, pH > 11 - blue-violet. During the titration of calcium salts and other metals in the presence of murexide, a change in the red color of the solution to a blue-violet color is observed at the equivalence point.

Currently, complexometric methods have been developed for the determination of more than 80 chemical elements.

Laboratory work No. 25
Complexometric quantification metal ions in solution

Equipment:burettes, analytical pipettes, volumetric flasks, titration flasks, glass funnels, graduated cylinders, conical flasks.

Reagents:solutions of ammonia-ammonium buffer, ammonia, ammonium chloride, standard solution of Trilon B, metal indicators - murexide, eriochrome black, test solutions.

Obtain from the laboratory assistant the calcium salt solution to be tested in a 50 ml volumetric flask and adjust the volume to the mark with distilled water. Prepare an ammonia-ammonium buffer solution by using a measuring cylinder to take 20 ml of 20% solutions of ammonia and ammonium chloride into a 100 ml conical flask.

Add 10 ml of the test solution to each titration flask using an analytical pipette; then, using a graduated cylinder, add 2 ml of ammonia-ammonium buffer and 3 drops of murexide solution. Fill the burette with a standard solution of Trilon B with a molar concentration of 0.025 mol/l and titrate until the color changes from cherry-red to blue.

Based on the results of the analysis, calculate the molar concentration of the equivalent and titer of calcium in the test solution, as well as its mass in 50 ml of solution. Enter the obtained data into the table.

$V(Ca^{2+})$ ml	V (EDTA) ml	$C_H(Ca^{2+})$ mol/l	$T(Ca^{2+})$ g/ml	$m(Ca^{2+})$ g
10.0 10.0 10.0				

Laboratory work No. 26

Titration using the precipitation method. Preparation of 0.05 N solution of mercury(I) nitrate and standardizing it using a standard potassium chloride solution. Determination of chlorine ions in solution

Halides (C1~, Br~ and 1~), cyanides and thiocyanides are determined argentometrically. The working solution is a standard solution of silver nitrate AgNO3. Equivalent to 3AgNO3 = MAgNO3 = 169.874. Silver nitrate AgNO3 Properties. White crystalline substance (M = 169.874). In its pure form it is quite stable, but impurities of organic substances cause its decomposition with the formation of dispersed black silver. Light greatly accelerates this decomposition. The reagent leaves dark stains on the skin of hands, paper and fabrics. The wet preparation, as well as its solutions, decompose in the light, so the reagent and its solutions are stored in dark bottles with ground-in stoppers. Silver nitrate is highly soluble in water and organic solvents, almost insoluble in concentrated HNO3. The drug is analytical grade. contains no less than 99.8% AgNO3, parts - no less than 99.75%. Recrystallization. A chemically pure AgNO3 preparation is obtained by recrystallizing a conventional preparation from a weakly nitric acid solution and then drying the salt at 150°C in an oven to constant weight. Preparation of silver nitrate solutions Usually, solutions of approximately the required normality are prepared, and then their titer is determined using a sodium chloride solution. To prepare 0.1 n. a solution of 17 g of silver nitrate is dissolved in water and the solution is diluted with water to 1 liter. A solution is prepared from the recrystallized drug by precise weighing. Dissolve 16.9874 g of AgNOa in water, transfer to a 1-liter volumetric flask and dilute with water to the mark. The normality of the solution is exactly 0.1 N. and does not need verification. A solution of silver nitrate can also be prepared from pure metallic silver (fineness 999). To do this, dissolve 10.787 g of silver in 100 ml of diluted HNO3 (1:1), which does not contain hydrochloric acid. After dissolving the silver, the solution is boiled until nitrogen oxides are removed, cooled, transferred to a 1-liter volumetric flask and diluted with water to the mark. The solution is exactly 0.1 N in concentration. and does not need to install a title. It is not suitable for the determination of chlorides using the Mohr method, since its acidity with respect to nitric acid is approximately 0.5 N. Standardization of solutions of silver nitrate A solution of silver nitrate is standardized against a solution of sodium chloride x. hours, using a solution of potassium thiocyanate or by the gravimetric method. In the absence of sodium chloride x. h. it is obtained from a conventional reactive preparation. The following symbols are used in the chapter: M - molecular weight; A - atomic mass; E - equivalent; p - density; t - temperature.

Sodium chloride NaCl: Properties. White crystalline substance or fine crystalline powder; M=58.443; p=2.17; tmelt=801°C; boiling point=1439°C. Poorly soluble in concentrated HC1. The solubility of NaCl increases little with increasing temperature; at 25°C it is 36.1 g, and at 100°C - 39.6 g. Slightly soluble in methanol (1.41 g in 100 ml at 20°C), even less soluble in ethanol (0.09 g at 17 °C). The drug of all qualifications contains at least 99.8% NaCl Recrystallization. The saturated hot salt solution is filtered, cooled with ice and the solution is saturated with hydrogen chloride gas. In this case, NaCl crystals fall out. A funnel is attached to the end of the gas supply tube so that the crystallizing mass does not clog the outlet

of the tube. The crystals are sucked off on a Buchner funnel, washed several times with concentrated HC1, squeezed between sheets of filter paper, dried at 110 - 115 ° C, ground into powder in a mortar and calcined in a muffle furnace at 500 - 600 ° C to constant weight. Calcination can also be carried out on a gas burner by placing the crucible in the hole of an asbestos plate fixed in an inclined position in order to avoid combustion products of gases containing sulfur from entering the crucible. Recrystallized NaCl from a Buchner funnel can be placed in an evaporation dish, dried, then heated to a boil and poured into a completely clean and dry porcelain or ceramic plate, then broken into pieces and crushed in a porcelain mortar. The purified drug is stored in a bottle with a ground-in stopper for an indefinitely long time, since it is not hygroscopic. (Ordinary table salt is hygroscopic due to the fact that it contains an admixture of magnesium chloride.) If reagent x is available. hours, then before taking the sample it should be calcined at 500°C to constant weight. Preparation 0.1 n. sodium chloride solution. Convert 5.8443 g of sodium chloride x. hours in a volumetric flask, dissolve in water and dilute with water to 1 liter. The normality coefficient of the solution is found by dividing the actual mass of the sample by the theoretical one (5.8443). Standardization according to Mohr's method: Take 25.0 ml of 0.1 N. sodium chloride solution into a titration flask, add 25 ml of water and 0.5 ml of a 10% aqueous solution of potassium chromate K2CrO4. Titration is carried out in the presence of a “witness”. To prepare the “witness”, 25.0 ml of 0.1 N is also placed in another similar flask. sodium chloride solution, 25 ml of water, 0.5 ml of 10% K2CrO4 solution and add 2 - 3 ml of silver nitrate solution. A solution of sodium chloride is titrated with a solution of silver nitrate until a weak but quite noticeable red-brown color appears, which persists after vigorous shaking and differs from the color of the “witness”. Titration should not be carried out in direct sunlight, as the AgCl precipitate decomposes, becoming lilac. Titration under electric light, when the yellow color is difficult to see, does not give good results. Near the end point of titration, the AgCl precipitate coagulates, forming large flakes that settle to the bottom. The last drops of AgNO3 solution are added slowly, vigorously stirring the solution in order to titrate the adsorbed C1- ions.

Laboratory work No. 22
Oxidometry preparation of 0.05 N KMnO4 solution and determining its exact normality using a standard solution of oxalic acid

The starting solution for establishing the concentration of potassium permanganate is oxalic acid dihydrate H2C2O4 * 2H2O. The reaction proceeds according to the equation: 5H2C2O42- + 2MnO4- + 6H+ = 10CO2 + 2Mn2+ + 8H2O

Progress

3) 4 2 Calculate the mass of oxalic acid crystal hydrate(H2C2O*2H2O) required to prepare 100 ml of 0.1 N. solution. Take the calculated portion of oxalic acid and transfer it to a 1000 ml volumetric flask. Dissolve in a small amount of distilled water.

The solution is thoroughly mixed.

4) Prepare three conical heat-resistant titration flasks. Add 15 ml of sulfuric acid solution (2N) to each, heat to 80-90°C, add 10 ml of the prepared oxalic acid solution. (The oxalic acid solution is added to the flask immediately before titration, since oxalic acid is destroyed at elevated temperatures.) The solution is quickly titrated with a solution of potassium permanganate, first adding 1-2 drops of the titrant and waiting, stirring, until the solution becomes colorless. Subsequent portions of the titrant can be added more quickly. The end of the titration is determined by the persistent pink color of the solution that appears when an excess drop of titrant is added. The burette is prepared for titration as described above. Titration is carried out 3 times. The arithmetic mean is taken as the measurement result. The molar concentration of potassium permanganate equivalent is calculated using the formula:

N KMnO4 = NH2C2O4 .VH2C2O4 / V KMnO4

Laboratory work No. 23
Iodometry. Preparation of 0.05 N sodium thiosulfate solution and standardization with potassium dichromate

*Iodometric titration*is called a titrimetric method of analysis, based on determining the amount of iodine spent to complete the reaction with a substance with reducing properties, or released as a result of the reaction of KI with a substance with oxidizing properties.

The basis of equilibrium: iodometric definitions is the following

[I3]- + 2ē « 3I-;*E0* = +0.545 V

Iodine and sodium thiosulfate are used as titrants in iodometric titration.

Task 1. Standardization of sodium thiosulfate solution

Potassium dichromate is used to standardize sodium thiosulfate solutions. The reactions of Na2S2O3 with K2Cr2O7 and other strong oxidizing agents proceed non-stoichiometrically, therefore, standardization of a sodium thiosulfate solution is carried out by substitution titration: when K2Cr2O7 reacts with excess KI, an amount of iodine equivalent to the first substance is formed, which is then titrated with the Na2S2O3 solution being standardized.

The end point of titration in iodometry is most often detected by the disappearance or appearance of color of the iodine-starch complex.

Progress

Add 15 ml of 10% KI solution into three titration flasks. Add 5 ml of H2SO4 solution (1:4) and 10 ml of 0.05 N solution to each flask. K2Cr2O7 solution. There is no need to measure solutions of potassium iodide and sulfuric acid with a pipette (you can use a cylinder), but a solution of K2Cr2O7 is necessary. (Why?)

The titration flasks are covered with a watch glass and placed in a dark place for approximately 5 minutes. (Why?) The burette is prepared for titration as usual by filling it with the sodium thiosulfate solution to be standardized. Begin the titration without an indicator, which is added at the end of the titration, when the color of the titrated solution turns pale yellow. (Why?) Starch is used as an indicator, after the addition of which the solution turns blue. The end point of titration is considered to be the moment the color of the analyzed solution changes from blue to pale green. Titration is carried out 3 times. Based on the average volume of sodium thiosulfate, its concentration is calculated

N (Na2S2O3) = N (K2Cr2O7) .V (K2Cr2O7) / V(Na2S2O3)

When performing subsequent iodometric determinations, the resulting value of sodium thiosulfate concentration is used in calculations.

Laboratory work No. 24
Complexometry. Preparation of a 0.05 N EDTA solution and standardization using a standard zinc solution

Target: To study the theoretical foundations of the complexometry method, which is widely used in analytical studies.

Tasks: Acquiring skills in complexometric titration and performing quantitative calculations. Develop skills and abilities in drawing up equations for complexation reactions.

Main questions of the topic:

2. Theoretical foundations of complexometry.
2. Classification of complexometry methods.
3.Standardization of titrants in complexometry.
4.Complexometry indicators, their principle of operation.
5. Calculations in complexometry.

Task 1.A sample of metallic magnesium was dissolved in hydrochloric acid and the resulting solution was titrated with 15.00 ml of EDTA solution with a molar concentration of 0.1500 mol/l. Calculate the mass of a sample of magnesium. Answer:*0.05468 g*

Task 2.A sample of magnesium bicarbonate weighing 3.500 g was dissolved in water and titrated with 12.05 ml of EDTA solution with a molar concentration of 0.05000 mol/l. Calculate the mass fraction of magnesium bicarbonate in the sample as a percentage. Answer: 2.518%

Task 3.A sample of mercury (II) nitrate monohydrate weighing2,900 gdissolved in water to obtain 50.00 ml of solution. An aliquot of 5.00 ml was titrated with 11.06 ml of EDTA

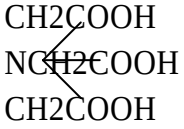
solution with a molar concentration of 0.07500 mol/L. Calculate the mass fraction of mercury (II) nitrate in the sample as a percentage. Answer: 93.33%

Task 4. Sample of manganese (II) nitrate hexahydrate weighing4,500 gdissolved in water and prepared 200.0 ml of solution. To titrate 10.00 ml of the resulting solution, 13.50 ml of EDTA solution with a molar concentration of 0.05000 mol/l was consumed. Calculate the mass fraction of manganese in the sample as a percentage. Answer: 16.48%

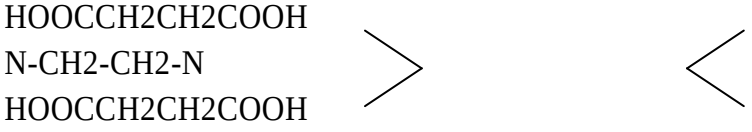
Theoretical foundations of the method. Analytical laboratories widely use analytical methods based on the use of reactions accompanied by the formation of complex compounds of cations with organic reagents - complexones. The resulting compounds are called intracomplex (claw-shaped, chelate) salts.

Complexons are usually called organic compounds that are derivatives of aminopolycarboxylic acids.

The simplest complexone is nitrilotriacetic acid (NTA, complexone I, abbreviated H2U):

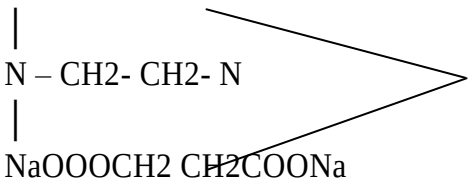


The most important is tetrabasic ethidenediaminetetraacetic acid (EDTA, complex II, abbreviated H4U):



Complexons, along with carboxyl groups (-COOH), contain amine nitrogen (-N). Due to this structure, these compounds are distinguished by multi(poly)dentity, i.e. the ability to form several coordination bonds with complexing metal ions at once.

In practice, the disodium salt of ethylenediamine-tetraacetic acid (EDTA, Na-EDTA, complexon III or Trilon B, abbreviated as Na2H2U) is usually used:



The ethylenediaminetetraacetic acid ion forms up to six bonds with the metal ion through the oxygen atoms of carboxyl groups and nitrogen atoms. One complexone ion replaces several

monodentate ligands. When titrating metal complexing salts with EDTA, the following reactions occur:

$Na_2H_2У \rightarrow 2\ Na^+ + H_2У^{2-}$
$Me^{2+} + H_2У^{2-} \leftrightarrow MeУ^{2-} + 2\ H^+$
$Me^{3+} + H_2U^{2-} \leftrightarrow MeU^- + 2\ H^+$
$Me^{4+} + H_2U^{2-} \leftrightarrow MeU + 2\ H^+$

According to the above equations, 1 mole of cations reacting with NaEDTA, regardless of their oxidation state, binds 1 mole of Na-EDTA. The equilibria of these transformations are shifted to the right, because the resulting complex compounds are very strong. In addition, in accordance with the Le Chatelier-Brown principle, the completeness of these reactions increases with increasing pH of the solution, i.e. when binding hydrogen ions with alkali. However, it should be borne in mind that when the pH of the solution increases, metal hydroxide may precipitate. Therefore, when using complexones for analytical purposes, it is necessary to create an optimal pH value of the solution, depending on the strength of the complex and the solubility of the corresponding hydroxide. For example, iron (III) ion forms both a strong complex with Na-EDTA and a very poorly soluble hydroxide. Therefore, the complexation reaction can occur at a pH no higher than 3.

The Ca^{2+} cation forms a less stable complex and a relatively highly soluble hydroxide. It reacts most fully with Na-EDTA at pH 9-10. A certain pH value of the solution is achieved using buffer solutions.

The equivalence point in complexometry is established using indicators, which are organic dyes that form colored complex compounds with cations (metal indicators). The resulting complex compounds are less stable than intracomplex salts formed by the cations being determined with complexones. Therefore, during the titration with a complexon of a solution containing a colored complex compound formed by cations with an indicator, a change in the color of the solution is observed at the equivalence point. This is explained by the fact that the complex compound of the indicator is destroyed and the indicator is released in a free form. Since the color of the complex compound of the indicator differs from the color of the free indicator, a change in the color of the titrated solution occurs. This can be represented schematically as follows:

$Me^{2+} + Hind^- \leftrightarrow Meind^- + H^+$
colorless colored colored different color

$Meind^- + H_2E^{2-} \leftrightarrow VtE^{2-} + Hind^- + H^+$
colored colorless colored

Thus, the indicator metal reacts to changes in the concentration of the cation in the same way as an acid-base indicator behaves when the pH of the titrated solution changes.

The indicator for ions of magnesium, copper, zinc, manganese, aluminum, etc. is eriochrome black T. The indicator itself is blue, and its complexes with metals are red. The reaction equation can be represented as follows:

$Me^{2+} + Hind^{2-} \leftrightarrow Meind^{-} + H^{+}$
blue red
$Meind^{-} + Na_2H_2Y + OH^{-} \leftrightarrow Na_2MeY + Hind^{2-} + H_2O$

Another widely used indicator metal is murexide (ammonium purpurate), which forms stable complex compounds with cations of calcium, nickel, cobalt, copper, etc.

Murexide is a dark red powder, the aqueous solution of which is colored violet, varying depending on the environment: pH < 9 - red-violet, pH > 11 - blue-violet. During the titration of calcium salts and other metals in the presence of murexide, a change in the red color of the solution to a blue-violet color is observed at the equivalence point.

Currently, complexometric methods have been developed for the determination of more than 80 chemical elements.

Laboratory work No. 25
Complexometric quantification
metal ions in solution

Equipment:burettes, analytical pipettes, volumetric flasks, titration flasks, glass funnels, graduated cylinders, conical flasks.

Reagents:solutions of ammonia-ammonium buffer, ammonia, ammonium chloride, standard solution of Trilon B, metal indicators - murexide, eriochrome black, test solutions.

Obtain from the laboratory assistant the calcium salt solution to be tested in a 50 ml volumetric flask and adjust the volume to the mark with distilled water. Prepare an ammonia-ammonium buffer solution by using a measuring cylinder to take 20 ml of 20% solutions of ammonia and ammonium chloride into a 100 ml conical flask.

Add 10 ml of the test solution to each titration flask using an analytical pipette; then, using a graduated cylinder, add 2 ml of ammonia-ammonium buffer and 3 drops of murexide solution. Fill the burette with a standard solution of Trilon B with a molar concentration of 0.025 mol/l and titrate until the color changes from cherry-red to blue.

Based on the results of the analysis, calculate the molar concentration of the equivalent and titer of calcium in the test solution, as well as its mass in 50 ml of solution. Enter the obtained data into the table.

$V(Ca^{2+})$ ml	V (EDTA) ml	$C_H(Ca^{2+})$ mol/l	$T(Ca^{2+})$ g/ml	$m(Ca^{2+})$ g

10.0 10.0 10.0				

Laboratory work No. 26
Titration using the precipitation method.
Preparation of 0.05 N solution of mercury(I) nitrate and standardizing it using a standard potassium chloride solution. Determination of chlorine ions in solution

Halides (C1~, Br~ and 1~), cyanides and thiocyanides are determined argentometrically. The working solution is a standard solution of silver nitrate AgNO3. Equivalent to 3AgNO3 = MAgNO3 = 169.874. Silver nitrate AgNO3 Properties. White crystalline substance (M = 169.874). In its pure form it is quite stable, but impurities of organic substances cause its decomposition with the formation of dispersed black silver. Light greatly accelerates this decomposition. The reagent leaves dark stains on the skin of hands, paper and fabrics. The wet preparation, as well as its solutions, decompose in the light, so the reagent and its solutions are stored in dark bottles with ground-in stoppers. Silver nitrate is highly soluble in water and organic solvents, almost insoluble in concentrated HNO3. The drug is analytical grade. contains no less than 99.8% AgNO3, parts - no less than 99.75%. Recrystallization. A chemically pure AgNO3 preparation is obtained by recrystallizing a conventional preparation from a weakly nitric acid solution and then drying the salt at 150°C in an oven to constant weight. Preparation of silver nitrate solutions Usually, solutions of approximately the required normality are prepared, and then their titer is determined using a sodium chloride solution. To prepare 0.1 n. a solution of 17 g of silver nitrate is dissolved in water and the solution is diluted with water to 1 liter. A solution is prepared from the recrystallized drug by precise weighing. Dissolve 16.9874 g of AgNOa in water, transfer to a 1-liter volumetric flask and dilute with water to the mark. The normality of the solution is exactly 0.1 N. and does not need verification. A solution of silver nitrate can also be prepared from pure metallic silver (fineness 999). To do this, dissolve 10.787 g of silver in 100 ml of diluted HNO3 (1:1), which does not contain hydrochloric acid. After dissolving the silver, the solution is boiled until nitrogen oxides are removed, cooled, transferred to a 1-liter volumetric flask and diluted with water to the mark. The solution is exactly 0.1 N in concentration. and does not need to install a title. It is not suitable for the determination of chlorides using the Mohr method, since its acidity with respect to nitric acid is approximately 0.5 N. Standardization of solutions of silver nitrate A solution of silver nitrate is standardized against a solution of sodium chloride x. hours, using a solution of potassium thiocyanate or by the gravimetric method. In the absence of sodium chloride x. h. it is obtained from a conventional reactive preparation. The following symbols are used in the chapter: M - molecular weight; A - atomic mass; E - equivalent; p - density; t - temperature.

Sodium chloride NaCl: Properties. White crystalline substance or fine crystalline powder; M=58.443; p=2.17; tmelt=801°C; boiling point=1439°C. Poorly soluble in concentrated HC1. The solubility of NaCl increases little with increasing temperature; at 25°C it

is 36.1 g, and at 100°C - 39.6 g. Slightly soluble in methanol (1.41 g in 100 ml at 20°C), even less soluble in ethanol (0.09 g at 17 °C). The drug of all qualifications contains at least 99.8% NaCl Recrystallization. The saturated hot salt solution is filtered, cooled with ice and the solution is saturated with hydrogen chloride gas. In this case, NaCl crystals fall out. A funnel is attached to the end of the gas supply tube so that the crystallizing mass does not clog the outlet of the tube. The crystals are sucked off on a Buchner funnel, washed several times with concentrated HC1, squeezed between sheets of filter paper, dried at 110 - 115 ° C, ground into powder in a mortar and calcined in a muffle furnace at 500 - 600 ° C to constant weight. Calcination can also be carried out on a gas burner by placing the crucible in the hole of an asbestos plate fixed in an inclined position in order to avoid combustion products of gases containing sulfur from entering the crucible. Recrystallized NaCl from a Buchner funnel can be placed in an evaporation dish, dried, then heated to a boil and poured into a completely clean and dry porcelain or ceramic plate, then broken into pieces and crushed in a porcelain mortar. The purified drug is stored in a bottle with a ground-in stopper for an indefinitely long time, since it is not hygroscopic. (Ordinary table salt is hygroscopic due to the fact that it contains an admixture of magnesium chloride.) If reagent x is available. hours, then before taking the sample it should be calcined at 500°C to constant weight. Preparation 0.1 n. sodium chloride solution. Convert 5.8443 g of sodium chloride x. hours in a volumetric flask, dissolve in water and dilute with water to 1 liter. The normality coefficient of the solution is found by dividing the actual mass of the sample by the theoretical one (5.8443). Standardization according to Mohr's method: Take 25.0 ml of 0.1 N. sodium chloride solution into a titration flask, add 25 ml of water and 0.5 ml of a 10% aqueous solution of potassium chromate K2CrO4. Titration is carried out in the presence of a “witness”. To prepare the “witness”, 25.0 ml of 0.1 N is also placed in another similar flask. sodium chloride solution, 25 ml of water, 0.5 ml of 10% K2CrO4 solution and add 2 - 3 ml of silver nitrate solution. A solution of sodium chloride is titrated with a solution of silver nitrate until a weak but quite noticeable red-brown color appears, which persists after vigorous shaking and differs from the color of the “witness”. Titration should not be carried out in direct sunlight, as the AgCl precipitate decomposes, becoming lilac. Titration under electric light, when the yellow color is difficult to see, does not give good results. Near the end point of titration, the AgCl precipitate coagulates, forming large flakes that settle to the bottom. The last drops of AgNO3 solution are added slowly, vigorously stirring the solution in order to titrate the adsorbed C1- ions.

Laboratory work No. 27
Ionometry. Determination of nitrates by ionometric method

Purpose of work: To master the ionometric method of analysis. Apply the method to determine the nitrate content in soil and plant samples.

Express method for determining nitrate nitrogen in soil

1. Essence of the method

The essence of the method is to extract nitrates with a 1% solution of potassium alum or 0.05% K2SO4 solution at a soil to solution ratio of 1:2.5 and subsequent determination of nitrates in the extract using
ion selective electrode. The method is used to determine nitrates in all soils, except saline ones, in which the mass fraction of chloride ion is 50 times or more greater than the mass fraction of nitrates.

2. Experimental part

Reagents, chemical glassware and equipment

- Universal ion meter EV-74;
- Ion-selective electrode for nitrates (EPM-1, EPM-11, EM-NO3-01). Before work, it is filled with a 0.1 M KNO3 solution (1.5 ml) and a 0.005 M KCl solution. The electrode is kept in a 0.1 M KNO3 solution for 24 hours. During non-working hours, the nitrate membrane electrode is stored in a 10-3 M KNO3 solution, and the reference electrode is stored in distilled water;
- Potassium alum Al2(SO4)3·K2SO4·24H2O (10 g/l);
- Standard solutions. 0.1 M solution of KNO3 (10.11 g of salt is dissolved and brought to 1 l with a 1% solution of potassium alum). From this solution, working standard solutions (0.01 M, 0.001 M, 0.0001 M) are prepared by diluting with an extraction solution and used to construct a calibration graph.

Sampling technique

Soil samples are analyzed in a state of natural moisture, but no more than 5 hours after their collection, or brought to an air-dry state by drying at 400C (samples can be stored in their natural state for no more than two days at 1-5 0C).

A soil sample in an air-dry state is taken for analysis from a box with a spatula or spoon, after first mixing the soil to the entire depth of the box. The sample is poured onto a flat surface, mixed thoroughly,
distributed in a layer of no more than 1 cm and selected from at least five points.

Performing an experiment

A sample of air-dry soil, sifted through a sieve with holes of 1-2 mm, or raw soil, sifted through a sieve with holes with a diameter of 5 mm, weighing 20 g, is placed in jars or conical flasks with a capacity of 100 cm3, 50 cm3 of a 1% solution of potassium alum is added or 0.005% potassium sulfate solution and stir for 3 minutes. In the resulting suspension, the activity of the nitrate ion is measured using an ion-selective electrode for nitrates. When determining nitrates in soil with natural moisture, a sample weighing 5-10 g is simultaneously collected to determine soil moisture.
Nitrate ion activity can be measured in pNO3 or measured in “mV”.
pNO3 = -log aNO3, (1)

where aNO3 is the activity of nitrate ion.

It should be remembered that the concepts of activity and ion concentration are not identical, although they are closely related: a = cγ (where a is the activity of the ion; c is the ion concentration; γ is the average activity coefficient). In infinitely dilute solutions, when the concentration tends to zero, γ = 1, then
a=c. Thus, we determine not the concentration of the ion, but its activity.
In practice, this point is usually neglected.
The ion-selective method is quite accurate and, thanks to the use of simple equipment and the speed of analysis, has become widespread in research.
The content of nitrate nitrogen in the soil is calculated using the formula:

N-NO3 (mg/kg) = 10-NO3·14(V/m)·103, (2)

where 14 is the atomic mass of nitrogen, g;
V – volume of extraction solution, cm3;
m – mass of soil sample, g;
103 – conversion factor in mg;
pNO3 is the negative logarithm of the concentration of nitrate ions.

Transformation of the formula made it possible to simplify the calculations. With the ratio soil and solution 1:2.5 content:

N-NO3 mg/kg soil = Antilog (4.54 – p NO3). (3)

Determination of nitrates in plants by ionometric method

1. Essence of the method

The method boils down to measuring the activity of nitrate ion in a salt suspension
1% solution of potassium alum at the ratio of sample volumes and
solution 1:4.

2. Experimental part

Ground samples weighing 12.5 g are placed in a 250 ml flask, pour
50 ml of 1% solution of potassium alum and shake for 30 minutes.
The activity of the nitrate ion in the resulting suspension is measured. The nitrogen content of nitrates (mg/kg) in the analyzed material is calculated using formula (2).
Transformation of the formula made it possible to simplify the calculations. With the ratio sample and solution 1:4 content:
N-NO3 mg/kg = Antilog (4.75 – p NO3) (4)

Test questions and assignments

1. What are the main types of ion selective electrodes? How are they structured, what characteristics do they have?
2. Basic techniques of ionometric analysis. Calibration graph method. Concentrated element method. Additive method.

3. Describe the main indicator of an ion-selective electrode – the selectivity coefficient. What kind of characteristic is response time?
4. Solid ion-selective electrodes. Fluoride and enzyme electrodes. What limitations does a fluoride electrode have in operation?
5. Liquid ion-selective electrodes. Their structure and application.

Laboratory work No. 28

Potentiometry. Determination of strong or weak acids and alkalis.

Goal of the work:

1. Check the correctness of the theoretical calculations for calculating the activity coefficient in the first approximation according to the Debye-Hückel theory by comparing the calculated and experimental values of f.
2. Determine the degree of dissociation of salicylic acid, compare the data obtained with those calculated using the Ostwald equation.

The content of the work:

1. Prepare a solution of a strong electrolyte (hydrochloric acid) and a weak electrolyte (salicylic acid).
2. Measuring the pH of a hydrochloric acid solution at various concentrations and calculating the activity coefficient.
3. Measuring the pH of a salicylic acid solution at various concentrations and calculating the degree of dissociation.

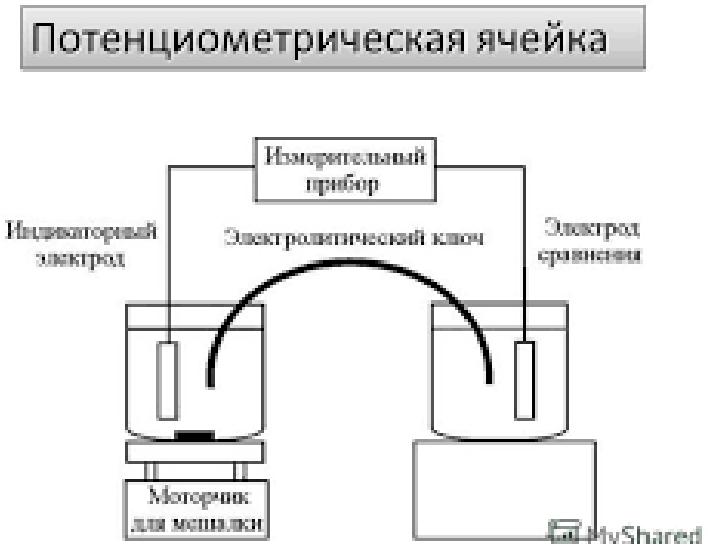
Potentiometric methods of analysis are based on the use of the dependence of the electrochemical potential of the indicator electrode on the activity (concentration) of the analyte in the analyzed solution. Ideally, this dependence is described by the Nernst equation:

Eme = Emeo ± lga(Men+), nFRT 3.2

where E is the measured EMF of the electrochemical circuit, mV;

a is the activity of the ion being determined.

The potentiometric cell consists of two electrodes: an indicator electrode and a reference electrode (Fig. 2)



Rice. 2 Diagram of a potentiometric cell

The potential of the reference electrode (standard) is maintained constant by establishing an equilibrium of a certain reaction on it and serves as a reference point. The potential of the indicator electrode depends on the activity of the detected ion in the analyzed solution.

Depending on the type of electrochemical reaction occurring on the indicator electrode, several types of electrodes can be distinguished:

Type of indicator electrode	**Electrochemical reaction determining the electrode potential**
1.Redox Pt | Ox, X (redox electrode) – an inert metal in combination with a redox system	XOx + mX + ne =yRed + Zz Mn+ + ne = M E = E0 + M n+ a nF RT ln
2. Electrode of the first kind	MA +ne = M + An- E = E0 + A n- a nF RT ln
3. Electrode of the second type - a redox reaction occurs on it, leading to the dissolution or precipitation of a sparingly soluble salt	Kij – selectivity coefficient, ai, aj, zi, zj – activities and charges of the detected and interfering ions

In the first three types of electrodes, the potential is determined by the process of electron transfer between ions in a solution with a metal:

1) Redox electrodes -electrodes made of inert material (for example, Pt, Au) serve as electron carriers from the reduced form to the oxidized one, and their potential is a function of the ratio of the activities of the oxidized and reduced forms of the analyte.

An example of a redox electrode used in pH measurements is the quinhydrone electrode. Quinhydrone is a poorly soluble molecular compound of quinone and hydroquinone - C6H4O2 · C6H4(OH)2. In solution, quinhydrone breaks down, forming a reversible redox system:

Quinone + 2e + 2H+ = Hydroquinone

The state of equilibrium between the oxidized and reduced forms depends on the concentration of hydrogen ions in the solution. A saturated solution of hydroquinone with a platinum electrode immersed in it is called a quinhydrone electrode.

2) Electrodes of the first kind- metals, which are a reduced form of a reversible redox system (Pb, Ag, Cu, etc.). When such an electrode is immersed in an electrolyte solution containing an ion of the same name as the metal of the electrode, a potential difference is created between the electrode and the solution, which depends on the activity of the corresponding metal ion. Gas electrodes (for example, hydrogen) also belong to the first type electrodes. These electrodes do not have wide practical significance.

3) Electrodes of the second kind– are metal electrodes coated with a thin layer of a sparingly soluble metal compound from which the electrode is made and placed in a solution of a salt containing the same anion as in the sparingly soluble salt on the metal surface (for example, AgCl/Ag, KCl). Electrodes of this type are sensitive to the corresponding anions present in the solution and the potential difference depends on the activity of these anions. They are widely used in practice and serve either as indicator electrodes for the determination of anions or as reference electrodes. A significant drawback of these electrodes is that they lose their functionality in the presence of oxidizing agents.

experimental part

Reagents: HCl solution – 0.1 M, salicylic (2-hydroxybenzoic acid), analytical grade, M (C6H4(OH)COOH) = 138.12 g/mol, Kdiss = 1.1·10-3

Cutlery, dishes, equipment: universal ion meter (pH meter), glass electrode - indicator, silver chloride electrode - reference electrode, measuring pipettes for 25 ml and 5 ml, beakers for 50-100 ml.

Part A. Determination of activity coefficient

strong electrolyte

Work order

According to the instructions of the teacher, working solutions with a volume of 25 ml with a concentration of 0.01 M and 0.001 M are prepared from a 0.1 M solution of hydrochloric acid by serial dilution.

Determine the pH values of three solutions, starting with the most dilute one. Between measurements, the electrodes are washed with distilled water, the pH is checked using distilled water, then the drops of water are carefully blotted with filter paper (DO NOT WIP). At the end of the work, the washed electrodes are left in distilled water (NOT IN AIR).

Write down the electrochemical circuit diagram.

Enter the results of determinations and calculations based on theoretical and experimental data into a table and draw conclusions.

Part B. Determination of the degree of dissociation of a weak electrolyte

Work order

Having received a centimolar solution of salicylic acid from the teacher, prepare 50 ml of a millimolar solution by diluting the original acid solution tenfold. Pour solutions with salicylic acid into cups to measure pH.

Measure the pH of two solutions, starting with the diluted one. Readings are taken on the upper pH scale in a narrow range. Between measurements, the electrodes are washed with distilled water, with well-washed electrodes the pH of distilled water should be between 5 and 6, then carefully blot the water drops with filter paper (DO NOT WIP). At the end of the work, the washed electrodes are left in distilled water (NOT IN AIR).
Write down the electrochemical circuit diagram, enter the calculations and experimental data into the table.

Table

Solution no.	**From solution**	**pH exp.**	**α exp.**	**α theoretical**

Questions to the topic:

1. Why does the redox potential change? What relationship is expressed by the Nernst equation? Explain the meaning of the quantities included in it.
2. What factors influence the direction of the redox reaction?
3. How does a galvanic cell work? What reactions occur during its operation? How does the emf of a galvanic cell occur?
4. How are the electrodes used in potentiometry classified?
5. Reference electrodes – silver chloride and calomel. Their devices, functions, operating principles, electrode reactions.
6. Classification of indicator electrodes. Their function and differences from reference electrodes.
7. Give examples of metal indicator electrodes of the 1st and 2nd kind. Explain the mechanism of their action.

LABORATORY WORK No. 29

Potentiometric titration.

Determination of iron in solution.

1) Titration of a mixture of 2 reducing agents (Sn^{2+} and Fe^{2+}) with a solution of $K_2Cr_2O_7$

The determination is based on the preliminary reduction of Fe^{3+} to Fe^{2+} with tin chloride $SnCl_2$ and subsequent titration of a mixture of two reducing agents (Sn^{2+} and Fe^{2+}) with a solution of $K_2Cr_2O_7$. In this case, the Sn^{2+} ion is titrated first, and then the Fe^{2+} ion:

3SnCl42- + Cr2O72- + 14H+ + 6C1->3SnCl62- + 2Cr3+ + 7H2O

6Fe2+ + Cr2O72- + 14H+>6Fe3+ + 2Cr3+ + 7H2O

The titration curve is characterized by two jumps: the first corresponds to the oxidation of Sn2+, and the second to the oxidation of Fe2+. The volume (V2-V1) corresponds to the volume of potassium dichromate consumed for the titration of iron.

Reagents:

Potassium dichromate K2Cr2O7, 0.1 M (1/6 K2Cr2O7) titrated solution. Tin chloride SnCl2, solution with a mass fraction of 5%. Hydrochloric acid HC1, diluted solution (1:1).

Dishes:

Volumetric flask (100 ml), pipette (10 ml), graduated cylinder (50 ml), burette (25 ml).

Equipment:

Installation for potentiometric titration, indicator electrode - platinum, reference electrode - silver chloride.

Completing of the work:

1. Preparation of titrant solution. Calculate the mass of a sample of K2Cr2O7 required to prepare 100 ml of 0.1 M (1/6 K2Cr2O7) potassium dichromate solution. The sample is weighed on an analytical balance, quantitatively transferred to a 100 ml volumetric flask, dissolved in a small volume of water and adjusted to the mark with water.

2. Analysis of the test solution. The solution to be analyzed is taken into a 100 ml volumetric flask, diluted to the mark with water, and mixed thoroughly. An aliquot of 10 ml of this solution is transferred to an electrochemical cell, 50 ml of a dilute solution (1:1) of HCl is added using a graduated cylinder and the solution is heated almost to boiling. A SnCl2 solution is added dropwise from a burette to the hot solution until completely discolored, and then another 1-2 drops of a SnCl2 solution.

The setup for potentiometric titration is prepared for operation. A platinum electrode is placed in a hot solution and the circuit is closed using a salt bridge filled with a saturated solution of KS1.

The burette is filled with a solution of K2Cr2O7, a magnetic stirrer is turned on, and the mixture to be analyzed is titrated, adding the titrant slowly drop by drop. After each infusion, the titrant volume and instrument readings are recorded. When tin (T) has been titrated (the first titration step), the K2Cr2O7 solution is poured in larger portions (0.2 ml each), and near

the second titration step the titrant is added dropwise again. Integral and differential titration curves are constructed and titrant volumes corresponding to the first (V1) and second (V2) equivalence points are found. Titration is repeated two to three times. Based on the data obtained, the mass of Fe3+ ions in solution is calculated.

2) Complexometric titration with EDTA solution

The iron (III) content can also be determined by complexometric titration with an EDTA solution (disodium salt of ethylenediaminetetraacetic acid - Na2H2Y). The iron complexonate formed during titration is characterized by a stability constant of FeY- = 1025.1.

Instruments and reagents:

Installation for potentiometric titration; platinum indicator electrode; silver chloride reference electrode; pipette with a capacity of 1 ml; CH3COOH solution, 50%; EDTA standard solution, 0.05 M; analyzed solution FeCl3, 0.03 M.

Completing of the work:

A solution of an iron (III) salt in a titration cell is diluted with 100 ml of distilled water, 1 ml of a 50% CH3COOH solution is added, electrodes are immersed in the solution and the EMF of the circuit is measured. Add EDTA from the burette in 1 ml portions, measuring the EMF of the circuit. The E - V curve is used to determine the equivalence point. Iron content is calculated using titrimetric analysis formulas.

Questions for self-control:

1. The essence of potentiometry.
2. Methods for titrimetric determination of iron ions in solution.
3. Complexometry and its features.
4. What is the difference between simple complexometry and potentiometric complexometry?
5. Where is potentiometric complexometry used?

Laboratory work No. 30
Conductometric determination of hydrochloric and acetic acids

Goal of the work:

1. Master the skills of conductometric titration
2. Learn to construct conductometric titration curves.

The content of the work:

1. Preparing the device for operation.
2. Standardization of NaOH solution to HCl.

3. Analysis of the test solution.

The determination is based on the sequential interaction with a solution of a strong base of acids that differ from each other in the degree of ionization. First of all, a strong acid interacts, which causes a sharp decrease in the electrical conductivity of the solution due to the binding of highly mobile hydrogen ions. When titrating a weak acid, the conductivity usually increases, since a well-dissociating salt is formed instead of a weak electrolyte. After the equivalence point, the conductivity increases sharply due to the appearance of hydroxyl ions with high mobility in the solution. The volume of alkali V1 corresponds to the titration of hydrochloric acid, the volume V2 corresponds to the titration of the sum of hydrochloric and acetic acids.

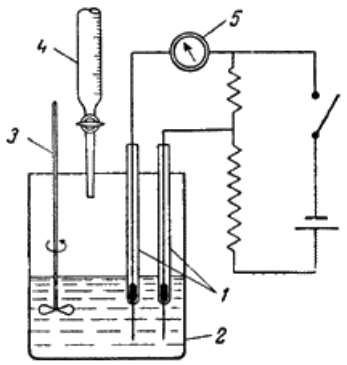
experimental part

Reagents:sodium hydroxide – 0.1 M solution, hydrochloric acid – 0.5 M titrated solution, nitric acid – diluted solution 1:1.

Cutlery, dishes, equipment:installation for conductometric titration complete with a conductometer, volumetric flasks (50 ml), pipettes (10 ml).

Preparing the device for operation

Assemble the installation for conductometric titration in accordance with the diagram shown in Fig. 8. Obtain an electrolytic cell from a teacher or laboratory assistant and wash the platinum electrodes. To do this, pour nitric acid (1:1) into the cell until the electrodes are completely immersed and keep them in this solution for 2-3 minutes. Then the acid is poured into the bottle in which it is stored, and the electrodes and cell are washed under running tap water, and then rinsed twice with distilled water. The device is connected to the network and prepared for operation. The burette is washed and filled with NaOH solution.



Rice. 8. Installation for conductometric titration

The cell consists of a glass and two platinum electrodes (1), immersed in the test solution (2). The electrodes are fixed in a lid, which has a hole for a burette (4) and a stirrer (3).

Standardization of NaOH solution to HCl

Place 10 ml of titrated HCl solution into a 50 ml volumetric flask, dilute to the mark with water and mix thoroughly. Take 10 ml of the resulting solution into the electrolytic cell, add distilled water until the electrodes are completely immersed, turn on the magnetic stirrer and begin titration, adding NaOH solution in 0.5 ml portions after

adding each portion of the titrant, measure the electrical conductivity in the solution. Titration is continued until a break is detected in the titration curve, after which readings are taken at another 4–5 points. Based on the data obtained, a titration curve is constructed in the coordinates instrument reading – titrant volume. Find the volume of titrant at the equivalence point and calculate the concentration of the NaOH solution.

Analysis of the test solution

The test solution containing a mixture of HCl and CH3COOH is placed in a 50 ml volumetric flask and diluted to the mark with water. Using a pipette, 10 ml of the resulting solution is taken into the electrolytic cell, water is added until the electrodes are completely immersed, and the stirrer is turned on. Titrate with NaOH solution, adding it in 0.5 ml portions and recording the electrical conductivity of the solution at each point. Titration is stopped after two breaks are detected in the titration curve - from a sharp drop in readings to a smooth, and then a sharp increase in values. A titration curve is constructed, from which V1 and V2 are found - the titrant volumes at the first and second equivalence points: V1 corresponds to the neutralization of HCl, and (V2 - V1) to the neutralization of CH3COOH. The mass in the solution taken for analysis is also calculated.

Questions to the topic:

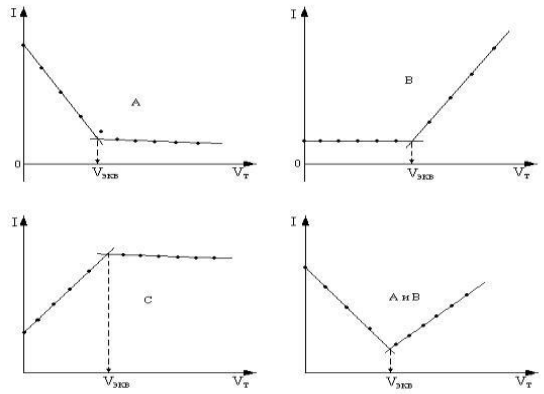
1. Measurement of what property is the basis of conductometric analysis? In what units is this property measured and using what devices?
2. What is electrical conductivity? What determines the electrical conductivity of conductors of the first and second kind?
3. What characterizes the specific and equivalent (molar) conductivity of solutions? How can you calculate electrical conductivity? What factors determine electrical conductivity?
4. How to practically determine electrical conductivity?
5. What is the difference between direct and indirect conductometry?
6. What is conductometric titration and how to practically carry it out? For what purposes can conductometric titration be used?
7. What is the shape of the titration curve of a mixture of strong and weak acids with an alkali?
8. How to find the volumes of alkali consumed for the titration of each component of a mixture of acids?

LABORATORY WORK No. 31

Amperometric analysis. Determination of the amount of potassium dichromate

Amperometric titration

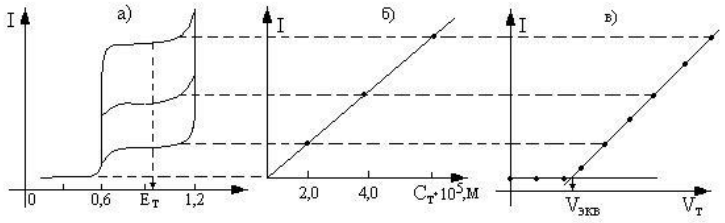
The analysis method is based on recording the dependence of the current on the volume of injected titrant. The most commonly used current titration is the analyte (A), the titrant (B), the reaction product (C) and the analyte and titrant (A and B) simultaneously (Fig. 4.4):



Rice. 4.4. Amperometric titration curves.

In this case, the electroactive component loses (or gains) the ability to discharge as a result of precipitation, complexation, or oxidation-reduction reactions occurring during titration.

A necessary condition for carrying out amperometric titration is the correct choice of the working electrode potential and maintaining its value constant during the titration. The choice of the titration potential Et is due to the need to use in quantitative analysis a linear function connecting the concentrations of the component being determined and its analytical signal (Fig. 4.5).



Rice. 4.5.Stages of amperometric determination (see work 10-E).

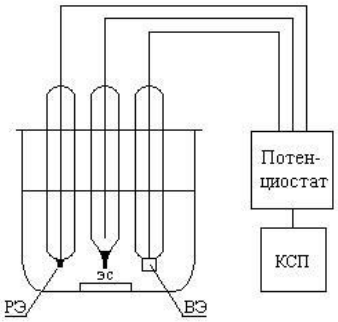
a) current-voltage curves of iron (II) solutions with concentration C1÷C3: (2.0 ÷6.0) 10 -5 mol/l; b) calibration dependence for iron (II) at ET;

c) amperometric current titration curve of iron (II) at ET.

Amperometric determination of potassium dichromate

This is a method for determining the content of oxidizing agents (K2Cr2O7 and KMnO4). It can be used for express analysis of solutions of oxidizing substances along with coulometric and potentiometric methods (works 16-E, 3-E). Based on the oxidation of the electroactive ligand of the ferrocyanide (II) complex during a redox reaction.

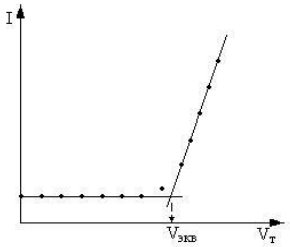
The determination is carried out using a three-electrode voltammetric sensor (Fig. 4.6):



Rice. 4.6. Three-electrode sensor.

fixing the dependence of the current in the RE – SE circuit on the volume of the added titrant (Fig. 4.7).

The determination is carried out by recording the dependence of the current in the RE-VE circuit (Fig. 4.6) on the volume of the added titrant (Fig. 4.7).



Rice. 4.7. Titration curve.

Determined substance **–potassium dichromate**

Titrant - solution**K4[Fe(CN)6].**

Background – 0.5 M Na2SO4.

The essence of the method.

Chemical reaction. In a strongly acidic environment, hexacyanoferrate (II) ions are oxidized by potassium dichromate to hexacyanoferrate (III) ions:

Cr2O72- + [Fe(CN)6]4- + 14 H+ → [Fe(CN)6]3- + 2Cr3+ +7H2O

The electrochemical reaction causes an increase in the recorded current after reaching the equivalence point due to the Faraday component caused by the oxidation of ferrocyanide (II) ions:

$$[Fe(CN)_6]^{4-} \rightarrow [Fe(CN)_6]^{3-} + \bar{e}$$

Provided the working electrode potential is correctly selected, the oxidation current of Fe (II) is directly proportional to its concentration in solution.

Reagents. 1. Supporting electrolyte solution (2MH_2SO_4).

2. Sample solution (in a 100 ml flask).
3. Titrant solution (0.03M$K_4[Fe(CN)_6]$).
4. Distilled water.

Method of determination.

1. After washing the cell with distilled water, add 10 ml of background into it using a cylinder and 10 ml of sample solution with a pipette.
2. Turn on the potentiostat. Set the titration potential.
3. After establishing the current, enter its value into the table.
4. Add 0.05 ml of titrant.
5. Alternate steps 3 and 4 sequentially.
6. Titration is completed after obtaining 4-5 experimental points in the second section of the curve (after the equivalence point).
7. Reproduce the resulting curve on graph paper using the two tangent method and find the equivalence point.
8. Calculate the potassium dichromate content:

$$m = \frac{C_T \cdot V_{T_{экв.}} \cdot M_{экв.}}{1000} \cdot \frac{V_K}{V_П}$$

- molar mass equivalent $K_2Cr_2O_7$

где $M_{экв.} = \frac{M}{z}$

Laboratory work No. 32

Polarographic method for analyzing a mixture of metals

Polarographic method of analysisis one of the electrochemical methods. It is based on deciphering current-voltage curves, called polarograms, which are obtained by electrolysis of the solution under study in a special electropolarographic cell.

In this cell, mercury flowing from a thin capillary - the cathode with a dripping period of 2-7 s and a diameter of approximately 1 mm - is used as one electrode, called the working one. The second electrode, the anode, is the reference electrode. It is a layer of mercury with a large surface at the bottom of the vessel.

A gradually increasing voltage is applied to the electrodes from an external current source if there are substances in the analyzed solution that can be oxidized or reduced; the current increases after reaching a certain value of the applied voltage, called the half-wave potential. This dependence of the current on the applied voltage is expressed by a polarographic wave and is recorded on the polarograph's recorder.

To quantify a substance, a directly proportional relationship is used between the strength of the limiting current, the expressed height of the polarographic wave, and the concentration of the substance in the solution. To obtain strictly quantitative patterns, an excess of foreign electrolyte—background—is introduced into the analyzed solution.

Lithium salts and other diluted salts, acids, and alkalis are used as a background. The presence of oxygen in the analyzed solution interferes with the analysis, so it is removed by passing an inert gas through the solution.

For polarography, polarographs of various brands are used. Almost all metal cations, many anions, inorganic and organic substances capable of electrochemical oxidation or reduction can be polarographed.

The high sensitivity of the method is combined with sufficient accuracy. The speed of analysis, the objectivity of the results obtained, combined with good reproducibility, distinguishes the polarographic method from other physicochemical research methods.

This method has found wide application in sanitary-chemical analysis for the study of food products for the content of heavy metal salts, as well as drinking water, surface water and wastewater for the content of chromium, lead, zinc, and copper salts. Lead, chromium, manganese, zinc, cadmium, copper, formaldehyde and other toxic substances are determined in the air using the polarographic method.

Voltammetric polarograph

“Determination of Cu2+, Cd2+, Ni2+, Zn2+ ions in their joint presence”

Before performing work you must:

-study the theory of the method in accordance with the work program;

-understand the experimental methodology (preparation of solutions for polarography, development device And acquisition some operator skills);

- pass the interview WITHteacher And get permission completing of the work.

The polarographic method makes it possible to determine several substances in a mixture without separation, if the release potentials of the substances being determined do not coincide.

The proximity of the values of these potentials is not always an obstacle to polarography without preliminary separation of substances: it is possible to select a background electrolyte that forms complexes with different stability with the ions being determined. The stronger the complex, the more the release potential shifts towards negative values. For Cu2+, Cd2+, Ni2+ and Zn2+ ions it is most advantageous as
background use a mixture of NH4OH with ammonium salts. Half-wave potentials
tetraammine complexes are respectively equal to -0.56; -0.81; -1.09: -1.36 IN
relative to the potential of the saturated calomel electrode, which
taken as polarographic zero.

$$a = \frac{0.059tg}{z}$$

An aliquot of the test solution is placed in a volumetric flask
with a capacity of 50 ml, add 25 ml of ammonia buffer mixture, 0.5 g dry
Na2SO3, 20 drops of 0.5% solution gelatin And top up before tags
distilled water and, after standing for 5 minutes, polarograph (according to
instructions for the polarograph). Standard solutions are prepared similarly. For
constructing a calibration graph, it is enough to prepare three solutio
different concentrations containing ions present in the test substance.
For example, solutions containing by 1; 1.5; 2 ml workers standard
solutions of all ions.

The analysis of the test solution is repeated using the method of additives and standard. The polarograms are processed, E 1/2 is determined, and the wave height h is measured. The value of E 1/2 determines which wave of the polarogram corresponds to each ion. Then, using these methods, the amount of each ion in the analyzed sample is determined.

Problematic issues

1.What is the essence of the polarographic method?
2.What does a polarogram show?
3. How to prove that the NH4OH + NH4Cl mixture is more favorable as a background,
than KCl, HC1, H2SO4, Na2H2Y, NH4Cl, NH4OH, CH3COOH?
4. How to determine the number of electrons participating in the electrode process, having a polarogram in hand?
5. How to experimentally determine the dependence of lg on the height of the mercury column? What is she like? What does deviation from addiction indicate?
6. Questions 1,2,5 contain factors influencing the results of the analysis? What is the impact?
7. How can I use the Ilkovich, Levich equation to calculate the concentration of a depolarizer?
8. Describe the operation of a self-recording polarograph.
9. Indicate the main directions of development of polarography and characterize two of them.

LABORATORY WORK No. 33

PHOTOMETRIC DETERMINATION OF IRON IONS WITH SULPHOSALICYLIC ACID

Essence of the method:

The method is based on the formation of a colored complex compound of divalent iron ions with 1,10-phenanthroline. Ferric iron is preliminarily reduced with ascorbic acid.

Equipment, reagents and solutions

Photoelectric calorimeter.

Hydrochloric acid diluted 1:1 and 0.1 mol/dm .

Ascorbic acid, solution concentration 10 g/dm .

Sodium acetate according to GOST 199, solution concentration 70 g/dm .

1,10-phenanthroline (o-phenanthroline), solution concentration 2.5 g/dm at 0.1 mol/dm hydrochloric acid solution.

Iron oxide.

Standard iron solution: 1.4298 g of iron oxide is placed in a 250 ml conical flask. , add 100 cm hydrochloric acid solution (1:1) and heated in a water bath until completely dissolved. Then the solution is cooled and transferred into a 1000 cm3 volumetric flask. , add water to the mark and mix. Standard solution with iron mass concentration 1 mg/cm (solution A).

Iron calibration standard solution: pipet 10 cm standard solution A into a 1000 mL volumetric flask , add water to the mark and mix. Calibration standard solution with mass concentration of iron 0.01 mg/cm (solution B).

Preparing for analysis

In 100 cm3 volumetric flasks measured with burette 0; 2; 4; 8; 10; 15; 20 and 25 cm calibration standard solution B, which corresponds to 0; 0.02; 0.04; 0.08; 0.10; 0.15; 0.20 and 0.25 mg iron. Add water to a volume of 25 cm , add 2 cm hydrochloric acid solution (1:1), 2 cm each ascorbic acid solution, 5 cm each o-phenanthroline solution and 20 cm sodium acetate solution. Add water to the mark and mix. After 30 minutes, the optical density of the solutions is measured on a photoelectric calorimeter, using a light filter with a light transmission

range of 450-500 nm, in a cuvette with a thickness of the calorimetered layer of 10 mm.

The reference solution is a solution that does not contain iron.

Carrying out analysis

A sample of graphite weighing 1 g is placed in a glass with a capacity of 100-150 cm, pour 25 cm hydrochloric acid solution (1:1), cover with a watch glass or a glass or porcelain lid covered with glaze, and boil for 20 minutes. Then dilute with water to 50-60 cm and filter through a tight filter into a 250 ml volumetric flask . The residue on the filter is washed 4-6 times with hot water acidified with hydrochloric acid (1:100). The solution is cooled, water is added to the mark and mixed (stock solution).

From the stock solution into a 100 cm3 volumetric flask an aliquot is selected depending on the mass fraction of iron and added with a control solution solution to a volume of 20 cm3 in accordance with Table 1.

Table 1

Mass fraction of iron, %	Volume of aliquot part, cm	
	Analyzed solution	Control solution
Up to 0.3 incl. St. 0.3" 1.0" "1.0" 2.5"	20 5 2	- 15 18

Add 2 cm ascorbic acid solution, 5 cm o-phenanthroline solution, 20 cm sodium acetate solution, add water to the mark and mix.

The optical density of the resulting solution is measured.

The reference solution is the control experiment solution.

Based on the optical density value, the mass of iron in milligrams is determined from the calibration graph.

Processing the results

Mass fraction of iron (X_{Fe}) as a percentage calculated by the formula

$$X_{Fe} = \frac{m_1 \cdot V \cdot 100}{V_1 \cdot m \cdot 1000},$$

Mass fraction of iron (III) oxide $(X_{Fe_2O_3})$ as a percentage calculated by the formula

$$X_{Fe_2O_3} = 1{,}43 \cdot X_{Fe},$$

where 1.43 is the conversion factor of the mass fraction of iron to the mass fraction of iron (III) oxide;

- mass fraction of iron in graphite, %.

2.5.3. Allowable discrepancies between the results of parallel determinations should not exceed the values indicated in Table 2.

table 2

Mass fraction of iron (iron oxide), %	Allowable discrepancy, %
Up to 0.10 incl.	0.005
St. 0.10 " 0.50 "	0.02
" 0.50 " 1.0 "	0.05
"1.0" 2.5"	0.1
" 2.5	0.2

PHOTOMETRIC METHOD FOR DETERMINING IRON WITH SULPHOSALICYLIC ACID

Essence of the method

The method is based on the formation of a colored iron trisulfosalicylate complex in an ammonia environment.

Equipment, reagents and solutions

Sulfosalicylic acid, solution concentration 100 g/dm .

Hydrochloric acid diluted 1:1.

Ammonia aqueous.

Calibration standard solution of iron (solution B), prepared according to clause 2.2.

Preparing for analysis

Construction of a calibration graph

In 100 cm3 volumetric flasks measured with burette 0; 1; 2; 5; 10; 20; thirty; 40 and 50 cm calibration standard solution B, which corresponds to 0; 0.01; 0.02; 0.05; 0.10; 0.20; 0.30; 0.40 and 0.50 mg iron.

10 cm is poured into each flask solution of sulfosalicylic acid, ammonia solution until a stable yellow color of the solution appears and 5 cm in excess. The solution is cooled, added to the mark with water and mixed.

The optical density of solutions is measured on a photoelectric calorimeter using a light filter with a light transmission range of 400-450 nm in a cuvette with a thickness of the calorimetered layer of 10-30 mm.

The reference solution is a solution that does not contain iron.

Carrying out analysis

A sample of graphite weighing 1-3 g is placed in a glass with a capacity of 100-150 cm, 25-50 cm is added hydrochloric acid solution (1:1), cover with a watch glass or a glass or porcelain lid covered with glaze, and boil for 20 minutes. Then dilute with water to 50-100 cm and filtered through a thick filter into a 250 cm3 volumetric flask. The residue on the filter is washed 4-6 times with hot water acidified with hydrochloric acid (1:100). The solution is cooled, water is added to the mark and mixed (stock solution).

An aliquot of 2-20 cm is taken from the main solution into a 100 cm3 volumetric flask , add 10 cm solution of sulfosalicylic acid, ammonia solution until a stable yellow color of the solution appears and 5 cm in excess.

Next, measure the optical density of the solution, as indicated in paragraph 3.3.

The reference solution is the control experiment solution.

The mass of iron in milligrams is determined from the optical density using a calibration graph.

X.

Processing the results

3.5.1. Mass fraction of iron (X_{Fe}) and iron oxide $(X_{Fe_2O_3})$ percentage is calculated using the formulas given in clauses 2.5.1 and 2.5.2.

3.5.2. Allowable differences between the results of parallel determinations should not exceed the values specified in Table 2.

Laboratory work No. 35

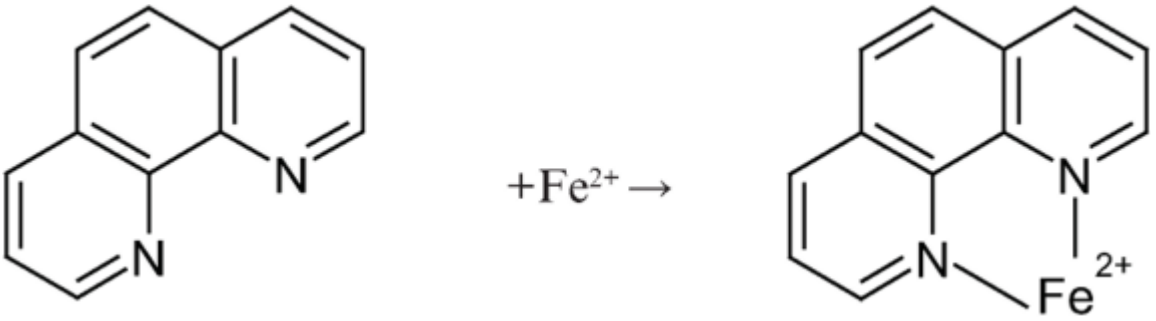
Spectrophotometric determination of iron (II) ions

Target. Acquire skills in determining iron ions using the spectrophotometric method.

The essence of the work.

To determine iron ions, it is transferred into a Fe(II) complex with 1,10-phenanthroline [Fe(CpH8N 2)]3+ and the optical density of its solution is measured using a spectrophotometer. The maximum light absorption is found from the absorption spectrum. Hydroxylamine (in the form of hydrochloride to increase solubility) is added to reduce Fe3+ to Fe2+ and prevent its reverse oxidation.

4Fe3+ + 2NH2OH -> 4Fe2+ + N2O + 4H+ + H2O.



Equipment and reagents:

Spectrophotometer with a set of cuvettes, volumetric flasks with a capacity of 250, 25 and 100 ml, pipettes for 1.00, 2.00, 5.00, 10.00 and 25.00 ml, distilled water, filter paper.

Standard solution of iron ions (//). To prepare a standard iron solution, weigh 0.0176 g of iron (II)-ammonium sulfate Fe(NH4)?(SO4)., • 6H?O, quantitatively transfer the portion into a 250 ml volumetric flask and dissolve in a sufficient amount of water. Then add 0.7 ml of concentrated sulfuric acid, dilute to the mark with distilled water and mix thoroughly. The resulting solution contains 10.0 mg/l iron (II) ions. If the mass of the sample differs from the specified one, calculate the corresponding concentration value.

1,10-phenanthroline solution. Dissolve 25 mg of 1,10-phenanthroline monohydrate in 25 ml of water. The solution is stored in a plastic container.

Hydroxylamine hydrochloride solution. Dissolve 10 g of the substance in 100 ml of water.

Sodium acetate solution. Dissolve 10 g of sodium acetate in 100 ml of water.

To reduce the time of the experiment, these solutions can be prepared in advance.

Conducting an experiment. IN100 ml volumetric flasks are pipetted with 1.00, 2.00, 5.00, 10.00 and 25.00 ml of a standard solution of iron (II) ions. 50 ml of water is placed in another identical flask to prepare a comparison solution (control solution). The 100 ml volumetric flask also contains the solution to be analyzed. Add 1.0 ml of hydroxylamine hydrochloride solution and 5.0 ml of 1,10-phenanthroline solution to each flask (including the flask with the analyzed solution). To establish the required pH value, add 8.0 ml of sodium acetate solution to each flask; in this case, a red color appears in the complex of iron (II) ions with 1,10-phenanthroline. (The complex is formed in the pH range = 2-9.) By adding sodium acetate, the acid present in the solution is neutralized and the pH value is adjusted to the desired range. After adding all the reagents, leave the solutions for 15-20 minutes for the color to fully develop (once developed, the color is stable for several hours). Turn on the spectrophotometer to warm up. Dilute each solution exactly to a volume of 100 ml. After dilution, the iron concentrations in standard solutions will be 0.1, 0.2, 0.5, 1.0 and 2.5 mg/l, respectively.

A solution with a concentration of 2.5 mg/l is transferred to a cuvette, having previously rinsed it with the same solution. If necessary, remove drops of solution from the outer surface of the cuvette using filter paper. Record the absorption spectrum in the range of 400-700 nm, using the control solution as a reference solution. The dependence of optical density on wavelength is plotted. Knowing the values of the molar concentration of iron (II) ions in solution and the length of the cuvette, it is possible to calculate the molar absorption coefficient of the complex of iron (II) ions with phenanthroline at the wavelength of maximum absorption.

Construct a calibration graph of the dependence of optical density on the concentration of standard solutions (mg/l) by measuring the optical densities of all standard solutions at the absorption maximum. Under the same conditions, the optical density of the analyzed solution is measured. From this graph, the concentration of iron (II) ions in it is calculated from the optical density of the analyzed solution. The protocol provides the total content of iron (II) ions in the sample (μg), the molar absorption coefficient of the complex and the spectrum of the complex of iron (II) ions with phenanthroline. After completion of work, the spectrophotometer is turned off, the cuvettes are removed and thoroughly washed with distilled water.

Photometric titration with indicator

Photometric titration with an indicator is used when the titrated substance, titrant and reaction product do not absorb light (colorless). Complexation reactions are most often used.

Substances that do not absorb light of a given wavelength (ελ(Ind) = 0), but form a compound with at least one of the substances of the titrated system that absorbs light of a given wavelength (ελ (AInd)>0, or ελ (BInd)>0 or ελ (AVInd)>0).

Laboratory work No. 36

Quantitative determination of Fe3+ by photometric method

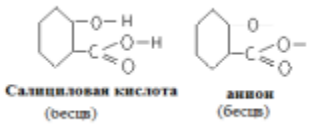
titration with salicylic acid indicator

The definition is based on the fact that salicylic acid and Fe3+ form a complex ion – iron salicylate, intensely colored with an absorption maximum at λ = 525 nm. This complex in an acidic environment (pH = 2.4) is less stable than the colorless complex with Na2-EDTA, therefore it is possible to carry out a quantitative determination of Fe3+ by photometrically titrating this ion and its salicylate in an acidic environment with a working solution of Na2-EDTA until complete discoloration is observed at the equivalence point.

Schematically, the interaction of the ion being determined with the indicator can be represented as follows:

Fe3+ + H2Sal [FeSal]+ + 2H+

In this scheme, the symbol Sal 2- denotes the salicylic acid anion



The complex ion [FeSal]+ has a purple color in an acidic environment (pH=2.4).

When titrating [FeSal]+ with a working solution of Na2-EDTA, destruction of [FeSal]+ as a less stable complex occurs and the formation of a colorless but more durable complex of iron (III) with Na2-EDTA, which can be represented by the diagram:

[FeSal]+ + [H2Tr]2- [FeTr]+ + H2Sal

Violet bestsev bestsev

1 Task. Determine the amount of substance and mass of Fe3+ in the analyzed solution by photometric titration.

2 Equipment, glassware and reagents:

1) device for photometric titration;

2. 50.0 ml volumetric flask;
3. microburette with a volume of 2.0 ml;
4. pipette with a volume of 1.0 or 2.0 ml;

5) working titrated solution of Trilon B, C(Na2-EDTA) = 0.01 mol/l;

6) the analyzed solution Fe3+ - iron (III) salicylate [FeSAl]+.

3 Execution of work:

1) prepare the device for operation according to the instructions for the device;

2) prepare the solution to be analyzed. To do this, place 1.0 ml of iron salicylate solution in a 50.0 ml volumetric flask and fill to the mark with distilled water, mix;

3) transfer the entire volume of the solution from the volumetric flask to the cuvette of the device with a magnetic stirrer at the bottom. The outer surface of the cuvette must be dry;

4) fill the microburette with the Na2-EDTA working solution and direct the burette nose into the cuvette with the solution. Turn on the stirrer;

2. titrate the [FeSal]+ solution with a Na2 - EDTA solution, adding 0.1 ml each and keeping a record;

Titrant volume, ml	0.0	0.1	0.2	0.3	etc.
Instrument readings					

6) complete the titration after receiving 5-6 identical instrument readings;

7) repeat the titration according to paragraphs 2-6 again;

8) based on the results of two titrations, construct two titration curves in the coordinates “instrument readings - V (Na2-EDTA)” and determine from the equivalence points two volumes of the Na2-EDTA working solution spent on interaction with 1.0 ml of [FeSal]+ solution, calculate average;

9) to solve the analytical problem, obtain from the teacher an unknown volume of [FeSal]+ solution into a clean volumetric flask with a volume of 50.0 ml and perform the work according to pp. 2-6;

10) based on the titration results, construct a titration curve and determine the volume of the Na2 - EDTA working solution spent on interaction with an unknown volume of [FeSal]+;

11. comparing the results of steps 8 and 10, find the volume of the control solution, check its correctness and calculate the absolute and relative errors of determination;

12) from the known concentration of the Na2–EDTA working solution (C(Na2-EDTA) = 0.01 mol/l), calculate the mass and amount of Fe3+ substance in the control solution.

Questions to the topic:

1. The device of the KFK-2 photocolorimeter. Absorption filters, their features and choice for analysis.
2. Basic concepts of the titrimetric method of analysis: titration, titration curve, T.E., end point of titration (T.T.T.), calculations in titrimetry.
3. Complexometric method of analysis, standard solutions, metal indicators.
4. Advantages and scope of photometric titration.
5. Laws of light absorption.
6. Methodology for performing laboratory work.

1.3 Practical work

Practical work No. 1
Processing and metrological assessment of the values of random and gross errors in the results of titrimetric analysis using mathematical statistics methods

After sampling and preparation of the sample, the stage of chemical analysis begins, at which the component is detected or its quantity is determined. For this purpose, the analytical signal is measured. In some cases, it is possible to directly determine its content. For example, with the gravimetric method, the mass of the component being determined, for example, moisture or a chemical element, is sometimes directly measured. In most methods, the analytical signal is the average of measurements of a physical quantity that is functionally related to the content of the component being determined. This can be current strength, electromotive force of the system, optical density, radiation intensity, etc.

If it is necessary to detect any componentusually the appearance of an analytical signal is recorded - the appearance of a precipitate, color, line in the spectrum - which must be reliably recorded. When determining the amount of a component, the value of the analytical signal is measured: sediment mass, current strength, spectrum line intensity, etc. Then the component content is calculated using the functional relationship “analytical signal - content” (y = f(c)), which is established by the calculated or empirically and can be presented in the form of a formula, table or graph. The content can be expressed as the absolute amount of the component being determined in moles, in

units of mass, or through the corresponding concentrations.

When measuring an analytical signal, take into account the presence of a useful analytical signal, which is a function of the content of the component being determined, and an analytical background signal caused by impurities of the component being determined and interfering components in solutions, solvents and the sample matrix, as well as noise arising in measuring instruments, amplifiers and other equipment. Typically, the analytical background signal is taken into account when conducting a control (blank) experiment, when a sample that does not contain the component being determined is passed through all stages of chemical analysis. The useful signal in this case will be an analytical signal equal to the difference between the measured analytical signal and the analytical background signal.

Based on the existing relationship between the analytical signal and the content, the concentration of the component being determined is determined using the methods of a calibration curve, standards or additives. The most common method is the calibration graph. In this case, a graph is constructed in the coordinates “analytical signal – component content” using comparison samples with different and precisely known contents of the component being determined. Then, having measured the value of the analytical signal (y) in the analyzed sample, the content of the determined component (c) is found according to the calibration graph (Figure 2.1).

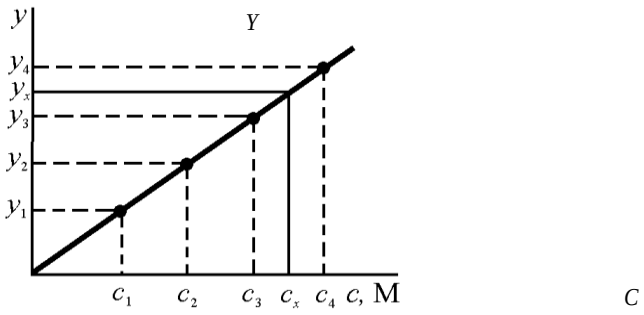


Figure 2.1 –Calibration graph method

Most often, straight-line calibration graphs are used, constructed for a certain range of determined contents.

Using the standard method, the analytical signal is measured in a comparison sample (reference sample) with a known component content and in the analyzed sample: uet = Scet and yx = Scx, where S is the proportionality coefficient.

If the value of S determined under identical conditions is known in advance, then the calculation can be carried out using the formula

$$c_x = \frac{y_x}{S}. \qquad (2.1)$$

Usually the ratio is used

$$\frac{y_{эт}}{y_x} = \frac{c_{эт}}{c_x}, \qquad (2.2)$$

where

$$c_x = \frac{y_x c_{эт}}{y_{эт}}. \qquad (2.3)$$

In cases where, when determining small quantities of a component, it is necessary to take into account the influence of the sample matrix on the value of the analytical signal, the additive method (calculated and graphical) is often used.

When determining the content by calculation method, two aliquots of the solution of the analyzed sample are taken and an additive of the determined component of known content is added to one of them. In both samples, the analytical signal is measured (yx and yx + ext). The unknown concentration of the component being determined is calculated using the following formula:

$$c_x = \frac{y_x V_{доб} c_{доб}}{y_{x+доб} V_{доб} + (y_{x+доб} - y_x) V}, \qquad (2.4)$$

where V add and c add are the volume and concentration of the added solution of the component being determined;

V– aliquot of the analyzed sample.

When determining the content of a component by graphical method, n aliquots of the analyzed sample are taken (1, 2, 3, ..., n). Known increasing amounts of the analyte are added to aliquots. In all aliquots, the analytical signal is measured and a graph is plotted in the coordinates “analytical signal - content of the component being determined.” Extrapolation of the resulting straight line to the intersection with the x-axis gives a segment located to the left of the conventional coordinate zero, the value of which on the selected scale and units of measurement corresponds to the desired content (cx) of the component being determined (Figure 2.2).

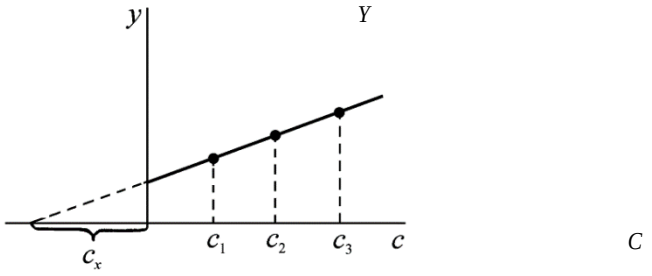


Figure 2.2 –**Additive Method**

The standard method and the addition method are applicable for the linear calibration function. The calibration graph method allows the use of both linear and nonlinear “analytical signal – content” functions. In the latter case, a larger number of experimental data is required, and the result of determining the component content is, as a rule, less accurate. In all the considered methods, comparison samples (standards) with precisely determined component content are used.

Methods of analysis that use reference samples are so-called relative methods of chemical analysis. There are few absolute (standard-free) methods in analytical studies (for example, gravimetry methods, direct coulometry, some variants of radiochemical

methods).

The most reliable results are obtained when standard samples are used as comparison samples - specially prepared materials, the composition and properties of which have been reliably established and officially certified by special state metrological institutions.

When conducting chemical analysis, they usually do not limit themselves to a single determination, but carry out several parallel determinations (usually 3–5) for the same sample under the same conditions. The average result of parallel determinations is called the result of analysis and is denoted by c or x. The deviation of the analysis result from the true content of the determined component (μ) is called error, or determination error. Along with detecting or determining the content of a component, it is important to assess the reliability of the results obtained and measurement errors.

2.2. Panalysis errors. Presentation of analysis results

There are two main metrological characteristics by which the results of the analysis are judged:

- reproducibility of determination results;
- correctness, i.e., compliance of the obtained result with the content of the component being determined in the sample.

Metrological support for quantitative analysis is based on the methods of mathematical statistics; the following general terms are used:

- Variable (x), or random value, is a measured or calculated numerical value or characteristic. The corresponding numerical value can be used for statistical processing. A variable quantity, for example, can be a measured quantity or an outcome.
- True value (true value; μ, τ) is a value that characterizes a certain parameter, uniquely defined under the conditions existing at the time when this parameter is being considered. This is an ideal value that can only be achieved when all sources of measurement error are eliminated and the entire population is selected.
- Reproducibility (precision, reproducibility) is the degree of closeness between independent measurement results obtained using an experimental technique under specified conditions. The smaller the random experimental error affecting the result, the more accurate this technique is. A measure of reproducibility or non-reproducibility is the absolute (S) or relative (Sr) standard deviation, calculated from the results of several parallel observations. Based on the International Vocabulary of Basic and General Terms in Metrology. ISO, 1993, the term is often used in the sense of “correctness.” To avoid confusion in the use of terms, it should be clear that precision refers only to variance, and not to deviation from the true (in the traditional sense) value.
- Repeatability is the degree of consistency of independent results obtained using the same method or identical analyzed material under the same conditions (the same performer, the same instrument, the same laboratory and small intervals between measurements). The measure of convergence is the standard deviation, used with a

qualifying term, i.e., standard deviation of convergence (repeata-bility standard deviation).

•Accuracy and precision. Correctness is the degree of closeness of a measurement result to the true or conditionally true (actual) value of the measured quantity or, in the absence of a standard of the measured quantity, the degree of closeness of the average value obtained on the basis of a large series of measurement results (or test results) to the accepted reference value. The indicator of correctness is usually the value of systematic error.

In turn, precision is the degree of proximity to each otherindependent measurement results obtained under specific specified conditions. This characteristic depends only on random factors and is not related to the true or conditionally true value of the measured value. A measure of precision is usually calculated as the standard (mean square) deviation of measurements taken under specified conditions. The quantitative values of precision measures depend significantly on the given conditions. Extreme indicators of precision - repeatability, convergence and reproducibility - are regulated in most state standards as methods.

•Student's t-distribution is a continuous one-dimensional distribution with one parameter - the number of degrees of freedom. The shape of the Student distribution is similar to the shape of the normal distribution (the greater the number of degrees of freedom, the closer the distribution is to normal). The difference is that the tails of the Student distribution tend to zero more slowly than the tails of the normal distribution. Typically, the Student distribution appears in problems related to estimating the mathematical expectation of normally distributed random variables.

Let x1, ..., xn be independent random variables, normally distributed with mathematical expectation (μ) and variance (σ2). Then we can obtain the following estimates for the parameters μ and σ2:

$$\tilde{\mu} = \frac{1}{n}(x_1 + \ldots + x_n); \qquad (2.5)$$

$$\tilde{\sigma} = \frac{1}{n}\sum_{i=1}^{x}(x_i - \tilde{\mu})^2. \qquad (2.6)$$

In this case, the estimate of the mathematical expectation is not exactly equal to μ, but only fluctuates around this value. The difference between the true mathematical expectation and the one calculated based on the sample, divided by the scaling factor

$$T = \frac{\tilde{\mu} - \mu}{\sigma : \sqrt{n}}, \qquad (2.7)$$

has a distribution called the Student distribution with n degrees of freedom.

•Random value, random variable (random value, random variable) is any observable quantity that changes when the general set of conditions in which it occurs is repeated. Depending on the case, it takes on certain values with certain probabilities. Thus, its values form a set of elementary random events. The probability distribution of random variables is its most important characteristic. Random variables can be discrete or

continuous, depending on what set of events (discrete or continuous) their values "run through."

*Normalized random variable*is the ratio of a given random variable to its square deviation.

•The normal distribution (Gaussian distribution) is used to assess the reliability of products that are affected by a number of random factors, each of which has a slight effect on the resulting effect (there are no dominant factors). It is known that the sum of a sufficiently large number of independent (or weakly dependent) random variables, subject to any distribution laws (subject to some non-rigid restrictions), approximately obeys the normal law, and this is true the more accurately the greater the number of random variables is summed. The main constraint imposed on the summable random variables is that they all uniformly play a relatively small role in the total. If this condition is not met and, for example, one of the random variables turns out to be sharply dominant in its influence on the sum over all others, then the distribution law of this prevailing random variable will impose its influence on the sum and determine its main features of the distribution law.

Classification of errors. Errors are classified according to the method of expression and the nature of the reasons causing the errors.

1. ByAccording to the method of expression (calculation), errors are divided into absolute and relative.

Result error(measurements, determinations, etc.) (error of result; e) – deviation of the result (measurements, determinations, etc.) from the true value (μ) of the measured quantity:

$$e = \overline{X} - \mu. \qquad (2.8)$$

If necessary, then calculate the errors of single determinations (e1 = X1 –μ).

Errors can be positive or negative depending on whether the analysis overestimates or underestimates the error.

The measurement error, expressed in units of the measured value, is called the absolute measurement error.

Relative error (relative error, er) is the error divided by the true value:

$$e_r = \frac{e}{\mu} = \frac{\left|\overline{X} - \mu\right|}{\mu}. \qquad (2.9)$$

Relative error in percentage(percentage relative error, er(%)) is obtained by multiplying the relative error by 100:

$$e_r(\%) = \frac{e}{\mu} = \frac{\left|\overline{X} - \mu\right|}{\mu} \cdot 100. \qquad (2.10)$$

2. Based on the nature of the reasons causing errors, systematic, random and gross errors (misses) are distinguished.

Random errors– these are measurement errors that change randomly during repeated measurements of the same quantity, carried out with the same care. The reasons for the

occurrence of random errors are unknown. Random errors determine the reproducibility of the analysis method and make the analysis result inaccurate. They can change the measurement result in both directions, increasing or decreasing it. Random errors cannot be excluded from measurement results, but with a certain number of repeated measurements they can be taken into account if the numerical characteristics of the distribution law of random measurement errors are known. These numerical characteristics establish a relationship between the true value of a quantity and the quantity values obtained from measurements. This kind of connection determines the probability that the true value of a quantity is within a certain interval of values of this quantity.

Gross errors (misses)are called measurement (determination) errors that significantly exceed those expected under given conditions. They are usually caused by the negligence or incompetence of the experimenter.

Systematic error– component of the error of the measurement (determination) result, which remains constant or changes naturally during repeated measurements (determinations) of the same quantity. A systematic error is caused by a permanent cause. The presence and magnitude of systematic errors characterize the correctness of the analysis technique and its result. Systematic errors make the analysis itself incorrect.

Systematic errorsare considered as errors, the magnitude of which can be measured and taken into account.

Based on the nature of their influence on the final result, systematic errors are divided into additive (constant), independent of the content of the component being determined, and multiplicative (proportional), depending on the content of the component being determined. Additive errors arise, for example, when the dummy signal is not taken into account in instrumental methods of analysis; multiplicative - in titrimetry when the titrant titrant (concentration) is incorrectly set. Multiplicative errors are very effective but are detected and installed using standard additions.

It is impossible to list all sources of systematic errors. Typical components of measurement error are methodological, instrumental components and errors introduced by the operator - subjective (individual) errors.

Individual(subjective) errorsarise as a result- due to ignorance, negligence, bias or physical defects of the experimenter.For example, they can appear when the sample is transferred incorrectly, in particular, during the selection and transfer of an aliquot volume with a measuring pipette while blowing a solution out of it to “speed up” the analysis.

Instrumental errors– errors caused by the imperfection of devices or the influence of external factors on them, primarily ambient temperature.

Systematic errors of this type can be eliminated by calibrating the glassware at the appropriate temperature. Periodic verification of analytical instruments minimizes the systematic component of instrumental errors.

The main contribution to the overall error is made by methodological errors, which are determined by the determination method. Methodological errors may be caused by errors

in sampling, converting the sample into a form convenient for analysis, and operations of concentration and separation of components.

The typical and most widespread methodological error in titrimetric methods of analysis is the indicator error. It occurs when the end point of the titration is fixed.

When processing analysis results, systematic errors should be identified and eliminated or, if possible, assessed.

To detect systematic error, use one of the following methods to check the significance of the difference:

- between the result of the analysis of a standard reference material (SRM) or a certified mixture (AC), which is obtained using a developed or used method, and the certified content (certificate data) of the component being determined in the RM or in the AC (this is the most reliable a method for identifying systematic errors and certifying the correctness of a method or analysis technique);
- between the analysis results obtained using this and alternative (arbitration) analysis techniques;
- between the analysis results obtained in this and alternative (arbitration) laboratories;
- between the analysis results obtained using two different portions of the analyte (variation method, varying the sample size); by doubling (the doubling method) or increasing the sample size by a multiple of times, a constant (additive) systematic error can be detected by changing the found content of the determined component;
- between the result of the analysis of a given substance and the content of the analyte component in this substance, calculated from the result of the analysis of a substance with a known addition of the analyte component (addition method).

In all of these cases, the significance of the difference between the compared results a1 and a2 is established using the t-test. A systematic error is considered significant if:

$$\frac{|a_1 - a_2|}{\bar{S}\sqrt{\frac{1}{n_1} + \frac{1}{n_2}}} > f(P, f = n_1 + n_2 - 2), \qquad (2.11)$$

Where

$$\bar{S} = \sqrt{\frac{S_1^2(n_1 - 1) + S_2^2(n_2 - 1)}{n_1 + n_2 - 2}}, \qquad (2.12)$$

Where S_1^2 And S_2^2 – variances characterizing the random scattering of results for a1 and a2, respectively;

$n_1$and n2 – the number of experiments when obtaining results a1 and a2;

R–confidence probability;

f–number of degrees of freedom.

One of the ways to reduce and eliminate systematic errors is relativization (from the English relative - relative), when, under identical conditions, individual operations are carried out in such a way that systematic errors are leveled, for example, conducting a control experiment. In this case, errors caused by contamination from reagents, water,

and utensils are leveled out; errors in the sample preparation stage, etc.

Errors of unknown nature– these are errors whose values are unknown and difficult to identify and eliminate. They can be detected only after eliminating other systematic errors and subsequent careful examination of all stages, operations and conditions of the analysis. Typically, in such cases, the technique of randomization is used (from the English random - randomly) - converting systematic errors into random ones. The possibility of randomization is based on the fact that the systematic error of a single phenomenon (method, device, analysis performer) when considered in a wider class of similar phenomena (a group of methods, a series of devices, a team of analysts) becomes a variable value, i.e., it acquires the features of a random error and is assessed using mathematical statistics methods.

WITHstatistical processing of the results of direct equal-precision observations(definitions)

All measurements in metrology are divided into direct and indirect.

In direct direct measurements, the numerical value of the measured value x is obtained by direct comparison of this value with a standard (for example, the mass of an object when weighed on a cup balance - with the mass of weights, the volume of a solution - with a graduated burette scale, etc.). Typically, the results of such measurements are obtained directly from the readings of the measuring device.

The result of each direct measurement includes a random error, which depends on a large number of random factors.

If deviations caused by random factors are comparable in absolute value to the sensitivity of the instrument, then they are detected by the instruments, and with n measurements of the same quantity, results x1, x2, xi, xn are obtained, which may differ from each other within the sensitivity of the measurement data .

The description of the results obtained from replicate measurements (determinations) should include the following characteristics: number of measurements, arithmetic mean, standard deviation, confidence interval limits and, if known, the true value, as well as an estimate of the limits of systematic error.

Number of measurements(number of observations, n) – total number of data received in the series, sample size. This number must always be specified. If the general population is considered, the designation N is used.

Number of degrees of freedom (degrees of freedom, f) – a statistical value showing the number of variables that can be assigned arbitrarily when characterizing a sample; in the simplest case, when they have n measurements (definitions) and one parameter under study (average value) – $f = n - 1$.

Confidence level(confidence level), or confidence probability, is the probability that the expected value of the studiedparameter lies within a certain interval ($P = 1 - \alpha$). Confidence probability (P) is the proportion of cases in which the average (x) for a given number of definitions will lie within certain limits. The confidence probability is associated with the two-sided – upper and lower – limit of the spread of the sample mean

value. From the point of view of mathematical statistics, the higher the confidence probability, the higher the reliability of the result obtained. As a rule, they use a confidence probability P equal to 0.95, or a two-sigma criterion (2σ), but in particularly important cases they take P = 0.99 - the 3σ criterion. The confidence probability can also be expressed as a percentage.

The complementary value of α is known as the significance level. Significance level α = (1 – P) – the maximum probability that the error will exceed a certain limiting (critical) value (+Δxcr), i.e. such a value that the occurrence of this error can be considered as a consequence of a significant (non-random) cause. In different literary sources, the level of significance is designated differently: α, β.

Arithmetic mean, average value(arithmetic mean, average, $\bar{x}$) – the sum of all values of a series (sample) of observations divided by the number of observations:

$$\bar{x} = \frac{\sum x_i}{n}. \qquad (2.13)$$

In all sum determination processes (hereinafter, unless otherwise noted), summation limits are considered from 1 to n.

Deviation(deviation, d) – the difference between the random variable and the arithmetic mean of the sample to which it belongs:

$$d = x_n - x_{\min}. \qquad (2.14)$$

Scope(samples)(range, R) – the difference between the largest and smallest observed value in the sample:

$$R = \text{xmax} - \text{xmin}. \qquad (2.15)$$

This parameter is especially useful for small samples (n < 10) as an alternative measure of dispersion.

Standard deviation(standard deviation) is estimated as the positive square root of the value obtained by dividing the sum of squared differences of all elements of the sample and the average of this sample by the number of degrees of freedom (in the simplest case, the number of measurements minus one). The sample standard deviation (S) is expressed by the following formula:

$$S = \sqrt{\frac{\sum (x_i - \bar{x})^2}{n-1}}. \qquad (2.16)$$

Relative standard deviation(relative standard deviation,*Sr*) – standard deviation divided by the sample mean:

$$S_r = \frac{S}{\bar{x}}. \qquad (2.17)$$

Relative standard deviation expressed as a percentage(percentage standard deviation, Sr (%)), is obtained by multiplying the value of the relative standard deviation by 100.

It is recommended that the relative standard deviation, not expressed as a percentage, be used when reporting results to avoid confusion when results are also expressed as a percentage. It is not recommended to use the term coefficient of variation instead of the

term relative standard deviation.

Dispersion (variance, $V_{\bar{x}}$) is the square of the standard deviation, expressed by the formula

$$V_{\bar{x}} = \frac{\sum d_i^2}{n-1} = \frac{\sum (x_i - \bar{x})^2}{n-1}. \qquad (2.18)$$

When assessing the reproducibility of the results obtained, the variance of the average (sample) is also calculated using the formula

$$V_{\bar{x}} = \frac{\sum (x_i - \bar{x})^2}{n(n-1)} \qquad (2.19)$$

and standard deviation of the mean ($S_{\bar{x}}$):

$$S_{\bar{x}} = \frac{S}{\sqrt{n}} = \sqrt{\frac{\sum (x_i - \bar{x})^2}{n(n-1)}}. \qquad (2.20)$$

To denote the standard deviation of the average in the English literature, the term population standard deviation, or standard error, with the symbol "σ" is used.

Evaluation of the correctness of the measurement result (analysis). After gross errors have been checked (in the case of individual suspicious measured values) and eliminated, the boundaries of the confidence interval (C) are assessed, the confidence interval $(\bar{x} \pm C)$ and, if necessary, assessing the correctness of the result.

Confidence interval limits (confidence levels about the mean) – symmetrical boundaries of the confidence interval (+C) for estimating the mean, into which the mathematical expectation (the population mean) falls with confidence probability (P). The numerical value of C is calculated using the equation

$$C = \frac{t_{P,j} \cdot S}{\sqrt{n}}, \qquad (2.21)$$

or

$$WITH = tP,j \cdot Si, \qquad (2.22)$$

where tP, j is the table value of Student's t-test.

Typically, a P value of 0.95 is used to calculate confidence limits, but higher reliability is required for critical measurements (P = 0.99).

It should be noted that if, when developing a technique, n parallel measurements are performed, and the analysis technique subsequently provides for the production of results from m parallel measurements (usually n ≥ 10, m = 2–3), then the limits of the confidence interval for ordinary analyzes should be calculated using the formula

$$C = \frac{t_{P,j} \cdot S}{\sqrt{m}}, \qquad (2.23)$$

and not according to formulas (2.21) and (2.22) (where S is the standard deviation for a sample of n experiments). Otherwise, the C value of the series analysis will be too low.

Confidence interval (confidence interval) is described as $\bar{x} \pm C$. If the reproducibility

of measured values (results of observations, determinations) is characterized by a standard deviation, then the result (of measurement, analysis) is characterized by a confidence interval. The confidence interval limits the area within which, in the absence of systematic errors, the true value of the result (measurement, analysis) is located with a predetermined confidence probability P:

$$\bar{x} \pm C; \qquad (2.24)$$

$$\bar{x} - C < \mu < \bar{x} + C; \qquad (2.25)$$

$$\bar{x} - t_{P,j} \cdot S_{\bar{x}} < \mu < \bar{x} + t_{P,j} \cdot S_{\bar{x}}; \qquad (2.26)$$

$$\bar{x} - t_{P,j} \cdot \frac{S}{\sqrt{n}} < \mu < \bar{x} + t_{P,j} \cdot \frac{S}{\sqrt{n}}. \qquad (2.27)$$

From equations (2.25–2.27) it follows that the value of the confidence intervaldepends on the sample size, i.e., on the number of experiments performed: with a decrease in the number of measurements, the confidence interval increases (with the same confidence probability) or, for a given confidence interval, the reliability of measurements decreases.

Significance of systematic error characterizes the measure of correctness of the determination results. The significance of the systematic error, i.e., the correctness of the analysis result, is judged depending on whether the true value of the value being determined falls within the established confidence interval or is outside it. If $|x - \mu| > C$, then we can talk about a significant systematic error (Δxc), the interval value of which is within the limits:

$$\bar{x} - \mu - C < \Delta x_c < \bar{x} - \mu + C. \qquad (2.28)$$

In this case, it is necessary to find out the cause of the systematic error. The task of freeing measurement results from systematic errors requires an in-depth analysis of the entire set of measurement data.

Regression and correlation analyzes are also widely used to detect and eliminate systematic errors.

2.4. ABOUTvaluation of gross errors (misses)

There are various methods for assessing and eliminating gross errors:

- elimination of gross errors by calculating the maximum relative deviation;
- checking the validity of measurement results according to the rule;
- determination of gross errors using the Q-criterion.

In series with a small number of measurements, the definition of misses is better assessed using the range of variation. To do this, n results are ordered by size. The value that can be considered as a gross error is denoted by x1. Then calculate for n = 3–7:

$$Q = \left| \frac{x_1 - x_2}{x_1 - x_n} \right| = \left| \frac{x_1 - x_2}{R} \right|; \qquad (2.29)$$

for n = 8–10:

$$Q = \left| \frac{x_1 - x_2}{x_1 - x_{n-1}} \right|, \qquad (2.30)$$

where Q is the range of variation (the difference between the largest and smallest values of a number of measurements).

The calculated Q value is compared with the critical value (Qcrit) at a confidence level of P = 0.90 (Table 2.1). If *Q*> Qcrit, then the result x1 is a miss and is discarded. If Q < Qcrit, then the result cannot be excluded, since it belongs to the sample population.

Table 2.1 – **Q-test values (confidence probability P = 0.90)**

N	Q_{Crete}	*n*	Q_{Crete}
3	0.94	7	0.51
4	0.76	8	0.47
5	0.64	9	0.44
6	0.56	10	0.41

Q-the criterion is not applicable to small samples (n < 5). In this case, it is necessary to collect more data or use other methods to detect a miss. After eliminating errors, sample data can be processed using mathematical statistics methods.

Practical work No. 2
Calculation of the result of titrimetric analysis. Solving problems to determine the concentration of a solution.

1. Acid-base titration

Example 16. To standardize the HNO3 solution, a sample of 1.7594 g of Na2B4O7 10H2O was dissolved in a 100.0 ml volumetric flask. The titration of an aliquot (V = 15.0 ml) of this solution required 12.7 ml of HNO3 solution. Calculate the molar concentration, molar equivalent concentration and titer of the acid solution.

Solution. During titration the following reaction occurs:

2HNO3 + Na2B4O7 +5H2O → 2NaNO3 + 4H3BO3

This means that the equivalence factor for Na2B4O7 · 10H2O is 1/2. Let us calculate the concentration of the prepared sodium tetraborate solution using the formula

C = m/(M V),

where C is the molar concentration of the equivalent, mol/l; m – mass, g; M – molar mass of equivalent, g/mol; V – volume of solution, l.

M(1/2 Na2B4O7 10H2O) = 190.69 g/mol,

C(1/2 Na2B4O7 10H2O) = 1.7594/(190.69 0.1) = 0.09226 mol/l.

Using the law of equivalents, we calculate the molar concentration of the equivalent of the HNO3 solution:

C(1HNO3) = 15.0 · 0.09226/12.7 = 0.1090 mol/l.

The equivalence factor (feq.) of HNO3 is equal to unity, therefore the value of the molar concentration of HNO3 coincides with the value of the molar concentration of the equivalent. The titer of the acid solution is calculated using the formula

$$T_{HNO_3} = \frac{C_{HNO_3} \cdot M(HNO_3)}{1000};$$

M(HNO3) = 63.013 g/mol [3];

$$T_{HNO_3} = \frac{0{,}1090 \cdot 63{,}013}{1000} = 0{,}006868 \text{ г/мл}.$$

Example 17will help you solve problems No. 151, 152, 163.

Example 17. 10.0 ml of a mixture of sulfuric and phosphoric acids was placed in a 250 ml volumetric flask, and the contents were brought to the mark. 15.0 ml of the resulting solution was placed into two titration flasks. To titrate the first sample with methyl orange, 27.4 ml of NaOH solution with a concentration of 0.09678 mol/l was used. To neutralize the second sample in the presence of phenolphthalein, 33.2 ml of NaOH solution of the same concentration was spent. Calculate the mass of sulfuric and phosphoric acids in the initial mixture.

Solution.Titration curves for sulfuric and phosphoric acids show that a change in methyl orange color will occur when H2SO4 is titrated in two stages and H3PO4 in the first stage. In this case the following reactions occur:

H2SO4 + 2NaOH = Na2SO4 + 2H2O }
H3PO4 + NaOH = NaH2PO4 + H2O; VT = 27.4 ml.

Coloring of phenolphthalein will occur when H2SO4 is completely titrated, and H3PO4 is titrated in two steps:

H2SO4 + 2NaOH = Na2SO4 + 2H2O }
H3PO4 + 2NaOH = Na2HPO4 + 2H2O VT = 33.2 ml.

Consequently, the difference in volume corresponds to the amount of titrant used for the titration of H3PO4 in one step.

Let's calculate the volume of NaOH solution used for the titration of phosphoric acid in one step:

ΔV = 33.2–27.4 = 5.8 ml.

Using the law of equivalents, we determine the concentration of phosphoric acid in solution:

C = 0.09678 · 5.8/15.0 = 0.03742 mol/l; M(H3PO4) = 97.9952.

The calculation was carried out based on the results of one-stage titration, therefore, the equivalence factor of H3PO4 is equal to 1. 250.0 ml of solution and 10.0 ml of the analyzed mixture contain the same amount of H3PO4:

m(H3PO4) =0.03742 · 250.0 · 10–3 · 97.9952 = 0.9168 g.

The volume spent on the titration of H2SO4 can be calculated by subtracting from the volume spent on the titration of the mixture in the presence of methyl orange the volume spent on the titration of H3PO4 in one step. Thus, Vp–ra (NaOH), used for titration of sulfuric acid,

Vp–ra (NaOH) = 27.4 – 5.8 = 21.6 ml.

The equivalence factor of H2SO4 is ½, since the titration took place in two steps. Let's calculate the concentration and mass of H2SO4:

C(1/2 H2SO4) = 0.09678 · 21.6/15.0 = 0.1394 mol/l;

m(H2SO4) = 0.1394 · 250.0 · 10–3 · (1/2 98.078) = 1.7086 g.

Problems 161, 162, 167, 168, 172 use the back titration method (see section 6.3). Example 14 on p. will help you in solving these problems. 18 [2].

2. Redox titration

Example 18will help you solve problems No. 198, 203, 204, 207, 209, 212, 213.

Example 18.To 20.00 ml of silver salt solution, 20.00 ml of 0.0200 mol/l K2CrO4 solution was added. The Ag2CrO4 precipitate was separated, the filtrate was acidified, and an excess of KI solution was added. 24.60 ml of 0.0400 mol/l Na2S2O3 solution was used to titrate the released iodine. Calculate the mass concentration of Ag+ in the original solution.

Solution. Let's write down the reaction equations:

$2Ag+ + CrO_4^{2-}$ (ex.) = Ag2CrO4 ↓ (13)

$2\,CrO_4^{2-}$ + 6 I– + 16 H+⇆2 Cr3+ + 3 I2 + 8 H2O (14)

$2\,S_2O_3^{2-}$ + I2⇆ $S_4O_6^{2-}$ + 2 I (15)

In the quantitative determination of Ag+, the methods of back titration and substituent titration are used sequentially.

Ion equivalence factor CrO_4^{2-} in the oxidation-reduction reaction (14) we determine using the half-reaction

CrO_4^{2-} + 8 H+ – 3ē = Cr3+ + 4 H2O → feq(CrO_4^{2-})= 1/3.

According to reaction (13), two Ag+ ions enter into a precipitation reaction with the ion CrO_4^{2-} Therefore, 2 Ag+ ions are equivalent to 3 electrons. To determine the equivalence factor of the Ag+ ion, we create the proportion:

2 Ag+ ions – 3 ē

1 Ag+ ion – x ē

Hence x = z = 3/2. Therefore, the equivalence factor of the Ag+ ion is 2/3.

Let's move from the molar concentrations of solutions to the molar concentrations of the equivalent:

c(1/3K2CrO4) = 0.0200 / (1/3) = 0.0600 mol/l;

c(1Na2S2O3) = 0.0400 / 1 = 0.0400 mol/l.

Further, the problem can be solved in two ways: 1) using the formulas of subsection 6.3 with the calculation of the number of moles of equivalent reactants; 2) by calculating the volume of excess reagent. We offer the second option.

Using the law of equivalents, we find the volume of the K2CrO4 solution that remains after reaction (13):

$$V(K_2CrO_4) = \frac{24{,}60 \cdot 0{,}0400}{0{,}0600} = 16{,}40 \text{ мл.}$$

Then reaction (14) took 20.00 – 16.40 = 3.60 ml of K2CrO4 solution.

Let's find the mass of Ag+ in solution. Since M(2/3Ag+) = 71.912 g/mol, then

m(Ag2+) = 3.60 · 10–3 · 0.0600 · 71.912 = 0.01553 g,

and its mass concentration:

ρ*(Ag+) = 0.01553 /20 · 10–3 = 0.7766 g/l.

3. Complexometric titration

Example 19will help you solve problems No. 225, 226, 230, 232, 234, 236, 243, 244.

Example 19.Calculate the mass fraction of Al2O3 in the silicate if a sample of 1.0220 g was transferred to solution, 25.00 ml of a solution of complexone III was added [C(1/2 comp. III) = 0.2151 mol/l], and the excess of the latter was titrated 9.83 ml of 0.1015 mol/l zinc sulfate solution.

Solution. The following reactions occur in solution:

Al3+ + H2Y2–⇆AlY– + 2H+

H2Y2– + Zn2+⇆ZnY2– + 2 H+

The calculations in the problem will be carried out using the back titration method (see subsection 6.3). The number of moles of Al3+ equivalent is determined by the difference:

n(1/2 Al3+) = n(1/2 set III) – n(1/2 ZnSO4).

Let's calculate the number of moles equivalent of added complexone III:

n(1/2 set III) = C(1/2 set III) · V(1/2 set III);

n(1/2 set III) = 0.2151 · 25.00 · 10–3 = 5.38 · 10–3 mol.

Let us convert the concentration of the ZnSO4 solution into the molar concentration of the ZnSO4 equivalent, taking into account that feq.(ZnSO4) = 1/2 (see subsection 6.2):

C (1/2 ZnSO4) = C (ZnSO4): 1/2 = 0.1015: 1/2 = 0.2030 mol/l;

n(1/2 ZnSO4) = 0.2030 · 9.83 · 10–3 = 2.00 · 10–3 mol.

Then the number of moles of Al3+ equivalent

n(1/2 Al3+) = 5.38 · 10–3 – 2.00 · 10–3 = 3.38 · 10–3 mol.

Let's calculate feq.(Al2O3) taking into account the scheme:

Al2O3 → 2 Al3+

feq. (Al2O3) = (1/2)/ 2 = 1/4.

Let's calculate m(Al2O3) taking into account M(1/4 Al2O3) = 25.4903:

m(Al2O3) = n(1/2 Al3+) · M(1/4 Al2O3) = 3.38 · 10–3 · 25.4903 = = 0.0862 g;

ω = 0.0862 / 1.0220 · 100 = 8.43%.

1.4 Independent work

Subjects of independent work

The importance of organic reagents in the analysis of cations and anions in complex compounds
Areas of application and remaining buffer solutions
Kreshkov's proton-electron-hydride concept of acids and bases
Use of organic reagents in analytical chemistry
Bichromatometric determination of iron (II) in solution
Chemical, physicochemical and physical methods of separation and concentration, extraction and chromatographic methods of concentration.
Methods of gas, liquid and gas-liquid chromatography.
Ion exchange chromatography
Thin layer chromatography.
Liquid chromatography
Adsorption-liquid chromatography
Exclusion chromatography
Electrochemical analysis methods
Polyarographic analysis method
Photometric determination of the amount of nickel in steel
Differential spectrophotometric analysis
Atomic fluorescence analysis method
IR spectra of aromatic hydrocarbons and heteroaromatic compounds.
Analysis of IR spectra of carbonyl-containing compounds
Characteristic bands in the IR spectra of alkanes, alkenes and alkynes
Nuclear magnetic resonance spectroscopy
Spectroscopy of the carbon-13 nucleus
Two-dimensional correlation NMR spectroscopy. COSY spectra. View of a 2D spectrum
Application of NMR spectroscopy in organic chemistry: main characteristics of one-dimensional NMR spectra

1.5.Glossary

Absolute concentration -substances present in small quantities are collected in less volume or mass.

Ion activity –this is the proportion of ions of a substance that manifests itself in action.

Analytical chemistry- the science of determining the chemical composition of substances and partly their chemical structure.

Analytical signal– physical quantity functionally related to the content of the component.

Buffer capacity– the number of mole equivalents of a strong acid or alkali that must be added to 1 liter of a buffer solution to change the pH value by one.

Buffer solution –it is a solution containing a protolytic equilibrium system capable of maintaining a virtually constant pH value when diluted or when small amounts of acid or alkali are added.

Heterogeneous reactions- these are reactions that are characterized by the presence of an interface between the reagents, where their interaction takes place.

Hydrolysis by anioncharacterizes salts formed by a weak acid and a strong base.

Hydrolysis by cationand anion occurs in solutions of salts formed by a weak acid and a weak base.

Hydrolysis by cationcharacterizes salts formed by a strong acid and a weak base.

Hydrolysis of saltsis a protolytic process of interaction of salt ions with water molecules, as a result of which low-dissociation molecules or ions are formed.

Homogeneous reactions– characterized by the absence of an interface between the reagents, so their interaction occurs throughout the entire volume of the system.

Bulk isolation and concentration– several components are released at one time.

Diffusion stages of a heterogeneous chemical process– this is the supply of reagents and the removal of reaction products.

Problems of analytical chemistryas areas of knowledge: solving general issues of analysis (for example, the development of its metrology); development of analytical methods; solving specific analysis problems (for example, creating analytical chemistry of pesticides).

Law of acting masc: the rate of a chemical reaction is directly proportional to the product of the concentrations of the reacting substances.

Ostwald's dilution law– expression of the law of mass action, reflecting the relationship between the degree of dissociation of the electrolyte and its concentration for the process of electrolytic dissociation.

Inhibitor– a substance that reduces the rate of a chemical reaction.

The ionic strength of a solution is a value that depends on the concentrations and all the ions present in the solution, and is a measure of the electrostatic interaction between them.

True solutions– these are homogeneous systems with particle sizes at the level of 10-10 - 10-9 m.

Catalyst- This is a substance that accelerates a chemical reaction, but is not consumed in the process.

Electrolyte dissociation constant– the ratio of the product of ion concentrations in a solution of a weak electrolyte to the concentration of its undissociated part.

Chemical equilibrium constant– of a reversible process is equal to the ratio of the equilibrium concentrations of the final products to the product of the equilibrium concentrations of the starting substances raised to powers equal to the stoichiometric coefficient in the formulas of the corresponding substances in the chemical reaction equation.

Solution concentration– a quantity measured by the amount of dissolved substance in a certain volume or mass of solution (solvent).

Mass fraction– the ratio of the mass of the solute to the mass of the solution, multiplied by 100%.

Molal concentrationis the ratio of the amount of solute to the mass of solvent.

Molar concentration –the ratio of the amount of solute to the volume of solution.

Normalityis the number of equivalents of a substance in 1 liter of solution.

Van't Hoff's rule When the temperature increases by 10 degrees, the reaction rate increases 2-4 times.

Le Chatelier's principle: If a system in a state of equilibrium is influenced by changing the concentration of reagents, pressure or temperature in the system, then the equilibrium always shifts in the direction of the reaction, the occurrence of which weakens this influence.

Solvent- a component whose state of aggregation does not change during the formation of a solution.

Strong electrolytes– substances with a degree of electrolytic dissociation greater than 0.7.

Chemical reaction ratedetermined by the change in the concentration of reactants per unit time.

Weak electrolytes– substances with a degree of electrolytic dissociation less than 0.1.

Degree of salt hydrolysisis the ratio of the number of molecules that have undergone hydrolysis to the total number of salt molecules.

Degree of electrolytic dissociation- shows the ratio of the number of molecules disintegrated into ions to the total number of dissolved molecules.

Title –is the mass of solute in 1 ml of solution.

Chemical kinetics- a branch of chemistry that studies the mechanisms of chemical reactions and the rates of their occurrence.

Chemical equilibrium– a state of a reversible process in which the rates of forward and reverse reactions are equal.

Electrolytic dissociation– the process of decomposition of a substance into ions, occurring as a result of its electrostatic interaction with polar solvent molecules.

Electrolytes– substances whose solutions or melts conduct electric current.

Activation energy– the minimum energy of interacting particles, sufficient for all particles to enter into a chemical reaction.

Part 2. "Qualitative analysis"

Ammonium phosphate schemebased on the different solubilities of metal phosphates and chlorides.

Material analysisdetermines in what form the component of interest to us is present in the analyzing object and what is the content of these forms.

Group reagentsselectively deposit a certain group of atoms.

Unmasking- the transformation of a masked substance into a form capable of reacting normally characteristic of it.

Isotope analysis- this is the determination of the isotopic composition of a substance.

Masking indexis the logarithm of the ratio of the total concentration of the interfering substance to its concentration remaining unbound.

Qualitative analysis– this is a type of analysis that is focused on identifying the chemical composition of the analyzed sample: determining the presence of certain cations or anions.

Kinetic cloakingis based on an increase in the difference between the rates of reaction of the masked and determined substances with the same reagent.

Acid-base schemecation analysis is based on the different solubilities of chloride, sulfate and hydroxide cations in mineral acids, sodium hydroxide and ammonia.

Masking- This is the inhibition or complete suppression of a chemical reaction in the presence of substances that can change its direction or speed.

Minimum concentrationshows at what minimum concentration of the ion being determined in the solution this reaction is still possible for detection in a certain volume of the test solution.

Molecular analysisis the detection and identification of chemical compounds.

General reagentallows you to isolate a precipitate of a mixture of substances, which is subjected to further separation and analysis, taking advantage of differences in chemical properties.

Opening minimumis the smallest mass of the ion being determined that can be detected using a given reaction in the smallest volume of the test solution.

Limit dilution– the greatest dilution of a solution containing 1 g of the analyte ion, at which this reaction is still noticeable (precipitation, gas evolution, color change).

Selective (selective) reactions- these are reactions during which similar external effects occur not for the presence of one ion, but for several ions.

Hydrogen sulfide schemecation analysis is based on the different solubilities of metal sulfides, chlorides, hydroxides and carbonates.

Specific reaction To determine an ion, a reaction is considered to be one that allows it to be detected in the presence of other ions.

Structural - group analysis- this is the determination of functional groups of organic compounds - carboxyl, hydroxyl, amine, etc.

Phase analysis– analysis of inclusions in a heterogeneous object, for example in minerals.

Response sensitivitycharacterized by minimum concentration, opening minimum and dilution limit.

Elemental analysisis a determination of the elemental composition of a sample.

O‘ZBEKISTON RESPUBLIKASI
OLIY TA’LIM, FAN VA INNOVATSIYALAR VAZIRLIGI

NAMANGAN DAVLAT UNIVERSITETI

"TASDIQLAYMAN"
O‘quv ishlari bo‘yicha prorektori
D.Xolmatov
2023-yil

ANALITIK KIMYO
FANINING

O‘QUV DASTURI

2-kurs, kunduzgi ta’lim shakli uchun

Bilim sohasi:	**500000-Tabiiy fanlar, matematika va statistika**
Ta’lim sohasi:	**530000- Fizika va tabiiy fanlar**
Ta’lim yo’nalishi:	**60530100-Kimyo (turlari bo‘yicha)**

Namangan – 2023

Fan/Modul kodi AK1420		O‘quv yili 2023/2024	Semestr 3-4	ECTS-Kreditlar 10+10=20
Fan/Modul turi Majburiy		Ta‘lim tili O‘zbek		Haftadagi dars soatlari 3-semestr - *8 soat* 4-semestr - *10 soat*
1	**Fanning nomi**	**Auditoriya mashg'ulotlari(soat)**	**Mustaqil ta’lim (soat)**	**Jami yuklama (soat)**
	Analitik kimyo	270	330	600

I. Fanning mazmuni

Fanni o‘qitishdan maqsad - Fanni o’qitishdan maqsad-Talabalarga analitik kimyo fanining nazariy asoslarini, asosiy tushunchalari va usullarini, atrof-muhitdagi har xil obyektlarning elementar kimyoviy tuzulishini, sifat miqdoriy aniqlanishni taminlaydigan metodlarning ma’lumotlaridan foydalanib chuqur bilim berish hamda ularni amaliyotga tadbiq etish ko’nikmasini hosil qilishdan iborat.

Fanning vazifasi - analitik kimyoning predmeti va vazifalari, reaksiyani amalga oshirishning shart-sharoitlari va bajarish usullari, namuna olish va uni analizga tayyorlash, analizning gravimetrik, titrimetrik, elektrokimyoviy va spektroskopik usullari, moddalarning sifat va miqdoriy tarkibini aniqlashni, analitik reaksiyalarni bajarish usullari, nur yutilishi va chiqarilishiga asoslangan analiz usullarini optik va elektrkimyoviy analiz qonuniyatlari, aralashmalar tarkibidagi moddalarni sifat va miqdoriy tarkibini aniqlash, pH-metrlar, spektofotometrlar, fotoelektrmetrlar, alanga fotometrlar, atom-absorbsion spektrometrlar, polyarograflar va amperometrlarda ishlash, miqdoriy analizning gravimetrik, titrimetrik, elektrokimyoviy va spektroskopik usullari va boshqalar bo’yicha bilim berish, amaliy ko’nikma va malaka xosil qilish.

II. ASOSIY NAZARIY QISM(MA’RUZA MASHG’ULOTLARI)

II.I. Fan tarkibiga quyidagi mavzular kiradi:

1-mavzu. Analitik kimyo fani, tadqiqot doirasi, maqsadi va vazifalari.

“Analitik kimyo” fani turli murakkab ob’ektlar (suv, tuproq, xavo, qotishmalar, geologik, biologik, atrof-muhit ob’ektlari va xok.) analizini amalga oshirishni o’rganadi. Fanning maqsadi kimyoviy analizning nazariy asoslari va metodlarini ishlab chiqish, atrof-muhitdagi har xil ob’ektlarning elementar kimyoviy tuzilishini, sifat va miqdoriy aniqlashni ta’minlaydigan metodlar ishlab chiqish va o’rgatishdan iborat.

2-mavzu. Kimyoviy analizning metrologik asoslari.

O’lchash, o’lchash usullari va asboblari. O’lchash natijalariniing xaqiqiyligini ta’minlaydigan asosiy prinsiplar va uslublar. Analizdagi xatoliklar klassifikatsiyasi: sistematik, tasodifiy, qo’pol, absolyut va nisbiy xatoliklar. Analizning asosiy bosqichlari. Namunani analiz qilinadigan shaklga o’tkazish, bosim va xarorat ta’sirida parchalash va xok.

3-mavzu. Kimyoviy muvozanatning asosiy turlari.

Kimyoviy qaytar reaktsiyalar. Massalar ta’siri qonuni. Analitik kimyoda muvozanatning asosiy turlari: kislota-asosli muvozanat, kompleks hosil qilish, oksidlanish-qaytarilish, cho’ktirish. Analitik va muvozanat kontsentratsiya. Elektrostatik kuchlarning elektrolit tabiatiga va reaktsion qobiliyatga ta’siri, aktivlik koeffitsienta. Eritmaning ion kuchi. Chekli va kengaytirilgan Debay va Gyukkel qonunlari. Moddaning standart xolatdagi aktivligi. Muvozanat konstantalari (termodinamik, kontsentratsion va shartli) ular orasidagi bog’liqlik.

4-mavzu. Kislota-asosli rsaktsiyalarda muvozanat.

Kislota va asoslar haqida xozirgi zamon tushunchalari. Brensted-Louri nazariyasi. Asosli va

kislotali konstantalari. Har xil ko'rinishdagi protolitik eritmalarda pHini hisoblash. Protolit kuchiga ta'sir etuvchi omillar. Bufer eritmalar va ularning xossalari. Bufer sigimi. Bufer sistemalarda **pH** ni hisoblash.

5-mavzu. Kompleks hosil kilish reaktsiyalarida muvozanat.

Analitik kimyoda ishlatiladigan komplekslarning turlari. Analitik ahamiyatga ega bo'lgan kompleks birikmalarning xossalari: barqarorlik, eruvchanlik, rangdorlik, uchuvchanlik. Barqarorlik konstantalari (umumiy bosqichli). Hosil bo'lish funktsiyasi. Kompleks birikmalar dissotsiatsiyasi. Kompleks birikmalar va ko'sh tuzlar. Kompleks birikmalar va organik reagentlarni har xil analiz usullarida ishlatilish imkoniyatlari

6-mavzu. Oksidlanish-qaytarilish reaktsiyalari.

Elektrod potentsiapi, Nernst tenglamasi. Standart va formal potentsiallar bilan bog'liqligi. Oksidlanish-qaytarilish reaktsiyalarining yo'napishi. Oksidlanish-qaytarilish reaktsiyalarining mexanizmi. Analizda qo'llaniladigan asosiy organik va anorganik oksidlovchilar va qaytaruvchilar. Aniqdanadigan elementni oldindan oksiddash va qaytarish usullari.

7-mavzu. Cho'ktirish reaktsiyalari.

Eruvchanlik ko'paytmasi va eruvchanlik. Ularga ta'sir etuvchi omillar. Bo'laklab va sistematik cho'ktirish

8-mavzu. Miqdoriy analiz.

Miqdoriy analiz. Metodning mohiyati. Bevosita va bilvosita aniqlash usullari. Gravimetrik analizda xatoliklar. Aniqlashning umumiy sxemasi. Tortim, cho'kmaning miqdori va eritmaning hajmi. Amorf va kristall cho'kmalar, yirik kristaplarni olish sharoitlari. Gomogen cho'ktirish, cho'kmaning etilishi. Cho'kmaning ifloslanish sabablari. Birgalashib cho'kishning sinflanishi (adsorbtsiya, okklyuziya, izomorfizm). Analitik tarozilar, ularning turlari va sezgirliklari. Tortish texnikasi. Gravimetrik analizga misollar.

9-mavzu. Titrimetrik analiz usullari.

Titrimetrik analiz usullarining sinflanishi. Titrimetrik analizda ishlatiladigan reaktsiyalarga qo'yiladigan talablar. Kislota-asosli titrlash. Titrlash egrilari. Titrlash sakramasi va unga ta'sir etuvchi omillar. Titrlashning indikator xatoliklari. Oksidlanish-qaytarilish reaktsiyalari asosida titrlash. Titrlash xatoliklari. Amaliyotda ishlatilishi. Permanganatometriya. Iodometriya. Bixromatometriya. Kompleksonometrik titrlash. Kompsonometrik titrlashning amaliyotda qo'llanilishi. Suvning qattiqligini aniqlash. Cho'ktirish reaktsiyasi asosida titrlash. Titrlash egriligini tuzish. Titrlash aniqdigiga adsorbilanish xodisasining ta'siri. Titrlash egrisi tavsifiga cho'kma eruvchanligi, kontsentratsiya va haroratning ta'siri. Indikatorlar. Titrlash xatoliklari. Indikatorlar. Titrlash xatoliklari. Folgard, Mor, Fayans usullari. Cho'ktirish reaktsiyasi asosida titrlashning amaliyotda ishlatilishi.

10-mavzu. Optik analiz usullari.

Elektromagnit nurlanish spektri: Uning to'lqin va korpuskulyar tabiati. Elektromagnit nurlanishni xarakterlovchi kattaliklar (to'lqin uzunlik, chastota, to'lqin soni, energiya). *Molekulyar spektroskopiya usullari.* Modda tomonidan yoruglik nurining yutilishi. Buger-Ber - Lambert qonuni. Optik zichliklarning additivlik xossasi. Yorug'lik yutilishining molyar koeffitsienta. Buger-Ber -Lambert qonunidan chetlanish va uning sabablari. Fotometrik reaktsiyalar. Spektrofotometrik usulning metrologik xarakteristikalari. Aniqlanadigan kontsentratsiyaning quyi chegarasi. Sezgirligi. Tanlash (selektivlik). Selektivlikni cheklaydigan omillar. Spektral va fizik- kimyoviy xalaqitlar. Spektrofotometrik usulning qo'llanilish soxalari. Oddiy fotometrning tuzilishi, asosiy qismlari va ishlash printsipi.

11-mavzu. Atom-absorbtsion spektrometriya.

Atom-absorbtsion spektrometriya usulining asoslari. Atomlarning optik nurlarni yutishi. Atom bug'ining optik zichligi. Elektrotermik atomizator, tuzilishi va ishlash printsipi. Elektrotermik atomizatorning ustunligi va kamchiliklari. Atom-absorbtsion spektrometr. Optik (spektral) halaqitlar; fon hosil qiluvchi nurlanish, fon nurlanishining yutilishi. Fonning signalini ajratish. Miqdoriy analiz usullari; tashqi standartlar (darajapash grafigi), qo'shimcha ko'shish.

12-mavzu. Atom-emission spektrometriya.

Atom-emission spektrometriya usulining asoslari. Atomlarning asosiy va qo'zg'algan xolatlari. Atomlarning Boltsman qonuniga ko'ra sathlarga taqsimlanishi. Energetik sathlar orasidagi o'tishlar va spektr chiziqlarning hosil bo'lishi. Tanlash qoidalari. Spektr chiziqlarni xarakterlovchi kattaliklar: chiziqning joyi, intensivligi, yarimkengligi. Usulning metrologik xarakteristikalari: sezgirligi, aniqlanadigan kontsentratsiya oraligi, natijalarning takrorlanishi. Qo'llanish sohalari.

13-mavzu. Molekulyar lyuminestsentsiya.

Lyuminestsentsiyaning ta'rifi, turlari va boshqa nurlanishlardan farqi. Molekulyar lyuminestsentsiyaning asosiy xarakteristikalari. Lyuminestsentsiya va lyuminestsentsiyani qo'zgatish spektrlari. Lyuminestsentsiyaning energetik va kvant chiqishlari. Lyuminoforlar. Lyuminestsent analizning spektrofotometrik analizdan ustunligi va kamchiliklari. Xemilyuminestsentsiya xodisasi va uning analizda ishlatilishi. Molekulyar lyuminestsent analizda ishlatiladigan asboblar va texnik vositalar.

14-mavzu. Elektrokimyoviy analiz usullari.

Elektrokimyoviy analiz usullarining umumiy tavsifi va sinflanishi. Elektrokimyoviy zanjir. Indikatorli elektrod va solishtirma elektrodlar. Elektrokimyoviy muvozanat potentsiali. Tok o'tayotganda elektrokimyoviy zanjirlarda kuzatiladigan xodisalar: kuchlanishning qarshilik ta'sirida pasayishi, kontsentratsion va kinetik qutblanishlar. Elektrokimyoviy analiz usullarining sezgirligi va tanlanuvchanligi.

15-mavzu. Elektrogravimetrik analiz.

Elektrogravimetrik analiz. Metodning qo'llanilish soxalari, qulayligi va kamchiliklari. Doimiy elektrod potentsiali va doimiy tok kuchida elementning ajralishi. Ichki elektroliz metodi, uni mikroelementlarni kontsentrlash va aniqlashda qo'llanilishi. Ishchi elektrodning doimiy potentsiali va doimiy tok kuchida simob va qattik elektrodlarni qo'llash orkali elementlarni ajratish. Elektrolitik ajratishda, kompleks hosil bo'lishdan foydalanish. O'ta sof materiallar analizida simob katodidan foydalanish.

16-mavzu. Bevosita potentsiometriya.

potentsiometriya. Potentsialni o'lchash. Nernst tenglamasi. Qaytar va qaytmas oksidlanish-qaytarilish sistemalari. Indikatorli elektrodlar. Ionometriya, ion selektiv elektrodlar, sinflanishi. Ionometriyaning amaliyotda ishlatilishi. Potentsiometrik titrlashda ishlatiladigan reaktsiya turlari. Kislota va ishqorlar miqdorini aniqlash. Kislotalar aralashmasini, ko'p asosli kislota va asoslar aralashmasini miqdoriy analiz qilish.

17-mavzu. Kulonometriya.

Kulonometriyaning nazariy asoslari. Faradey qonunlari. Elektr miqdorini aniqlash usullari. Bevosita va bilvosita kulonometrik analiz (kulonometrik titrlash). Kulonometrik titrantni ichki va tashqi generatsiyalash. Kulonometrik titrlashning boshqa titrimetrik usullarga nisbatan afzalliklari va kamchiliklari. Kulonometrik titrlashning amaliyotda qo'llanilishi.

18-mavzu. Konduktometriya.

Bevosita va bilvosita konduktometrik usullar. Past va yuqori chastotali konduktometriya.

Konduktometrik bo’g’in (yacheyka)va ishlatiladigan elektrodlar. Konduktometrik titrlash egri chiziqdari va ularga ta’sir etuvchi omillar. Konduktometrik usullarning amaliyotda qo’llanilishi.

19-mavzu. Voltampermetriya.

Indikatorli elektrod va solishtirma elektrodlar. Simob elektrodining afzalliklari va kamchiliklari. Voltampermetriya egriligi (polyarogramma)ni olish va tavsiflash. Ilkovich tenglamasi. Polyarografik to’lqin uchun Ilkovich - Geyrovskiy tenglamasi. Yarim to’lqin potentsiali va unga ta’sir etuvchi omillar. Polyarogafik sifat va miqdoriy analiz. Voltamperometrik analiz usullarining takomillashtirilgan xillari.

20-mavzu. Amperometriya.

Amperometrik titrlash, usulning mohiyati. Indikatorli elektrodlar. Indikatorli elektrod potentsialini tanlash. Bir va ikki indikatorli kutblangan elektrodlar yordamida amperometrik titrlashlar, titrlash egrilarining ko’rinishlari.

21-mavzu. Xromatografik analiz usullari.

Xromatografiyaning mohiyati. Harakatli va harakatsiz fazalar haqida tushuncha. Harakatli va harakatsiz fazalar agregat xolati, ajratish mexanizmi va ishlash mexanizmiga ko’ra xromatografik usullarning klassifikatsiyasi. Xromatografik analizni maqbullashtirish. Xromatografik sifat va miqdor analiz usullari

22-mavzu. Mass-spektrometriya usuli.

Mass-spektrometriya usuli, sinflanishi, analitik tavsiflari, ionlanish manbalari. Detektorlar; Faradey elektrometri va elektron ko’paytirgich. Organik va noorganik kimyoda qo’llaniladigan mass- spektrometrlarning farqi. Mass-spektrometriyaning noorganik moddalarning element tarkibini aniqlashda qo’llanilishi. Organik moddalarning molekulyar massasini topish.

Ma’ruza mashg’ulotlari mazmuni va unga ajratilgan soatlar		
№	**Mavzular**	**Soati**
	3- Semestr	
1	**Analitik kimyo fani, tadqiqot doirasi, maqsadi va vazifalari**	2
2	**Kimyoviy analizning metrologik asoslari**	2
3	Analiz xatoliklari	2
4	Namuna olish	2
5	**Kimyoviy muvozanatning asosiy turlari**	2
6	Aktivlik	2
7	**Kislota-asosli rsaktsiyalarda muvozanat**	2
8	Bufer eritmalar	2
9	**Kompleks hosil kilish reaktsiyalarida muvozanat**	2
10	Kompleks birikmalar va qo’sh tuzlar	2
11	**Oksidlanish-qaytarilish reaktsiyalari**	2
12	Analizda qo’llaniladigan oksidlovchi va qaytaruvchilar.	2
13	**Cho’ktirish reaktsiyalari**	2
14	Bo’laklab va sistematik cho’ktirish	2
15	**Miqdoriy analiz**	2
16	Gravimetrik analiz	2
17	Amorf va kristall cho’kmalar	2
18	Analitik tarozilar	2
19	**Titrimetrik analiz usullari**	2
20	Kislota-asosli titrlash	2
		40
	4- Semestr	

21	Kislota-asosli titrlashning xatoliklari	2
22	Oksidlanish-qaytarilish reaktsiyalari asosida titrlash	2
23	Permanganatometriya. Iodometriya. Bixromatometriya	2
24	Kompleksonometrik titrlash	2
25	Suvning qattiqligini aniqlash	2
26	Cho'ktirish reaktsiyasi asosida titrlash	2
27	Indikatorlar. Titrlash xatoliklari.	2
28	Folgard, Mor, Fayans usullari	2
29	**Optik analiz usullari**	2
30	*Molekulyar spektroskopiya qonunlari*	2
31	**Fotometrik analiz usullari**	2
32	**Atom-absorbtsion spektrometriya**	2
33	**Atom-emission spektrometriya**	2
34	**Molekulyar lyuminestsentsiya**	2
35	**Elektrokimyoviy analiz usullari**	2
36	**Elektrogravimetrik analiz**	2
37	**Bevosita potentsiometriya**	2
38	**Kulonometriya**	2
39	**Konduktometriya**	2
20	**Voltampermetriya**	2
41	**Amperometriya**	2
42	**Xromatografik analiz usullari**	2
43	Xromatografik sifat va miqdor analiz usullari	2
44	**Mass-spektrometriya usuli**	2
45	Mass-spektrometriyaning qo'llanilishi	2
	Jami	**50 soat**
	Umumiy soat:	**90 soat**

III.1. AMALIY MASHG'ULOT MAVZULARINI

1-amaliy mashg'ulot. Kimyoviy analizning metrologik asoslari. O'lchash, o'lchash usullari va asboblari.

O'lchash, o'lchash usullari va asboblari. O'lchash natijalariniing xaqiqiyligini ta'minlaydigan asosiy prinsiplar va uslublar. Analizdagi xatoliklar klassifikatsiyasi: sistematik, tasodifiy, qo'pol, absolyut va nisbiy xatoliklar. Analizning asosiy bosqichlari. Namunani analiz qilinadigan shaklga o'tkazish, bosim va xarorat ta'sirida parchalash va xok. Analitik tarozilar, ularning turlari va sezgirliklari. Tortish texnikasi. Gravimetrik analizga misollar.

2-amaliy mashg'ulot. Elektrostatik kuchlarning elektrolit tabiatiga va reaktsion qobiliyatga ta'siri, aktivlik koeffitsienta. Eritmaning ion kuchi. Chekli va kengaytirilgan Debay va Gyukkel qonunlari

Elektrogravimetrik analiz. Metodning qo'llanilish soxalari, qulayligi va kamchiliklari. Doimiy elektrod potentsiali va doimiy tok kuchida elementning ajralishi. Ichki elektroliz metodi, uni mikroelementlarni kontsentrlash va aniqlashda qo'llanilishi. Ishchi elektrodning doimiy potentsiali va doimiy tok kuchida simob va qattik elektrodlarni qo'llash orkali elementlarni ajratish. Elektrolitik ajratishda, kompleks hosil bo'lishdan foydalanish. O'ta sof materiallar analizida simob katodidan foydalanish.

3-amaliy mashg'ulot. Analitik ahamiyatga ega bo'lgan kompleks birikmalarning xossalari: barqarorlik, eruvchanlik, rangdorlik, uchuvchanlik. Barqarorlik konstantalari

Analitik ahamiyatga ega bo'lgan kompleks birikmalarning xossalari: barqarorlik, eruvchanlik, rangdorlik, uchuvchanlik. Barqarorlik konstantalari (umumiy bosqichli). Hosil bo'lish funktsiyasi. Kompleks birikmalar dissotsiatsiyasi. Kompleks birikmalar va ko'sh tuzlar. Kompleks birikmalar va organik reagentlarni har xil analiz usullarida ishlatilish imkoniyatlari

4-amaliy mashg'ulot. I, II, III guruh kationlari aralashmasi analizi

I, II, III guruh kationlari aralashmasi analizi I-guruh kationlarining xususiy va umumiy reagentlari, II-guruh kationlarning umumiy va xususiy reagentlari, III-guruh kationlarning umumiy va xususiy reagentlari analizi.

5-amaliy mashg'ulot. IV, V, VI guruh kationlari aralashmasi analizi.

IV, V, VI guruh kationlari aralashmasi analizi. IV-guruh kationlarining xususiy va umumiy reagentlari, V-guruh kationlarning umumiy va xususiy reagentlari, VI-guruh kationlarning umumiy va xususiy reagentlari analizi.

6-amaliy mashg'ulot. I, II, III guruh anionlari aralashmalari analizi. Quruq tuzlar aralashmasi analizi.

I, II, III guruh anionlari aralashmalari analizi. Quruq tuzlar aralashmasi analizi. I-guruh anionlarining xususiy va umumiy reagentlari, II-guruh anionlarning umumiy va xususiy reagentlari, III-guruh anionlarning umumiy va xususiy reagentlari analizi.

7-amaliy mashg'ulot. Massalar ta'siri qonuniga doir masalalar yechish.

Massalar ta'siri qonuniga doir masalalar yechish. Miqdoriy analiz, analiz hatoliklari. Tasodifiy, qo`pol hatoliklar.

8-amaliy mashg'ulot. Titrimetrik analiz metodlarining sinflanishi. Standart eritmalar. Kislota va asoslarni aniqlash

Titrimetrik analiz usullarining sinflanishi. Titrimetrik analizda ishlatiladigan reaktsiyalarga qo'yiladigan talablar. Kislota-asosli titrlash. Titrlash egrilari. Titrlash sakramasi va unga ta'sir etuvchi omillar. Titrlashning indikator xatoliklari. Oksidlanish-qaytarilish reaktsiyalari asosida titrlash. Titrlash xatoliklari. Amaliyotda ishlatilishi.

9-amaliy mashg'ulot. Titrimetrik analizda olingan natijalarning tasodifiy va qo'pol xato qiymatlarini matematik statistika usullari yordamida qayta ishlash va metrologik baholash.

Analizda olingan natijalarning tasodifiy va qo'pol xato qiymatlarini matematik statistika usullari yordamida qayta ishlash va metrologik baholash. Qo`pol va tasodifiy hatoliklarga doir masalalar yechish ko`nikmalarini hosil qilish.

10-amaliy mashg'ulot. Titrimetrik analizda natijalarni hisoblash. Eritmalar konsentratsiyalarini hisoblashga doir masalalar yechish

Permanganatometriya. Iodometriya. Bixromatometriya. Kompleksonometrik titrlash. Kompsonometrik titrlashning amaliyotda qo'llanilishi. Suvning qattiqligini aniqlash. Cho'ktirish reaktsiyasi asosida titrlash. Titrlash egriligini tuzish. Titrlash aniqdigiga adsorbilanish xodisasining ta'siri. Titrlash egrisi tavsifiga cho'kma eruvchanligi, kontsentratsiya va haroratning ta'siri. Indikatorlar. Titrlash xatoliklari. Indikatorlar. Titrlash xatoliklari. Folgard, Mor, Fayans usullari. Cho'ktirish reaktsiyasi asosida titrlashning amaliyotda ishlatilishi.

11-amaliy mashg'ulot. Fizik-kimyovay analizda natijalarni hisoblash.

Fizik-kimyovay analizda natijalarni hisoblash. UB, IQ larda olingan natijalar asosida fo`rmulalarni hisoblab toppish.

12-amaliy mashg'ulot. Elektrokimyoviy analiz usullarining umumiy tavsifi va sinflanishi. Elektrokimyoviy zanjir. Indikatorli elektrod va solishtirma elektrodlar. Elektrokimyoviy muvozanat potentsiali.

Elektrokimyoviy analiz usullarining umumiy tavsifi va sinflanishi. Elektrokimyoviy zanjir. Indikatorli elektrod va solishtirma elektrodlar. Elektrokimyoviy muvozanat potentsiali. Indikatorlar va ular turlari.

13-amaliy mashg‘ulot. Potentsiometriya. Potentsialni o’lchash. Nernst tenglamasi. Kulonometriya, Konduktometriya

Potentsiometriya. Potentsialni o’lchash. Nernst tenglamasi. Kulonometriya, Konduktometriya. Patensiometrik titrlash asosida olingan natijalarni solishtrish.

14-amaliy mashg‘ulot. Polyarogafik sifat va miqdoriy analiz. Amperometrik titrlash, usulning mohiyati. Indikatorli elektrodlar. Indikatorli elektrod potentsialini tanlash.

Polyarogafik sifat va miqdoriy analiz. Amperometrik titrlash, usulning mohiyati. Indikatorli elektrodlar. Indikatorli elektrod potentsialini tanlash. Polyaragramma natijalarini hisoblash.

15-amaliy mashg‘ulot. Xromatografik analiz usullari. Xromatografiyaning mohiyati. Harakatli va harakatsiz fazalar haqida tushuncha.

Xromatografik analiz usullari. Xromatografiyaning mohiyati. Harakatli va harakatsiz fazalar haqida tushuncha. Qofg`oz xromatagrafiyasi, kalonkali xromatografiya.

16-amaliy mashg‘ulot. Mass-spektrometriya usuli. Mass-spektrometriya usuli. Mass-spektrometriyaning noorganik moddalarning element tarkibini aniqlashda qo’llanilishi.

Mass-spektrometriya usuli, sinflanishi, analitik tavsiflari, ionlanish manbalari. Detektorlar; Faradey elektrometri va elektron ko’paytirgich. Organik va noorganik kimyoda qo’llaniladigan mass- spektrometrlarning farqi. Mass-spektrometriyaning noorganik moddalarning element tarkibini aniqlashda qo’llanilishi. Organik moddalarning molekulyar massasini topish.

17-amaliy mashg‘ulot. Titrimetrik analiz metodlarining sinflanishi. Standart eritmalar. Kislota va asoslarni aniqlash

Titrimetrik analiz metodlarining sinflanishi. Standart eritmalar. Kislota va asoslarni aniqlash Titrimetrik analiz usullarining sinflanishi. Titrimetrik analizda ishlatiladigan reaktsiyalarga qo’yiladigan talablar. Kislota-asosli titrlash. Titrlash egrilari. Titrlash sakramasi va unga ta’sir etuvchi omillar. Titrlashning indikator xatoliklari. Oksidlanish-qaytarilish reaktsiyalari asosida titrlash. Titrlash xatoliklari. Amaliyotda ishlatilishi.

III.2. AMALIY MASHG‘ULOT MAVZULARINI TAQSIMLANISHI

№	Amaliy mashg‘ulot mavzulari	Soati
	3- Semestr	
1	**Kimyoviy analizning metrologik asoslari.** O’lchash, o’lchash usullari va asboblari.	2
2	Elektrostatik kuchlarning elektrolit tabiatiga va reaktsion qobiliyatga ta’siri, aktivlik koeffitsienta. Eritmaning ion kuchi. Chekli va kengaytirilgan Debay va Gyukkel qonunlari	4
3	Analitik ahamiyatga ega bo’lgan kompleks birikmalarning xossalari: barqarorlik, eruvchanlik, rangdorlik, uchuvchanlik. Barqarorlik konstantalari	4
4	I, II, III guruh kationlari aralashmasi analizi	2
5	IV, V, VI guruh kationlari aralashmasi analizi	4
6	I, II, III guruh anionlari aralashmalari analizi. Quruq tuzlar aralashmasi analizi	4
7	Massalar ta’siri qonuniga doir masalalar yechish	2

8	Titrimetrik analiz metodlarining sinflanishi. Standart eritmalar. Kislota va asoslarni aniqlash	4
		26
4- Semestr		
9	Titrimetrik analizda olingan natijalarning tasodifiy va qo'pol xato qiymatlarini matematik statistika usullari yordamida qayta ishlash va metrologik baholash	4
10	Titrimetrik analizda natijalarni hisoblash. Eritmalar konsentratsiyalarini hisoblashga doir masalalar yechish	4
11	Fizik-kimyovay analizda natijalarni hisoblash	2
12	Elektrokimyoviy analiz usullarining umumiy tavsifi va sinflanishi. Elektrokimyoviy zanjir. Indikatorli elektrod va solishtirma elektrodlar. Elektrokimyoviy muvozanat potentsiali.	4
13	**Potentsiometriya.** Potentsialni o'lchash. Nernst tenglamasi. Kulonometriya, Konduktometriya	4
14	Polyarogafik sifat va miqdoriy analiz. Amperometrik titrlash, usulning mohiyati. Indikatorli elektrodlar. Indikatorli elektrod potentsialini tanlash	4
15	**Xromatografik analiz usullari.** Xromatografiyaning mohiyati. Harakatli va harakatsiz fazalar haqida tushuncha.	4
16	Mass-spektrometriya usuli. Mass-spektrometriya usuli. Mass-spektrometriyaning noorganik moddalarning element tarkibini aniqlashda qo'llanilishi.	4
17	Farmatseftikada, Sud-med ekspertizada, mineralogiyada va sanoat sohalarida Analitik kimyoning roli	4
	Jami	**34**
	Umumiy jami	**60**

IV. 2.LABORATORIYA MASHG'ULOTLAR MAVZULARINI

1-labaratoriya mashg'ulot. Laboratoriyada ishlashning umumiy qoidalari. Havfsizlik texnikasi. Kimyoviy idishlar, ularni ishga tayyorlash

Laboratoriyada ishlashning umumiy qoidalari. Havfsizlik texnikasi. Kimyoviy idishlar, ularni ishga tayyorlash.kimyo labaratoriya hnasini ko`zdan kechirish v ishchi holatga keltrish.

2-labaratoriya mashg'ulot. I guruh kationlari (K^+, Na^+, NH_4^+) ning analitik reaktsiyalari

I guruh kationlari (K^+, Na^+, NH_4^+) ning analitik reaktsiyalari. K^+, Na^+, NH_4^+ kationlarning xususiy reagentlari vaularning ajratish usullari.

3-labaratoriya mashg'ulot. II guruh kationlari (Ag^+, Pb^{2+}, Hg_2^{2+}) ning analitik reaktsiyalari

II guruh kationlari (Ag^+, Pb^{2+}, Hg_2^{2+}) ning analitik reaktsiyalari. Ag^+, Pb^{2+}, Hg_2^{2} kationlarining umumiy va xususiy reaksiyalari.

4-labaratoriya mashg'ulot. III guruh kationlari (Ba^{2+}, Sr^{2+}, Ca^{2+}) ning analitik reaktsiyalari

III guruh kationlari (Ba^{2+}, Sr^{2+}, Ca^{2+}) ning analitik reaktsiyalari. Ba^{2+}, Sr^{2+}, Ca^{2+} kationlarining umumiy va xususiy reaksiyalari.

5-labaratoriya mashg'ulot. I, II, III guruh kationlari aralashmasi analizi

I, II, III guruh kationlari aralashmasi analizi. Aralashmaning birinchi guruh kationi, ikkinchi guruh kationi , guruh reagentlari.

6-labaratoriya mashg'ulot. IV guruh kationlari (Al^{3+}, Cr^{3+5+}, Zn^{2+}, Sn^{2+4+}) ning analitik

reaktsiyalari

IV guruh kationlari (Al^{3+}, Cr^{3+5+}, Zn^{2+}, Sn^{2+4+}) ning analitik reaktsiyalari. Guruh kationlarining umumiy va xususiy reagentlari.

7-labaratoriya mashg‘ulot. V guruh kationlari (Fe^{2+}, Fe^{3+}, Mn^{2+}, Bi^{3+}, Mg^{2+}, Sb^{3+5+}) ning analitik reaktsiyalari

V guruh kationlari (Fe^{2+}, Fe^{3+}, Mn^{2+}, Bi^{3+}, Mg^{2+}, Sb^{3+5+}) ning analitik reaktsiyalari. Guruh kationlarining xususiy va umumiy reagentlari.

8-labaratoriya mashg‘ulot. VI guruh kationlari (Cu^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}, Hg^{2+}) ning analitik reaktsiyalari.

VI guruh kationlari (Cu^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}, Hg^{2+}) ning analitik reaktsiyalari. Guruh kationlarining xususiy va umumiy reagentlari.

9-labaratoriya mashg‘ulot. IV, V, VI guruh kationlari aralashmasi analizi.

IV, V, VI guruh kationlari aralashmasi analizi. IV – guruh xususiy va umumiy reagent, V – guruh xususiy va umumiy reagent, VI – guruh xususiy va umumiy reagent,

10-labaratoriya mashg‘ulot. I guruh anionlari (SO_4^{2-}, SO_3^{2-}, $S_2O_3^{2-}$, CO_3^{2-}, HPO_4^{2-}, $B_4O_7^{2-}$, SiO_3^{2-}) ning xususiy reaktsiyalari.

I guruh anionlari (SO_4^{2-}, SO_3^{2-}, $S_2O_3^{2-}$, CO_3^{2-}, HPO_4^{2-}, $B_4O_7^{2-}$, SiO_3^{2-}) ning xususiy reaktsiyalari Guruh anionlarining xususiy va umumiy reagentlari.

11-labaratoriya mashg‘ulot. Ikkinchi (Cl^-, Br^-, J^-) va uchinchi (NO_3^-, NO_2^-, CH_3COO^-) guruh anionlarining analitik reaktsiyalari

Ikkinchi (Cl^-, Br^-, J^-) va uchinchi (NO_3^-, NO_2^-, CH_3COO^-) guruh anionlarining analitik reaktsiyalari Guruh anionlarining xususiy va umumiy reagentlari

12-labaratoriya mashg‘ulot. I, II, III guruh anionlari aralashmalari analizi

I, II, III guruh anionlari aralashmalari analizi. Birinchi guruh anionlari, ikkinchi guruh anionlari, uchunchi guruh anionlarining guruh reagentlari.

13-labaratoriya mashg‘ulot. Quruq tuzlar aralashmasi analizi

Quruq tuzlar aralashmasi analizi. Quruq tuzlardan na`muna olish, mineralla moddalar na`munaga tayorlash.

14-labaratoriya mashg‘ulot. Gravimetriya. Idishlarni olish va ularni ishga tayyorlash. Tigellarni doimiy massaga keltirish. Texnik va analitik tarozilar bilan ishlashni o’rganish.

Gravimetriya. Idishlarni olish va ularni ishga tayyorlash. Tigellarni doimiy massaga keltirish. Texnik va analitik tarozilar bilan ishlashni o’rganish.. idish hajmini o`lchash va hatoligini tekshirish.

15-labaratoriya mashg‘ulot. Eritmadagi sulfat ionlari miqdorini aniqlash.

Eritmadagi sulfat ionlari miqdorini aniqlash. Bariy hloridning standart eritmasini tayorlash.

16-labaratoriya mashg‘ulot. Idishlarni olish va ularni ishga tayyorlash. Pipetka va byuretka bilan ishlash texnikasini o’rganish.

17-labaratoriya mashg‘ulot. 250 ml li o’lchov kolbasining sig’imini tekshirish. Taxminiy 0,1 n 500ml NaOH eritmasini tayyorlash.

250 ml li o’lchov kolbasining sig’imini tekshirish. Taxminiy 0,1 n 500ml NaOH eritmasini tayyorlash. Xlorid kislotaning 0,1 n 500ml eritmasini tayyorlash.

18-labaratoriya mashg‘ulot. Oksalat kislotaning 0,1 n standart eritmasini tayyorlash va

uning yordamida 0,1n NaOH eritmasini standartlash.
Eritmadagi kislota miqdorini aniqlash.

Oksalat kislotaning 0,1 n standart eritmasini tayyorlash va uning yordamida 0,1n NaOH eritmasini standartlash. Eritmadagi kislota miqdorini aniqlash.

19-labaratoriya mashg‘ulot. Ammoniy tuzlari tarkibidagi ammiak miqdorini aniqlash.

Ammoniy tuzlari tarkibidagi ammiak miqdorini aniqlash. Kuchli kislotalarning sandart eritmasini tayorlash.

20-labaratoriya mashg‘ulot. Xlorid kislotaning taxminiy 0,1n 500ml eritmasini va buraning 0,1n standart eritmasini tayyorlash. Xlorid kislotani buraning standart eritmasi bilan standartlash.

Xlorid kislotaning taxminiy 0,1n 500ml eritmasini va buraning 0,1n standart eritmasini tayyorlash. Xlorid kislotani buraning standart eritmasi bilan standartlash.

21-labaratoriya mashg‘ulot. Texnik natriy gidroksiddagi soda miqdorini aniqlash.

Texnik natriy gidroksiddagi soda miqdorini aniqlash.

22-labaratoriya mashg‘ulot. Oksidimetriya. 0,05n $KMnO_4$ eritmasini tayyorlash va uning aniq normalligini oksalat kislotaning standart eritmasi bilan aniqlash.

23-labaratoriya mashg‘ulot. Iodometriya. Natriy tiosulfatning 0,05n eritmasini tayyorlash va uni kaliy bixromatning standart eritmasi bilan standartlash.

Iodometriya. Natriy tiosulfatning 0,05n eritmasini tayyorlash va uni kaliy bixromatning standart eritmasi bilan standartlash.. kaliy bixromat eritmasini standrtini tayorlash.

24-labaratoriya mashg‘ulot. Kompleksonometriya EDTA ning 0,05n eritmasini tayyorlash va ruxning standart eritmasi bilan standartlash.

Kompleksonometriya EDTA ning 0,05n eritmasini tayyorlash va ruxning standart eritmasi bilan standartlash.ruxninin tahminiy 0,05n eritmasidan 500ml tayorlash.

25-labaratoriya mashg‘ulot. Eritmadagi metall ionlari miqdorini kompleksonometrik aniqlash
Eritmadagi metall ionlari miqdorini kompleksonometrik aniqlash.

Analitik kimyoda ishlatiladigan komplekslarning turlari. Analitik ahamiyatga ega bo’lgan kompleks birikmalarning xossalari: barqarorlik, eruvchanlik, rangdorlik, uchuvchanlik. Barqarorlik konstantalari (umumiy bosqichli). Hosil bo’lish funktsiyasi. Kompleks birikmalar dissotsiatsiyasi. Kompleks birikmalar va ko’sh tuzlar. Kompleks birikmalar va organik reagentlarni har xil analiz usullarida ishlatilish imkoniyatlari

26-labaratoriya mashg‘ulot. Cho’ktirish metodi yordamida titrlash. 0,05n simob (I)-nitrat eritmasini tayyorlash va uni kaliy xloridning standart eritmasi bilan standartdash. Eritmadagi xlor ionlari miqdorini aniqlash.

27-labaratoriya mashg‘ulot. Ionometriya. Kation yoki anionlarni ion-selektiv elektrodlar yordamida ionini aniqlash.

Aniqlash suvli yoki suvsiz erituvchilar muhitida kislota asosli titrlashga asoslangan. Kuchli kislota yoki ishqor eritmasi suvli, kuchsiz kislota yoki asos eritmasi suvsiz erituvchilar muhitida titrlanadi. Ayrim olingan kislota eritmasini titrlash uchun protofil erituvchi yoki ayrim olingan asosni titrlash uchun protogen erituvchi tanlansa, kuchsiz elektrolitlar kuchli elektrolitlarga aylanadi.

28-labaratoriya mashg‘ulot. Potentsiometriya. Kuchli yoki kuchsiz kislotalar va ishqorlar miqdorini aniqlash

Aniqlash suvli yoki suvsiz erituvchilar muhitida kislota asosli titrlashga asoslangan. Kuchli kislota yoki ishqor eritmasi suvli, kuchsiz kislota yoki asos eritmasi suvsiz erituvchilar muhitida titrlanadi. Ayrim olingan kislota eritmasini titrlash uchun protofil erituvchi yoki ayrim olingan asosni titrlash uchun protogen erituvchi tanlansa, kuchsiz elektrolitlar kuchli elektrolitlarga aylanadi.

29-labaratoriya mashg‘ulot. Oksredmetrik (yodni) yoki kompleksonometrik (Fe^{3+} ionini) potentsiometrik titrlash.

Oksredmetrik (yodni) yoki kompleksonometrik (Fe^{3+} ionini) potentsiometrik titrlash. Yodni aniqlash oksidlash-qaytarilish reaksiyasi, u natriy tiosulfatning standart eritmasi yordamida titrlanadi. Bu ishni bajarishda oxirgi nuqtani topishning hisoblash usulidan foydalanishko‘zdatutilgan.

30-labaratoriya mashg‘ulot. Konduktometriya. Sirka kislotani bevosita konduktometrik aniqlash,

Konduktometriya. Sirka kislotani bevosita konduktometrik aniqlash, NaOH ning 0,5n li 500ml eritmasidan tayorlash. Sirka kislotani titrlash.

31-labaratoriya mashg‘ulot. Amperometrik analiz.
Kaliy bixromat miqdorini aniqlash

Amperometrik analiz. Kaliy bixromat miqdorini aniqlash. Amperometrik titrlash, usulning mohiyati. Indikatorli elektrodlar. Indikatorli elektrod potentsialini tanlash. Bir va ikki indikatorli kutblangan elektrodlar yordamida amperometrik titrlashlar, titrlash egrilarining ko’rinishlari.

32-labaratoriya mashg‘ulot. Polyarografik analiz metodi. Aralashmadagi metallarni sifat va miqdoriy aniqlash

Polyaragrafik titrlash, usulning mohiyati. Indikatorli elektrodlar. Indikatorli elektrod potentsialini tanlash. Bir va ikki indikatorli kutblangan elektrodlar yordamida amperometrik titrlashlar, titrlash egrilarining ko’rinishlari.

33-labaratoriya mashg‘ulot. Fotometrik analiz metodlari.
Eritmadagi temir yoki nikel (III) ionlari miqdorini aniqlash.

Fotometrik analiz metodlari. Eritmadagi temir yoki nikel (III) ionlari miqdorini aniqlash. Fotometrik analizning mohiyati. Kyuvettalar bilan ishlash. KFK-2, KFK-3 aparatlar bilan ishlash.

34-labaratoriya mashg‘ulot. Eritmadagi temirning miqdorini spektrometrik usul bilan aniqlash

Eritmadagi temirning miqdorini spektrometrik usul bilan aniqlash. Kyuvettalar bilan ishlash. KFK-2, KFK-3 aparatlar bilan ishlash.

35-labaratoriya mashg‘ulot. Fotometrik titrlash.

Fotometrik titrlash mohiyati , Kyuvettalar bilan ishlash. KFK-2, KFK-3 aparatlar bilan ishlash.

IV. 2.LABORATORIYA MASHG’ULOTLAR TAQSIMOTI		
№	**laboratoriya mashg’ulotlar mavzulari**	**Soat**
3- Semestr		
1	Laboratoriyada ishlashning umumiy qoidalari. Havfsizlik texnikasi. Kimyoviy idishlar, ularni ishga tayyorlash	2
2	I guruh kationlari (K^+, Na^+, NH_4^+) ning analitik reaktsiyalari	2
3	II guruh kationlari (Ag^+, Pb^{2+}, Hg_2^{2+}) ning analitik reaktsiyalari	2
4	III guruh kationlari (Ba^{2+}, Sr^{2+}, Ca^{2+}) ning analitik reaktsiyalari	2
5	I, II, III guruh kationlari aralashmasi analizi	2
6	IV guruh kationlari (Al^{3+}, Cr^{3+5+}, Zn^{2+}, Sn^{2+4+}) ning analitik reaktsiyalari	2
7	V guruh kationlari (Fe^{2+}, Fe^{3+}, Mn^{2+}, Bi^{3+}, Mg^{2+}, Sb^{3+5+}) ning analitik reaktsiyalari	2

8	VI guruh kationlari (Cu^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}, Hg^{2+}) ning analitik reaktsiyalari	2
9	IV, V, VI guruh kationlari aralashmasi analizi	2
10	I guruh anionlari (SO_4^{2-}, SO_3^{2-}, $S_2O_3^{2-}$, CO_3^{2-}, HPO_4^{2-}, $B_4O_7^{2-}$, SiO_3^{2-}) ning xususiy reaktsiyalari	2
11	Ikkinchi (Cl^-, Br^-, J^-) va uchinchi (NO_3^-, NO_2^-, CH_3COO^-) guruh anionlarining analitik reaktsiyalari	2
12	I, II, III guruh anionlari aralashmalari analizi	2
13	Quruq tuzlar aralashmasi analizi	2
14	Gravimetriya. Idishlarni olish va ularni ishga tayyorlash. Tigellarni doimiy massaga keltirish. Texnik va analitik tarozilar bilan ishlashni o'rganish.	4
15	Eritmadagi sulfat ionlari miqdorini aniqlash.	4
16	Idishlarni olish va ularni ishga tayyorlash. Pipetka va byuretka bilan ishlash texnikasini o'rganish.	2
17	250 ml li o'lchov kolbasining sig'imini tekshirish. Taxminiy 0,1 n 500ml NaOH eritmasini tayyorlash.	2
18	Oksalat kislotaning 0,1 n standart eritmasini tayyorlash va uning yordamida 0,1n NaOH eritmasini standartlash. Eritmadagi kislota miqdorini aniqlash.	4
19	Ammoniy tuzlari tarkibidagi ammiak miqdorini aniqlash.	4
20	Xlorid kislotaning taxminiy 0,1n 500ml eritmasini va buraning 0,1n standart eritmasini tayyorlash. Xlorid kislotani buraning standart eritmasi bilan standartlash.	4
21	Texnik natriy gidroksiddagi soda miqdorini aniqlash.	4
	III semester bo'yicha jami	**54**
	4- Semestr	
22	Oksidimetriya. 0,05n $KMnO_4$ eritmasini tayyorlash va uning aniq normalligini oksalat kislotaning standart eritmasi bilan aniqlash.	4
23	Iodometriya. Natriy tiosulfatning 0,05n eritmasini tayyorlash va uni kaliy bixromatning standart eritmasi bilan standartlash.	4
24	Kompleksonometriya EDTA ning 0,05n eritmasini tayyorlash va ruxning standart eritmasi bilan standartlash.	4
25	Eritmadagi metall ionlari miqdorini kompleksonometrik aniqlash	4
26	Cho'ktirish metodi yordamida titrlash. 0,05n simob (I)-nitrat eritmasini tayyorlash va uni kaliy xloridning standart eritmasi bilan standartdash. Eritmadagi xlor ionlari miqdorini aniqlash.	4
27	Ionometriya. Kation yoki anionlarni ion-selektiv elektrodlar yordamida ionini aniqlash.	6
28	Potentsiometriya. Kuchli yoki kuchsiz kislotalar va ishqorlar miqdorini aniqlash	6
29	Oksredmetrik (yodni) yoki kompleksonometrik (Fe^{3+} ionini) potentsiometrik titrlash.	6
30	Konduktometriya. Sirka kislotani bevosita konduktometrik aniqlash	6
31	Amperometrik analiz. Kaliy bixromat miqdorini aniqlash	4
32	Polyarografik analiz metodi. Aralashmadagi metallarni sifat va miqdoriy aniqlash	4
33	Fotometrik analiz metodlari. Eritmadagi temir yoki nikel (III) ionlari miqdorini aniqlash	6
34	Eritmadagi temirning miqdorini spektrometrik usul bilan aniqlash	4
35	Fotometrik titrlash	4
IV semester bo'yicha jami		**66**

Hammasi	120

	V.1. MUSTAQIL TA’LIM VA MUSTAQIL ISHLAR
№	Mavzu nomi
1	Kationlar va anionlar tahlilida kompleks birikmalar va organik reagentlarning ahamiyati
2	Bufer eritmalar tarkibi va ishlatilish sohalari
3	Kreshkovning kislota assolar to‘g‘risidagi proton-elektron-gidrid konseptsiyasi
4	Analitik kimyoda organik reagentlarning qo’llanilishi
5	Eritmadagi temir (II) ni bixromatometrik aniqlash
6	Ajratish va kontsentrlashning kimyoviy, fizik-kimyoviy va fizikaviy usullari va kontsentrlashning ekstraktsion va xromatografik usullari.
7	Gaz, suyuqlik va gaz-suyuqlik xromatografik usullari.
8	Ion almashinish xromatografiyasi
9	Yupqa qavat xromatografiyasi.
10	Suyuqlik xromatografiyasi
11	Adsorbtsion suyuqlik xromatografiyasi.
12	Ekslyuzion xromatografiya.
	III semester bo’yicha
1	Elektrokimyoviy analiz metodlari
2	Polyarografik analiz metodi
3	Po’lat tarkibidagi nikel miqdorini fotometrik aniqlash.
4	Differentsial spektrofotometrii analiz
5	Atom-fluorestsent analiz metodi
6	Aromatik uglevodoroddar va geteroaromatik birikmalarning IQ spektrlari. Karbonil tutgan birikmalarning IQ spektrlarining analitik tahlili
7	Alkanlar, alkenlar va alkinlarning IQ spektrlaridagi xarakteristik polosalar
8	Yadro magnit rezonansi spektroskopiyasi
9	Uglerod-13 yadrosining spektroskopiyasi
10	Ikki o’lchamli korrelyatsion YaMR spektroskopiya. COSYspektrlari. Ikki o’lchamli COSYspektrining ko’rinishi
11	PMR spektroskopiyani organik kimyoda qo’llash: Bir o’lchamli YaMR spektrlarining asosiy xarakteristikalari

VI.1. KURS ISHINING TAVSIYA ETILGAN MAVZULARI	
№	Kurs ishining mavzulari
1	Sanoatda suv va uni yumshatish usullari
2	Qon guruxlarini aniqlash usullari
3	Komplekslarning analizda ishlatilishi
4	Kungaboqar mevasining kimyoviy taxlili
5	Natriyli selitra taxlili
6	O’zbekiston tuproqlari kimyoviy tarkibi
7	Neft tarkibini taxlil qilish
8	Antibiotiklarning kimyoviy taxlili
9	Tilla buyumlarning kimyoviy taxlili

10	Mineral suvlarning kimyoviy taxlili
11	Inson organizmidagi yod tanqisligini aniqlash usullari
12	Analitik kimyo tarixi
13	Titrimetrik analiz
14	Qon tarkibidagi gemoglabin miqdorini aniqlash usullari
15	Gravimetrik analiz
16	Xromatografiyaning ayrim usullari
17	Qon tarkibitdagi qand miqdorini aniqlash
18	Qo'ng'ir ko'mirning kimyoviy tarkibi
19	Kimyoviy ifloslangan reaktivlarni tozalash usullari
20	Kimyoviy analizda tarozilar
21	Konduktometrik analiz usullari
22	Bufer eritmalar va ularning analizda ishlatilishi
23	Ekstraktsiya usuli
24	Analiz uchun namunaolish
25	Potentsiometrik analiz

VI. FAN O'QITILISHINING NATIJALARI (SHAKLLANADIGAN KOMPOTENSIYALAR)

Fanni o'zlashtirish natijasida talaba:

-analitik kimyoning predmeti va vazifalari, reaksiyani amalga oshirishning shart-sharoitlari va bajarish usullari, namuna olish va uni analizga tayyorlash, analizning gravimetrik, titrimetrik, elektrokimyoviy va spektroskopik usullar haqida tasavvurga ega bo'lish;

-moddalarning sifat va miqdoriy tarkibini aniqlashni, analitik reaksiyalarni bajarish usullarini, nur yutilishi va chiqarilishiga asoslangan analiz usullarini optik va elektrokimyoviy analiz qonuniyatlarini bilish va ulardan foydalana olishi;

-aralashmalar tarkibidagi moddalarni sifat va miqdoriy tarkibini aniqlash, pH-metrlar, spektofotometrlar, fotoelektrofotometrlar, alangali fotometrlar, atom-absorbsion spektrometrlar, polyarograflar, amperometrlarda ishlash, miqdoriy analizning gravimetrik, titrimetrik, elektrokimyoviy va spektroskopik usullarini bilish va ulardan foydalanish ko'nikmalariga ega bo'lishi kerak.

VII. TA'LIM TEXNOLOGIYALARI VA METODLARI:

ma'ruzalar;
interfaol keys-stadilar;
mantiqiy fikrlash, tezkor savol-javoblar;
guruhlarda ishlash;
taqdimotlarni tayyorlash;
individual loyihalar;
jamoa bo'lib ishlash va ximoya qilish uchun loyihalar

VIII. KREDITLARNI OLISH UCHUN TALABLAR

Fanga ajratilgan kreditlar talabalarga har bir semestr bo'yicha nazorat turlaridan ijobiy natijalarga erishilgan taqdirda taqdim etiladi.

Fan bo'yicha talabalar bilimini baholashda oraliq (ON) va yakuniy (YaN) nazorat turlari qo'llaniladi. Nazorat turlari bo'yicha baholash: 5 – "a'lo", 4 – "yaxshi", 3 – "qoniqarli", 2 – "qoniqarsiz" baho mezonlarida amalga oshiriladi.

Oraliq nazorat har semestrda bir marta yozma ish shaklida o'tkaziladi.

Talabalar semestrlar davomida fanga ajratilgan amaliy (seminar) mashg'ulotlarda muntazam, har bir mavzu bo'yicha baholanib boriladi va o'rtachalanadi. Bunda talabaning amaliy (seminar) mashg'ulot hamda mustaqil ta'lim topshiriqlarini o'z vaqtida, to'laqonli bajarganligi, mashg'ulotlardagi faolligi inobatga olinadi.

SHuningdek, amaliy (seminar) mashg'ulot va mustaqil ta'lim topshiriqlari bo'yicha olgan baholari oraliq nazorat turi bo'yicha baholashda inobatga olinadi. Bunda har bir oraliq nazorat turi davrida olingan baholar o'rtachasi oraliq nazorat turidan olingan baho bilan **qayta o'rtachalanadi**.

O'tkazilgan oraliq nazoratlardan olingan baho **oraliq nazorat natijasi** sifatida qaydnomaga rasmiylashtiriladi.

Yakuniy nazorat turi semestrlar yakunida tasdiqlangan grafik bo'yicha **og'zaki** shaklda o'tkaziladi.

Oraliq (ON) va yakuniy (YaN) nazorat turlarida:

Talaba mustaqil xulosa va qaror qabul qiladi, ijodiy fikrlay oladi, mustaqil mushohada yuritadi, olgan bilimini amalda qo'llay oladi, fanning (mavzuning) mohiyatini tushunadi, biladi, ifodalay oladi, aytib beradi hamda fan (mavzu) bo'yicha tasavvurga ega deb topilganda – **5 (a'lo) baho**;

Talaba mustaqil mushohada yuritadi, olgan bilimini amalda qo'llay oladi, fanning (mavzuning) mohiyatini tushunadi, biladi, ifodalay oladi, aytib beradi hamda fan (mavzu) bo'yicha tasavvurga ega deb topilganda – **4 (yaxshi) baho**;

Talaba olgan bilimini amalda qo'llay oladi, fanning (mavzuning) mohiyatini tushunadi, biladi, ifodalay oladi, aytib beradi hamda fan (mavzu) bo'yicha tasavvurga ega deb topilganda – **3 (qoniqarli) baho**;

Talaba fan dasturini o'zlashtirmagan, fanning (mavzuning) mohiyatini tushunmaydi hamda fan (mavzu) bo'yicha tasavvurga ega emas, deb topilganda – **2 (qoniqarsiz) baho** bilan baholanadi.

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2. Под ред. Золотова Ю.А. Основы аналитической химии, Задачи и вопросы. 3 изд:. М.: Высщ. шк. 2020. 413 с.
3. Турабов Н.Т., Аналитик кимё. Тошкент. «Ношир», 2019, 438 б.
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QO`SHIMCHA ADABIYOTLAR

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AXBOROT MANBALARI

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Namangan davlat universiteti tomonidan ishlab chiqilgan va tasdiqlangan

- "Noorganik kimyo" kafedrasining 2023-yil, 26-iyundagi 11-sonli majlisida muhokama qilingan va tasdiqqa tavsiya etilgan.

- Tabiiy fanlar fakulteti kengashining 2023-yil, 29-iyundagi 12-sonli majlisida ma'qullangan va tasdiqqa tavsiya etilgan.

- NamDU O'quv-uslubiy kengashining 2023-yil, 29-iyuldagi 12-sonli majlisida muhokama qilingan va tasdiqlangan.

Fan /Modul uchun mas'ul:

M.A.Ziyayev– NamDU, Noorganik kimyo kafedrasi katta o'qituvchisi, PhD

Taqrizchi:

O.G.Abdullayev – NamDU, Noorganik kimyo kafedrasi dotsenti, kimyo fanlari nomzodi

NamDU o'uv-uslubiy boshqarma boshlig'i	X. Mirzaaxmedov
Tabiiy fanlar fakulteti dekani	A.Baratov
Nooranik kimyo kafedrasi mudiri	T.Sattarov
Tuzuvchi	M.Ziyayev

REPUBLIC OF UZBEKISTAN
MINISTRY OF HIGHER EDUCATION, SCIENCE AND INNOVATION

NAMANGAN STATE UNIVERSITY

"APPROVED"
Vice-rector for shooting affairs
D. Kholmatov
"__" _____ 2023

WORKING TRAINING PROGRAM BY SUBJECTANALYTICAL CHEMISTRY

2nd course, for full-time education

Field of knowledge:	**500000-Natural sciences, mathematics and statistics**
Field of study:	**530000- Physics and natural sciences**
Field of study:	**60530100-Chemistry (by types)**

Namangan - 2023

Subject/Module Code AK1420		Academic year 2023/2024	Semester 3-4	ECTS-Credits 10+10 = 20
Subject/Module Type Mandatory		Language of education English		Class hours perweek 3rd semester - *8 hours* 4th semester - *10 hours*
1	The name of the subject	Auditorium training (hours)	Independent study (hours)	Total load (hours)
	Analytical chemistry	270	330	600

I. The content of science

The purpose of teaching science - The purpose of teaching science is to provide students with in-depth knowledge of the theoretical foundations, basic concepts and methods of analytical chemistry, the elementary chemical structure of various objects in the environment, using information on methods that ensure qualitative and quantitative determination, and their application in practice. is to form the skill of achievement.

The task of the science is the subject and tasks of analytical chemistry, the conditions and methods of carrying out the reaction, taking a sample and preparing it for analysis, gravimetric, titrimetric, electrochemical and spectroscopic methods of analysis, determining the qualitative and quantitative composition of substances, methods of performing analytical reactions, light absorption and the laws of optical and electrochemical analysis of emission-based analysis methods, determining the qualitative and quantitative composition of substances in blends, working with pH-meters, spectrophotometers, photoelectric meters, flame photometers, atomic absorption spectrometers, polarographs and amperometers, gravimetric, titrimetric, electrochemical and spectroscopic quantitative analysis imparting knowledge on methods and others, acquiring practical skills and qualifications.

II. MAIN THEORETICAL PART (LECTURE TASKS)

II.I. The subject includes the following topics:

Topic 1. Analytical chemistry science, research scope, purpose and tasks.

The science of "Analytical Chemistry" studies the analysis of various complex objects (water, soil, air, alloys, geological, biological, environmental objects and soil). The purpose of the science is to develop the theoretical foundations and methods of chemical analysis, to develop and teach methods that provide qualitative and quantitative determination of the elementary chemical structure of various objects in the environment.

Topic 2. Metrological bases of chemical analysis.

Measurement, measurement methods and tools. The main principles and methods that ensure the accuracy of measurement results. Classification of errors in analysis: systematic, random, gross, absolute and relative errors. The main stages of the analysis. Transferring the sample to an analyzable form, disintegrating it under the influence of pressure and temperature.

Topic 3. The main types of chemical equilibrium.

Chemical reactions . Law of mass action. The main types of equilibrium in analytical chemistry: acid-base equilibrium, complex formation, oxidation-reduction, precipitation. Analytical and equilibrium concentration. Effect of electrostatic forces on electrolyte nature and reactivity, activity coefficient. The ionic strength of the solution. Finite and extended Debye and Hückel laws. The activity of the substance in the standard state. Equilibrium constants (thermodynamic, concentration and conditional) and their relationship.

Topic 4. Equilibrium in acid-base reactions.

Modern concepts of acids and bases. Brensted-Lowry theory. Basic and acid constants. Calculation of pH in protolytic solutions of various types. Factors affecting protolith strength. Buffer solutions and their properties. Buffer capacity. Calculation of pH in buffer systems .

Topic 5. Equilibrium in complex formation reactions.

Types of complexes used in analytical chemistry. Properties of analytically important complex compounds: stability, solubility, color, volatility. Stability constants (general phase). Derivative function. Dissociation of complex compounds. Complex compounds and multiple salts. Possibilities of using complex compounds and organic reagents in various analytical methods

Topic 6. Redox reactions.

Electrode potential, Nernst equation. Connection with standard and formal potentials. Direction of oxidation-reduction reactions. The mechanism of oxidation-reduction reactions. The main organic and inorganic oxidizing agents and reducing agents used in the analysis. Methods of pre-oxidation and reduction of the detectable element.

Topic 7. Precipitation reactions.

Solubility Multiplier and Solubility. Factors affecting them. Piecemeal and systematic precipitation

Topic 8. Quantitative analysis.

Quantitative analysis. The essence of the method. Direct and indirect detection methods. Errors in gravimetric analysis. General scheme of detection. Gravity, amount of precipitate and volume of solution. Amorphous and crystalline precipitates, conditions for obtaining large crystals. Homogeneous precipitation, formation of precipitation. Causes of sediment pollution. Classification of co-precipitation (adsorption, occlusion, isomorphism). Analytical scales, their types and sensitivities. Pulling technique. Examples of gravimetric analysis.

Topic 9. Titrimetric analysis methods.

Classification of titrimetric analysis methods. Requirements for reactions used in titrimetric analysis. Acid-base titration. Titration curves. Titration rate and factors affecting it. Indicator errors of titration. Titration based on oxidation-reduction reactions. Titration errors. Use in practice. Permanganatometry. Iodometry. Bichromatometry. Complexonometric titration. Practical application of compsonometric titration. Determination of water hardness. Titration based on precipitation reaction. Plotting a titration curve. The effect of the phenomenon of adsorption on the accuracy of titration. Effect of precipitate solubility, concentration and temperature on titration curve description. Indicators. Titration errors. Indicators. Titration errors. Folgard, Mor, Faience methods. Practical use of titration based on precipitation reaction.

Topic 10. Methods of optical analysis.

The spectrum of electromagnetic radiation: Its wave and corpuscular nature. Magnitudes characterizing electromagnetic radiation (wavelength, frequency, wave number, energy). Methods of molecular spectroscopy. Substance absorption of light by Bouguer-Behr-Lambert law. Additivity property of optical densities . Molar coefficient of light absorption. Deviation from the Bouguer-Behr-Lambert law and its reasons. Photometric reactions. Metrological characteristics of the spectrophotometric method. Lower limit of detectable concentration. Sensitivity. Selection (selectivity). Factors limiting selectivity. Spectral and physical-chemical interference. Fields of application of the spectrophotometric method. The structure, main parts and working principle of a simple photometer.

Topic 11. Atomic absorption spectrometry.

the atomic absorption spectrometry method. Absorption of optical rays by atoms. Optical density of atomic vapor. Electrothermal atomizer, structure and principle of operation. Advantages and disadvantages of electrothermal atomizer. Atomic absorption spectrometer. Optical (spectral) effects; background radiation, absorption of background radiation. Separation of the background signal. Methods of quantitative analysis; external standards (step chart), additional addition.

Topic 12. Atomic emission spectrometry.

of atomic emission spectrometry . Ground and excited states of atoms. Distribution of atoms into levels according to Boltzmann's law. Transitions between energy levels and formation of spectral lines. Selection rules. Quantities characterizing spectrum lines: position, intensity, half-width of the line. Metrological characteristics of the method: sensitivity, detectable concentration range, reproducibility of results. Fields of application.

Topic 13. Molecular luminescence.

Definition, types and difference of luminescence from other radiations. The main characteristics of molecular luminescence. Luminescence and fluorescence excitation spectra. Energetic and quantum yields of luminescence. Luminophores. Advantages and disadvantages of fluorescent analysis over spectrophotometric analysis. Chemiluminescence phenomenon and its use in analysis. Instruments and techniques used in molecular fluorescence analysis.

Topic 14. Methods of electrochemical analysis.

General description and classification of electrochemical analysis methods. Electrochemical circuit. Indicator electrode and reference electrodes. Electrochemical equilibrium potential. Phenomena observed in electrochemical circuits during current flow: voltage drop due to resistance, concentration and kinetic polarizations. Sensitivity and selectivity of electrochemical analysis methods.

Topic 15. Electrogravimetric analysis.

Electrogravimetric analysis. Fields of application, convenience and disadvantages of the method. Element separation at constant electrode potential and constant current. Internal electrolysis method, its use in concentration and determination of trace elements. Separation of elements with the use of mercury and solid electrodes at a constant potential of the working electrode and a constant current. Use of complex formation in electrolytic separation. Use of mercury cathode in the analysis of ultrapure materials.

Topic 16. Direct potentiometry.

potentiometry. Measuring potential. Nernst equation. Reversible and irreversible redox systems. Indicator electrodes. Ionometry, ion selective electrodes, classification. Application of ionometry in practice. Types of reactions used in potentiometric titrations. Determination of the amount of acid and alkali. Quantitative analysis of acid blends, polybasic acid and base blends.

Topic 17. Coulometry.

Theoretical foundations of coulometry. Faraday's laws. Methods of determining the amount of electricity. Direct and indirect coulometric analysis (coulometric titration). Internal and external generation of coulombometric titrant. Advantages and disadvantages of coulometric titration over other titrimetric methods. Practical application of coulometric titration.

Topic 18. Conductometry.

Direct and indirect conductometric methods. Low and high frequency conductometry. Conductometric joint (cell) and used electrodes. Conductometric titration curves and factors affecting them. Application of conductometric methods in practice.

Topic 19. Voltammetry.

Indicator electrode and reference electrodes. Advantages and disadvantages of mercury electrode. Acquisition and description of voltammetry curve (polarogram). The Ilkovich equation. The Ilkovich-Geirovsky equation for a polarographic wave. Half-wave potential and factors affecting it. Polyarophagic qualitative and quantitative analysis. Improved types of voltammetric analysis methods.

Topic 20. Amperometry.

Amperometric titration, the essence of the method. Indicator electrodes. Selection of indicator electrode potential. Amperometric titrations using one and two indicator polarized electrodes, views of titration curves.

Topic 21. Chromatographic analysis methods.

The essence of chromatography. Understanding of mobile and stationary phases. Classification of chromatographic methods according to the state of aggregation of mobile and stationary phases, separation mechanism and mechanism of operation. Optimization of chromatographic analysis. Chromatographic methods of qualitative and quantitative analysis

Topic 22. Mass spectrometry method.

Mass spectrometry method, classification, analytical descriptions, sources of ionization. Detectors; Faraday electrometer and electronic multiplier. The difference between mass spectrometers used in organic and inorganic chemistry . Application of mass spectrometry in determination of element composition of inorganic substances. Finding the molecular mass of organic substances.

Content of lectures and hours allocated to it		
No	**M preferences**	**Hour**
	3 - Semester	
1	Analytical chemistry science, research scope, purpose and tasks	2
2	Metrological bases of chemical analysis	2
3	Analysis errors	2
4	Sampling	2
5	The main types of chemical industry	2
6	Activity	2
7	Equilibrium in acid -base reactions	2
8	Buffer solutions	2
9	Equilibrium in complex formation reactions	2
10	Complex compounds and double salts	2
11	Redox reactions	2
12	Oxidizing and reducing agents used in analysis.	2
13	Deposition reashares	2
14	Be a club and systematic sinking	2
15	Quantitative analysis	2
16	Gravimetric analysis	2
17	A morph and crystalline precipitates	2
18	Analytical scales	2
19	Titrimetrical analysis methods	2
20	Acid - base titration	2
		40

4 - Semester		
21	Errors in acid - base titration	2
22	Titration based on oxidation-reduction reactions	2
23	Permanganatometry. Iodometria. Bixrheumatometry	2
24	Complexonometric titration	2
25	Determination of water hardness	2
26	Titration based on precipitation reaction	2
27	Indicators. Titration errors.	2
28	Folgard, Mor, Faience methods	2
29	Optical analysis methods	2
30	Laws of molecular spectroscopy	2
31	Methods of photometric analysis	2
32	Atomic absorption spectrometry	2
33	Atomic emission spectrometry	2
34	Molecular fluorescence analysis	2
35	Electrochemical analysis methods	2
36	Electrogravimetric analysis	2
37	Direct potentiometry	2
38	Coulometry	2
39	Conductometry	2
40	Voltammetry	2
41	Amperometry _	2
42	X romatographic analysis methods	2
43	Chromatographic methods of qualitative and quantitative analysis _ _	2
44	Mass - spectrometric method	2
45	Application of mass spectrometry	2
	Total	**50 hours**
	General hour:	**90 hours**

III.1. SUBJECTS OF PRACTICAL TRAINING

1st practical training. Metrological bases of chemical analysis. Measurement, measurement methods.

Measurement, measurement methods. There are basic principles and methods that ensure the accuracy of measurement results. A nest classification: systematic, physical, coarse, absolute and relative classification. The main stages of the analysis. Transferring the sample to an analyzable form, disintegrating it under the influence of pressure and temperature. Analytical scales, their types and sensitivities. Pulling technique. Examples of gravimetric analysis.

2nd practical training. Effect of electrostatic forces on electrolyte nature and reactivity, activity coefficient. The ionic strength of the solution. Finite and extended Debye and Hückel laws

Electrogravimetric analysis. Fields of application, convenience and disadvantages of the method. Element separation at constant electrode potential and constant current. Internal electrolysis method, its use in concentration and determination of trace elements. Separation of elements with the use of mercury and solid electrodes at a constant potential of the working electrode and a constant current. Use of complex formation in electrolytic separation. Use of mercury cathode in the analysis of ultrapure materials.

3rd practical training. Properties of analytically important complex compounds: stability, solubility, color, volatility.
Stability constants

Properties of analytically important complex compounds: stability, solubility, color, volatility. Stability constants (general phase). Derivative function. Dissociation of complex compounds. Complex compounds and multiple salts. Possibilities of using complex compounds and organic reagents in various analytical methods

4th practical training. Analysis of the blend of group I, II, III cations

Analysis of blends of group I, II, III cations, specific and general reagents of group I cations, general and specific reagents of group II cations, analysis of general and specific reagents of group III cations.

5th practical training. Analysis of the blend of group IV, V, VI cations.

Analysis of the blend of group IV, V, VI cations. Analysis of specific and general reagents of group IV cations, general and specific reagents of group V cations, general and specific reagents of group VI cations.

6th practical training. Analysis of blends of group I, II, III anions. Analysis of dry salt blends.

Analysis of blends of group I, II, III anions. Analysis of dry salt blends. Analysis of specific and general reagents of group I anions, general and specific reagents of group II anions, general and specific reagents of group III anions.

7th practical training. Solving problems related to the law of mass action.

Solving problems related to the law of mass action. Quantitative analysis, analysis errors. Accidental, gross mistakes.

8th practical training. Classification of titrimetric analysis methods. Standard solutions. Determination of acids and bases

Classification of titrimetric analysis methods. Requirements for reactions used in titrimetric analysis. Acid-base titration. Titration curves. Titration rate and factors affecting it. Indicator errors of titration. Titration based on oxidation-reduction reactions. Titration errors. Use in practice.

9th practical training. Random and gross error values of results obtained in titrimetric analysis using mathematical statistics methods processing and metrological evaluation.

Processing and metrological assessment of random and gross error values of the results obtained in the analysis using mathematical statistics methods. Formation of problem-solving skills related to gross and accidental mistakes.

10th practical training. Calculation of results in titrimetric analysis. Solving problems for calculating concentrations of solutions

Permanganatometry. Iodometry. Bichromatometry. Complexonometric titration. Practical application of compsonometric titration. Determination of water hardness. Titration based on precipitation reaction. Plotting a titration curve. The effect of the phenomenon of adsorption on the accuracy of titration. Effect of precipitate solubility, concentration and temperature on titration curve description. Indicators. Titration errors. Indicators. Titration errors. Folgard, Mor, Faience methods. Practical use of titration based on precipitation reaction.

11th practical training. Calculation of results in physical-chemical analysis.

Calculation of results in physical-chemical analysis. Calculation of formulas based on the

results obtained in UB, IR.

12th practical training. General description and classification of electrochemical analysis methods. Electrochemical circuit. Indicator electrode and reference electrodes. Electrochemical equilibrium potential.

General description and classification of electrochemical analysis methods. Electrochemical circuit. Indicator electrode and reference electrodes. Electrochemical equilibrium potential. Indicators and their types.

13th practical training. Potentiometry. Measuring potential. Nernst equation. Coulometry, Conductometry

Potentiometry. Measuring potential. Nernst equation. Coulometry, Conductometry. Comparison of results obtained on the basis of potentiometric titration.

14th practical training. Polyarophagic qualitative and quantitative analysis. Amperometric titration, the essence of the method. Indicator electrodes. Selection of indicator electrode potential.

Polyarophagic qualitative and quantitative analysis. Amperometric titration, the essence of the method. Indicator electrodes. Selection of indicator electrode potential. Calculation of polyaragram results.

15th practical training. Chromatographic analysis methods. The essence of chromatography. Understanding of mobile and stationary phases.

Chromatographic analysis methods. The essence of chromatography. Understanding of mobile and stationary phases. Caucasian chromatography, column chromatography.

16th practical training. Mass spectrometry method. Element of mass spectrometry of inorganic substances use in determining the composition.

Mass spectrometry method, classification, analytical descriptions, sources of ionization. Detectors; Faraday electrometer and electronic multiplier. The difference between mass spectrometers used in organic and inorganic chemistry . Application of mass spectrometry in determination of element composition of inorganic substances. Finding the molecular mass of organic substances.

17th practical training. Classification of titrimetric analysis methods. Standard solutions. Determination of acids and bases

Classification of titrimetric analysis methods. Standard solutions. Determination of acids and bases. Classification of titrimetric analysis methods. Requirements for reactions used in titrimetric analysis. Acid-base titration. Titration curves. Titration rate and factors affecting it. Indicator errors of titration. Titration based on oxidation-reduction reactions. Titration errors. Use in practice.

III.2 . DISTRIBUTION OF TOPICS OF PRACTICAL TRAINING

No	Topics of practical training	Hour
	3- Semester	
1	Metrological bases of chemical analysis. Measurement, measurement methods and tools.	2
2	Effect of electrostatic forces on electrolyte nature and reactivity, activity coefficient.	2
3	The ionic strength of the solution. Finite and extended Debye and Hückel laws	2
4	Properties of analytically important complex compounds: stability, solubility, color, volatility.	2

5	Stability constants	2
6	Analysis of the blend of group I, II, cations	2
7	Analysis of the blend of group III, IV, cations	2
8	Analysis of the blend of group V, VI cations	2
9	Analysis of blends of group I, II, III anions.	2
10	Analysis of dry salt blends	2
11	Solving problems related to the law of mass action	2
12	Classification of titrimetric analysis methods.	2
13	Standard solutions. Determination of acids and bases	2
		26
	4 - Semester	
14	Processing and metrological assessment of random and gross error values of results obtained in titrimetric analysis using mathematical statistical methods.	2
15	Calculation of results in titrimetric analysis.	2
16	Solving problems for calculating concentrations of solutions.	2
17	Calculation of results in physical-chemical analysis.	2
18	General description and classification of electrochemical analysis methods. Electrochemical circuit.	2
19	Indicator electrode and reference electrodes.	2
20	Electrochemical equilibrium potential.	2
21	Potentiometry.	2
22	Measuring potential. Nernst equation.	2
23	Coulometry, Conductometry.	2
24	Polyarophagic qualitative and quantitative analysis . Amperometric titration, the essence of the method.	2
25	Indicator electrodes. Selection of indicator electrode potential.	2
26	Chromatographic analysis methods.	2
27	The essence of chromatography. Understanding of mobile and stationary phases.	2
28	Mass spectrometry method.	2
29	Application of mass spectrometry in determination of element composition of inorganic substances.	2
30	Role of Analytical Chemistry in Pharmaceutical, Forensic, Mineralogy and Industry.	2
	Total	**34**
	Grand total	**60**

IV. 2 . SUBJECTS OF LABORATORY TASKS

1- laboratory task. General rules of work in the laboratory . Security technique. Chemical containers, their preparation for work

General rules of work in the laboratory . H security technique. Chemical containers, preparing them for work, inspecting the chemical laboratory equipment and bringing it into working condition.

2 - laboratory task. Analytical reactions of Group I cations (K^+, Na^+, NH_4^+) .

Analytical reactions of group I cations (K^+, Na^+, NH_4^+) . K^+, Na^+, NH_4^+ special reagents and separation methods of cations.

3 - laboratory task. of group II cations (Ag^+, Pb^{2+}, Hg_2^{2+}). analytical reactions

Analytical reactions of group II cations (Ag^+, Pb^{2+}, Hg_2^{2+}) . Ag^+, Pb^{2+}, Hg_2^{2} general and specific reactions of cations.

4 - laboratory task. III group cations (Ba^{2+}, Sr^{2+}, Ca^{2+}). analytical reactions

Analytical reactions of group III cations (Ba^{2+}, Sr^{2+}, Ca^{2+}) . Ba^{2+}, Sr^{2+}, Ca^{2+} general and specific reactions of cations.

5 - laboratory task. Analysis of the blend of group I, II, III cations

Analysis of the blend of group I, II, III cations. Cation of the first group of the blend, cation of the second group, reagents of the group.

6 - laboratory task. Analytical reactions of group IV cations (Al^{3+}, Cr^{3+5+}, Zn^{2+}, Sn^{2+4+})

of group IV cations (Al^{3+}, Cr^{3+5+}, Zn^{2+}, Sn^{2+4+}) . General and specific reagents of group cations.

7 - laboratory task. Analytical reactions of Group V cations (Fe^{2+}, Fe^{3+}, Mn^{2+}, Bi^{3+}, Mg^{2+}, Sb^{3+5+})

Analytical reactions of Group V cations (Fe^{2+}, Fe^{3+}, Mn^{2+}, Bi^{3+}, Mg^{2+}, Sb^{3+5+}) . Specific and general reagents of group cations.

8 - laboratory task. Analytical reactions of group VI cations (Cu^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}, Hg^{2+}).

of group VI cations (Cu^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}, Hg^{2+}). Specific and general reagents of group cations.

9th laboratory task. Analysis of the blend of group IV, V, VI cations.

Analysis of the blend of group IV, V, VI cations. IV - special and general reagent group, V - special and general reagent group, VI - special and general reagent group,

1 0 - laboratory task. Group I's compounds (SO_4^{2-}·SO_3^{2-}, $S_2O_3$2-, $CO_3$2-, HPO_4^{2-}, $B^4O_7^{2-}$, SiO_3^{2-}) x usual reactions.

Group I compound (SO_4^{2-}·SO_3^{2-}, $S_2O_3$2-, $CO_3$2-, HPO_4^{2-}, $B^4O_7^{2-}$, SiO_3^{2-}) special and general reagents of group ions.

11 - laboratory task. Analytical reactions of second (Cl^-, Br^-, J^-) and third (NO_3^-, NO_2^-, CH_3COO^-) group anions

of second (Cl^-, Br^-, J^-) and third (NO_3^-, NO_2^-, CH_3COO^-) group anions Specific and general reagents of group anions

12 - laboratory task. Analysis of blends of group I, II, III anions

Analysis of blends of group I, II, III anions. Group reagents of first group anions, second group anions, third group anions.

1 3 - laboratory task. Analysis of dry salt blend

Analysis of dry salt blend. Sampling of dry salts, preparation of samples of mineral substances.

1 4 - laboratory task. Gravimetry. Getting dishes and preparing them for work. Bringing the crucibles to constant mass.

Learning to work with technical and analytical scales.

Gravimetry. Getting dishes and preparing them for work. Bringing the crucibles to constant mass. Learning to work with technical and analytical balances. Measuring the volume of the container and checking its error.

15th laboratory task. Determination of the amount of sulfate ions in the solution.

Determination of the amount of sulfate ions in the solution. Preparation of barium chloride standard solution.

16 - laboratory task. Getting dishes and preparing them for work. Learning the technique of working with a pipette and burette.

17 - laboratory task. Pour into a 250 ml measuring cup.
Prepare a solution of approximately 0.1 n 500 ml of NaO H.

Pour into a 250 ml measuring cup. _ _ _ Prepare a solution of approximately 0.1 n 500 ml of NaO H. Prepare 500 ml of 0.1 N hydrochloric acid solution.

18 - laboratory task. Preparation of 0.1 n standard solution of oxalic acid and standardization of 0.1 n NaOH solution using it.
Determination of the amount of acid in the solution.

Preparation of 0.1 n standard solution of oxalic acid and standardization of 0.1 n NaOH solution using it. Determination of the amount of acid in the solution.

19th laboratory task. Determination of the amount of ammonia in ammonium salts.

Determination of the amount of ammonia in ammonium salts. Preparation of sandal solution of strong acids.

20 - laboratory task. Preparation of approximately 0.1N 500ml solution of hydrochloric acid and 0.1N standard solution of borax. Standardization of hydrochloric acid with a standard solution of borax.

Preparation of approximately 0.1N 500ml solution of hydrochloric acid and 0.1N standard solution of borax. Standardization of hydrochloric acid with a standard solution of borax.

Laboratory task 21. Determination of soda content in technical sodium hydroxide.

Determination of soda content in technical sodium hydroxide.

Laboratory task 22. Oxidometry . Preparation of 0.05n $KMnO_4$ solution and its apparent normality is the standard of oxalic acid determination with solution.

Laboratory task 23. Iodometry. Prepare a 0.05n solution of sodium thiosulfate and standardize it with a standard solution of potassium bichromate.

Iodometry. Preparation of 0.05N solution of sodium thiosulfate and standardizing it with standard solution of potassium bichromate. Preparation of standard solution of potassium bichromate.

Laboratory task 24. Complexonometry Preparation of 0.05n solution of EDTA and standardization with zinc standard solution.

Complex ionometry Preparation of 0.05n solution of EDTA and standardization with standard solution of zinc. Preparation of 500ml of approximate 0.05n solution of zinc.

Laboratory task 25. Complexonometric determination of the amount of metal ions in the solution
Complexonometric determination of the amount of metal ions in the solution.

Types of complexes used in analytical chemistry. Properties of analytically important complex compounds: stability, solubility, color, volatility. Stability constants (general phase). Derivative function. Dissociation of complex compounds. Complex compounds and multiple salts. Possibilities of using complex compounds and organic reagents in various analytical methods

Laboratory task 26. Titration using the precipitation method. Preparation of 0.05N mercury(I)-nitrate solution and standardizing it with potassium chloride standard solution. Determination of the amount of chlorine ions in the solution.

Laboratory task 27. Ionometry. Ion determination of cations or anions using ion-selective electrodes.

The determination is based on acid-base titration in aqueous or non-aqueous solvent media. A solution of a strong acid or base is titrated in an aqueous solvent, and a solution of a weak acid or base is titrated in a non-aqueous solvent medium. If a protophilic solvent is chosen to titrate a given acid solution or a protogenic solvent to titrate a given base, weak electrolytes become strong electrolytes.

Laboratory task 28. Potentiometry. Determination of the amount of strong or weak acids and bases

The determination is based on acid-base titration in aqueous or non-aqueous solvent media. A solution of a strong acid or base is titrated in an aqueous solvent, and a solution of a weak acid or base is titrated in a non-aqueous solvent medium. If a protophilic solvent is chosen to titrate a given acid solution or a protogenic solvent to titrate a given base, weak electrolytes become strong electrolytes.

Laboratory task 29. Oxidometric (iodine) or complexonometric (Fe^{3+} ion) potentiometric titration.

Oxidometric (iodine) or complexonometric (Fe^{3+} ion) potentiometric titration. Determination of iodine is a redox reaction, which is titrated using a standard solution of sodium thiosulfate. It is intended to use the calculation method of finding the last point in the performance of this work.

30 - laboratory task. Conductometry. Direct conductometric determination of acetic acid,

Conductometry. Direct conductometric determination of acetic acid, preparation from 500 ml of 0.5N solution of NaOH. Titration of acetic acid.

31 - laboratory task. Amperometric analysis. Determination of the amount of potassium bichromate

Amperometric analysis. Determination of the amount of potassium bichromate. Amperometric titration, the essence of the method. Indicator electrodes. Selection of indicator electrode potential. Amperometric titrations using one and two indicator polarized electrodes, views of titration curves.

Laboratory task 32. Method of polarographic analysis. Qualitative and quantitative determination of metals in the blend

Polarographic titration, the essence of the method. Indicator electrodes. Selection of indicator electrode potential. Amperometric titrations using one and two indicator polarized electrodes, views of titration curves.

Laboratory task 33. Photometric analysis methods. iron or nickel (III) ions in the solution.

Photometric analysis methods. Determination of the amount of iron or nickel (III) ions in the solution. The essence of photometric analysis. Working with cuvettes. Working with KFK-2, KFK-3 devices.

34 - laboratory task. Spectrometric determination of iron in solution to determine by method

Determination of the amount of iron in the solution by spectrometric method. Working with cuvettes. Working with KFK-2, KFK-3 devices.

35 - laboratory task. Photometric titration.

photometric titration, Working with cuvettes. Working with KFK-2, KFK-3 devices.

IV. 2 . DISTRIBUTION OF LABORATORY TASKS		
No	**topics of laboratory tasks**	**Hour**
	3- Semester	
1	General rules of work in the laboratory . H security technique. Chemical containers, their preparation for work	2
2	Analytical reactions of group I cations (K^+, Na^+, NH_4^+) .	2
3	of group II cations (Ag^+, Pb^{2+}, Hg_2^{2+})	2
4	Analytical reactions of group III cations (Ba^{2+}, Sr^{2+}, Ca^{2+})	2
5	Analysis of the blend of group I, II, III cations	2
6	of group IV cations (Al^{3+}, Cr^{3+5+}, Zn^{2+}, Sn^{2+4+})	2
7	Analytical reactions of Group V cations (Fe^{2+}, Fe^{3+}, Mn^{2+}, Bi^{3+}, Mg^{2+}, Sb^{3+5+})	2
8	of Group VI cations (Cu^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}, Hg^{2+})	2
9	Analysis of the blend of group IV, V, VI cations	2
10	Group I compounds (SO_4^{2-}, SO_3^{2-}, $S_2O_3$2-, $CO_3$2-, HPO_4^{2-}, $B^4O_7^{2-}$, SiO_3^{2-}) x usual reactions	2
11	of second (Cl^-, Br^-, J^-) and third (NO_3^-, NO_2^-, CH_3COO^-) group anions	2
12	Analysis of blends of group I, II, III anions	2
13	dry salt blends	2
14	Gravimetry. Getting dishes and preparing them for work. Bringing the crucibles to constant mass.	2
15	Learning to work with technical and analytical scales.	2
16	Sample preparation for determining the amount of sulfate ions in the solution.	2
17	Determination of the amount of sulfate ions in the prepared solution.	2
18	Getting dishes and preparing them for work. Learning the technique of working with a pipette and burette.	2
19	Pour into a 250 ml measuring cup.	2
20	Prepare a solution of approximately 0.1 n 500 ml of NaOH.	2
21	Preparation of 0.1 n standard solution of oxalic acid and standardization of 0.1 n NaOH solution using it.	2
22	Determination of the amount of acid in the standard solution.	2
23	To determine the amount of ammonia contained in ammonium salts, bringing the sample to a state of gravity	2
24	Determining the amount of ammonia in ammonium salts brought to a state of tension	2
25	Preparation of approximately 0.1N 500ml solution of hydrochloric acid and 0.1N standard solution of borax.	2
26	Standardization of hydrochloric acid with a standard solution of borax.	2
27	Determination of soda content in technical sodium hydroxide.	2
	Total for the III semester	**54**

	4 - Semester	
28	Oxidometry.	2
29	Preparation of 0.05n $KMnO_4$ solution.	2
30	Its exact normality as a standard of oxalic acid determination with solution.	2
31	Iodometry.	2
32	Prepare a 0.05n solution of sodium thiosulfate.	2
33	Standardize it with a standard solution of potassium bichromate.	2
34	Complexonometry.	2
35	Preparation of 0.05n solution of EDTA.	2
36	Standardization with zinc standard solution.	2
37	Complexonometric determination of the amount of metal ions in the solution.	2
38	Titration using the precipitation method.	2
39	Preparation of 0.05N mercury(I)-nitrate.	2
40	Solution and standardizing it with potassium chloride standard solution.	2
41	Determination of the amount of chlorine ions in the solution.	2
42	Ionometry.	2
43	Ion determination of cations or anions using ion-selective electrodes.	2
44	Potentiometry.	2
45	Determination of the amount of strong or weak acids and bases.	2
46	Oxidometric (iodine) potentiometric titration.	2
47	Complexonometric (Fe^{3+} ion) potentiometric titration.	2
48	Conductometry. Direct conductometric determination of acetic acid.	2
49	Amperometric analysis.	2
50	Determination of the amount of potassium bichromate.	2
51	Method of polarographic analysis. Qualitative and quantitative determination of metals in the blend.	2
52	Determining the quality of mixed metals.	2
53	Determination of the amount of mixed metals.	2
54	Photometric analysis methods.	2
55	Determination of the amount of iron (III) ions in the solution.	2
56	Determination of the amount of nickel (III) ions in the solution.	2
57	Determination of the amount of iron in the solution by spectrometric method.	2
58	Photometric titration.	2
59	Gas, purification and gas-sleep chromatographic analysis methods.	2
60	Analysis of IR spectra.	
Total for the IV semester		**66**
All of lessons		**120**

	INDEPENDENT WORK
No	Subject Name
1	Importance of complex compounds and organic reagents in the analysis of cations and anions
2	Composition of buffer solutions and areas of use
3	Kreshkov's proton-electron-hydride concept of acid-bases
4	Application of organic reagents in analytical chemistry
5	Bichromatometric determination of iron (II) in solution
6	Chemical, physicochemical and physical methods of separation and concentration and extraction and chromatographic methods of concentration.
7	Gas, liquid and gas-liquid chromatographic methods.
8	Ion exchange chromatography
9	Thin layer chromatography.
10	Liquid chromatography
11	Adsorption liquid chromatography.
12	Exclusion chromatography.
	on the III semester
1	Electrochemical analysis methods
2	Polarographic analysis method
3	Photometric determination of nickel content in steel.
4	Differential spectrophotometric analysis
5	A tom-fluorescent analysis method
6	IR spectra of aromatic hydrocarbons and heteroaromatic compounds. Analytical analysis of IR spectra of compounds containing carbon
7	Characteristic bands in the IR spectra of alkanes, alkenes and alkynes
8	Nuclear magnetic resonance spectroscopy
9	Spectroscopy of carbon-13 nucleus
10	Two-dimensional correlation NMR spectroscopy. COZY spectra. View of the two-dimensional COZY spectrum
11	Applications of PMR spectroscopy in organic chemistry: Basic characteristics of one-dimensional NMR spectra

	V I .1. RECOMMENDED COURSE TOPICS
No	Topics of the course work
1	Water in industry and its mitigation methods
2	Methods of determining blood groups
3	Use of complexes in analysis
4	Chemical analysis of sunflower fruit
5	Analysis of sodium nitrate
6	Chemical composition of the soils of Uzbekistan
7	Oil content analysis to do
8	Chemical analysis of antibiotics
9	Chemical analysis of gold articles
10	Chemical analysis of mineral waters
11	Methods of determining iodine deficiency in the human body
12	History of Analytical Chemistry
13	Titrimetric analysis
14	Methods for determining the amount of hemoglobin in blood
15	Gravimetric analysis
16	Chromatography some methods

17	Determining the amount of sugar in the blood
18	Chemical composition of brown coal
19	Methods for cleaning chemically contaminated reagents
20	Scales in chemical analysis
21	Methods of conductometric analysis
22	Buffer solutions and their use in analysis
23	E k st rak ts iya method
24	Sampling for analysis
25	Analysis of the potentiometer

VI. RESULTS OF SCIENCE EDUCATION (DEVELOPED COMPETENCES)

As a result of mastering the subject, the student:

- to have an idea about the subject and tasks of analytical chemistry, the conditions and methods of reaction, taking a sample and preparing it for analysis, gravimetric, titrimetric, electrochemical and spectroscopic methods of analysis;
- to know and be able to use them to determine the qualitative and quantitative composition of substances, methods of performing analytical reactions, methods of analysis based on light absorption and emission, optical and electrochemical analysis;
- to determine the qualitative and quantitative composition of substances in blends, to work with pH meters, spectrophotometers, photoelectrophotometers, flame photometers, atomic absorption spectrometers, polarographs, ammeters, to know and use gravimetric, titrimetric, electrochemical and spectroscopic methods of quantitative analysis should be.

VII. EDUCATIONAL TECHNOLOGIES AND METHODS:

lectures;
interactive case studies;
logical thinking, quick questions and answers;
work in groups;
preparation of presentations;
individual projects;
projects for teamwork and protection

VII I. _ REQUIREMENTS FOR OBTAINING LOANS

Credits allocated to science are provided to students in case of positive results in each semester.

Intermediate (IC) and final (FC) control types are used to assess students' knowledge of science. Evaluation by control types: 5 - "excellent", 4 - "good", 3 - "satisfactory", 2 - "unsatisfactory" assessment criteria.

Midterm control is conducted once every semester in the form of written work.

semesters , students are regularly evaluated and graded on each subject in practical (seminar) training sessions . In this case, the student's timely and complete completion of practical (seminar) training and independent educational tasks, and his activity in training are taken into account.

In addition, the grades received for practical (seminar) training and independent educational tasks are taken into account in the assessment of the type of interim control. In this case, the average of the grades obtained during each intermediate control type **is re-averaged with the grade obtained from the intermediate control type** .

The assessment obtained from the intermediate controls is registered as **a result of the intermediate control .**

The final control type is conducted **orally at the end of the** semesters according to the approved schedule .

In intermediate (IC) and final (FC) control types :

A student makes independent conclusions and decisions, can think creatively, observes

independently, can apply the acquired knowledge in practice, understands the essence of science (topic), knows, can express, tell, and is considered to have an idea about science (topic) - **5 (excellent) grades**;

When the student conducts independent observation, can apply the acquired knowledge in practice, understands the essence of the science (subject), knows, can express, tell and has an idea about the science (subject) - 4 (good) **grade**;

When the student is able to apply the acquired knowledge in practice, understands the essence of science (topic), knows, can express, tell and has an idea about science (topic) - 3 (**satisfactory) grade**;

When it is considered that the student has not mastered the science program, does not understand the essence of the science (topic) and does not have an idea about the science (topic), he is evaluated with **a grade of 2 (unsatisfactory)**.

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2. Pod ed. Zolotova Yu.A. Basic analytical chemistry, Zadachi and voprosy. 3 izd: M.: Vysshch. shk. 2020. 413 p.
3. Turabov N.T., Analytical chemistry. Tashkent. "Publisher", 2019, 438 p.
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ADDITIONAL LITERATURE

1. Faizullayev O. Analytical chemistry. Tashkent, "Yangi asr avlodi", 2006, 488p.
2. Faizullayev O. Turabov N., Ro'ziev E., Kuvatov A., Muhamadiev N. Analytical chemistry. Laboratory training. Tashkent, "Yangi asr avlodi", 2006, 448 p.
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7. Christian G., Binom M. // Analytic chemistry, volume 1, 2009. 623 p.
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SOURCES OF INFORMATION

http://www.chem.msu.ru
http://www.rushim.ru
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- Approved and recommended for approval at the meeting No. 12 of the Faculty of Natural Sciences, 2023, "29"- 06.

- It was discussed and approved at the session No. 12 of NamDU Educational and Methodological Council of 2023 in "11"- 07.

Responsible for Subject/Module:

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Reviewer:
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Head of research-methodological department of NamSU: **Kh. Mirzaakhmedov**

Dean of the Faculty of Natural Sciences: **A. Baratov**

Head of Nooranik Chemistry Department: **T. Sattarov**

Compiled by: **M. Hakimov**

Tests

1. What law is the basis of titrimetric analysis?

A. Law of equivalents.

B. Law of constancy of composition.

C. Law of molar relations.

D. Law of weight relations.

2.Concentration titrants Vis expressedvarious ways,pick upDefinition of molar concentration expression.

A. Mass of the substance being determined in grams, interacting with 1 ml of titrant B. Number of moles of the substance in 1 liter of solution.

C. Mass of the substance in grams in 1 dm3 of solution.

D. The number of equivalents of a dissolved substance in 1 liter of solution.

3. Specify standards for acid-base titration.

1.Na2CO3 2.NaCl 3.Na_2B4O7 10H2O 4.K_2Cr2O7 5.H_2C2O4 2H2O

6

.

N

a

2

C

2

O

4

A

.

1

,

3

,

5

B. 2,3,4

S. 1,2,3

D. 4,5,6.

4. Indicate substances whose solutions can be used as titrants in acidometry.

1.H2SO4 2.HCl 3.NaOH 4.CON 5.NN_4HE 6.N_2C2O4 2H2O A. 3.4

B. 5.6

S. 1,2

D. 2.3

5. Specify the calculation formula for a sample for preparing a standard solution H2C2O4 2H2O

A.
N
E/
W
10
00
B.
W
E/
N
10
00
S.
E
10
00/
W
N
D.
W
N
E/
10
00

6. Requirements for standards. A. All of the above

B. The standard must have a large molar mass

C. Constant composition corresponding to a certain formula

D. Should be easy to clean by crystallization. Not absorb moisture and CO2 from the air

7. Indicate substances and solutions that can be used as titrants in the acidometry method.

1.NaOH 2.HCl 3.NH_3·H2O
4.H_2SO4
5.Na2CO3A. 2.4

B. 1,2

S. 2,3

D. 3.4

8. The meaning of the law of equivalents.

1. Substances react in multiple molar ratios 2. Substances react in equal molar ratios 3. Solutions of equal molarity react in equal volumes 4. Solutions of equal normality react in equal volumes

9. In titrimetric methods of analysis, depending on the required accuracy, different utensils are used. Select the appropriate measuring utensils for the cases below.

1. Preparation of a certain volume of solution of exact concentration. 2.Measuring small volumes of auxiliary materials.

3. Adding titrant to the analyzed solution (titration) 4. Measuring the volume of the test solution for analysis

A. volumetric flasks V.
graduated cylinders With. pipettes d. burettes

A. 1a, 2c, 3d, 4s

B. 1d,2a,3v,4s

S. 1a, 2c, 3c, 4d

D. 1s, 2c, 3s, 4d

10. Formula for calculating the true volume of a measuring container at a given temperature. A, B, C are correction factors, m is the mass of water in the nominal volume.

A.
m+∑ABC·V
nomin./1000
B. m.dH2O

C. m+dH2O

D. dH2O/m

11.To carry out analysis using the titrimetric method, you must have: A. Measuring glassware for accurately measuring volumes

B. Indicators or devices for fixing the end point of titration

C. Titrants

D. All of the above

12. Preparation of 300 ml of 0.1 N sulfuric acid solution from a more concentrated solution.

A. The calculated volume of acid is measured with a cylinder, poured into a flask and topped up with distillate to 300 ml. By water

B. The calculated volume of acid is measured with a cylinder, poured into a volumetric flask, diluted with water to 300 ml, stirred

C. The calculated volume of acid is measured with a pipette, transferred to a flask, diluted with water to 300 ml, mixed

D. The calculated volume of acid is measured with a pipette and transferred to a measuring cup flask,d

13. Standardization of prepared 0.1 N caustic alkali solution.

A. Titrate a sulfuric acid solution with an alkali solution, methyl orange indicator B. Titrate a sorrel acid solution with an alkali solution, phenolphthalein indicator C. Titrate an alkali solution with a sorrel acid solution, methyl orange indicator D. Titrate an alkali solution with a sulfuric acid solution, methyl orange indicator.

B. Calculation of N and T of NaOH solution is carried out using formulas. A. NSh=VK · ESh/VSh TSh=NK · ESh /1000

B. NSh = VSh · ESh / 1000 TSh = NSh · 1000/ ESh S. NSh = NK · VK/VSh T_{SCH}= NSh · ESh /1000 D. NSh = NK · VSh / VK T_{SCH}= NSh · ESh /1000

14. Requirements for standards.

A. The standard must have a large molar mass

B. Constant composition corresponding to a certain formula

C. Must be easily cleaned by crystallization. Not absorb moisture and CO2 from the air E. All of the above

15. Specify the definition of the concept of equivalence point, this is:
A. the moment during titration when the amount titrant equivalent quantitya ce

B. pH value at which titration with this indicator is completed

C. the pH value at which a visible change in the color of the indicator occurs. D. moment during titration when the pH of the solution is 7

16. What indicators can be used when titrating 0.1 N HCl and 0.1
1.Methyl orange rT-4 2.Phenolphthalein rT-9 3. Thymol blue pT=1.54. Thymolphthalein pT-10.9
5.Methyl yellow pT=1.75 6.Litmus pT=7

A. 1,2,3,4

B. 1,3,5,6

S. 2,4,5,6

D. 1,2,6

18. Provide a calculation formula for calculating the volume of a stronger NaOH solution required to prepare 300 ml of a 0.1 N solution.
A. V=W·N·E·100/1000·d·C% C% percentage concentration B. V=W·E·S%·100/1000·d·N
d density

C. V=d·1000·C%/W·N·E W volume 300 ml

D. V=W·N·E·d·100/1000·C% N normality 0.1 gEq/L

19. The meaning of the law of equivalents.
1. Substances react in multiple molar ratios 2. Substances react in equal molar ratios 3. Solutions of equal molarity react in equal volumes 4. Solutions of equal normality react in equal volumes

5. Solutions of equal percentage concentration react in equal volumes A. 3

B. 1.4

S. 1.5

D. 2.4

20. Standardization of the prepared 0.1 N H2SO4 solution. A. titrate NaOH with H2SO4 solution, methyl orange indicator
B. titrate NaOH solution with H2SO4 solution, phenolphthalein indicator C. titrate H2SO4 with NaOH solution, phenolphthalein indicator

D. titrated with H2SO4 with NaOH solution, methyl orange indicator

21. What indicators can be used when titrating 0.1 N HCl 0.1 N
1.Methyl orange rT-4 2.Phenolphthalein rT-9 3. Thymol blue pT=1.54. Thymolphthalein pT-10.9
5.Methyl yellow pT=1.75 6.Litmus pT=7

A. 1,2,6

B. 1,2,3,4

S. 1,3,5,6

D. 2,4,5,6

22. Specify the definition of the concept of equivalence point, this is:
A. pH value at which titration with a given indicator is completed B. pH value at which titration occurs

C. moment during titration when the amount titrant equivalent amount of a certain substance, a visible change in the color of the indicator.

D. moment during titration when the pH of the solution is 7

23. What indicator error occurs when titrating acetic acid with sodium hydroxide using the indicator methyl orange (pT=4)? pH in exact eq. equals 9
A. Basic B. Acid C. Hydrogen

D. Hydroxide

24. Determination of the mass of H2SO4 and H3BO3 in their joint presence is carried out as follows.

A. The mixture is titrated with NaOH and methyl orange indicator. In this case, H_2SO_4 is titrated, then glycerol is added and H_3BO_3 is titrated with the indicator phenolphthalein.

B. The mixture is titrated with a NaOH solution using phenolphthalein as an indicator, while H_2SO_4 is titrated and then glycerol is added and H_3BO_3 is titrated with methyl orange as an indicator.

C. The mixture is titrated with NaOH and methyl orange indicator, titrated with H_2SO_4, then phenolphthalein is added and titrated with H_3BO_3

E. The mixture is titrated with NaOH using the phenophthalein indicator, while H_2SO_4 is titrated. Then methyl orange is added and titrated with H_3BO_3.

25. Indicate in which case a hydroxide titration error occurs.

A. When undertitrating acids or overtitrating bases.

B. When weak acids are not titrated with alkali

C. When weak bases are not titrated with acid

D. When undertitrating alkalis and overtitrating acids with alkali

26. Indicate in what environment the indicator m.o. has the following colors. 1.In water (neutral environment)

a.red d. raspberry

2.In acid v.yellow e. colorless

3.In alkaline s.orangeA. 1d, 2a, 3e

B

.

1

c

,

2

c

,

3

e

C

.

1

c
,

2
a
,

3
c

D
.

1
e
,

2
c
,

3
c

27. Determine the equivalent of borax using the following reaction:
$$Na_2B_4O_7+2HCl+5H_2O\leftrightarrow 2NaCl+4H_3BO_3$$

A. $E_b=M/2$

B
.
E
b
u
r
a
=
M
/
5

S
.
E

b
=
M
/
4

D. Eb=M/3

28. Determination of the mass of H2SO4 is carried out using the following method:

1.Alkalimetry 2.Acidimetry 3.Direct4.Deputy 5.Reverse titration

A. 2.3

B. 1.3

S. 1.5

D. 1.4

29. Determination of the masses of H2SO4 and H3BO3 is carried out by the method: 1. Alkalimetry, 2. Acidimetry, 3.Ksammost, 4. Substitute,5.Back titration.

A. 1.3

B. 1.5

S. 1.4

D. 2.3

30. Acid-base titration jump. 1. A sharp change in pH at the equivalence point

2. Graphic representation of pH changes during the titration process. 3.0.1% of the substance is not titrated

Handout

1. **Analytical chemistry**–This is a branch of chemical science that develops, on the basis of the fundamental laws of chemistry and physics, fundamental methods and techniques for qualitative and quantitative analysis of the atomic, molecular and phase composition of matter.
2. **Substance analysis method**is a brief definition of the principles underlying the analysis of matter.
3. **Method of analysis**–a detailed description of all conditions and operations that ensure the regulated characteristics, including the accuracy and reproducibility of the analytical results.
4. **Qualitative chemical analysis**–This is the detection of chemical elements, ions, atoms, atomic groups, molecules in the analyzed substance.
5. **Quantitative chemical analysis**–This is a determination of the quantitative composition of a substance, i.e. establishing the number of chemical elements, ions, atoms, atomic groups, molecules in the analyzed substance.
6. **Instrumental (physical and physicochemical) methods of analysis**–These are methods based on the use of relationships between the measured physical properties of substances and their qualitative and quantitative composition.
7. **Analytical reaction**–chemical transformation of the analyzed substance under the action of a chemical reagent with the formation of products with noticeable analytical characteristics.
8. **Fractional analysis**– detection of an ion or substance in an analyzed sample using a specific reagent in the presence of all components of the sample.
9. **Systematic analysis**– provides for the separation of a mixture of analyzed ions into analytical groups with subsequent detection of each ion.
10. **Specific reagents and reactions**allow detection of an ion or substance in the presence of others, i.e. in a complex mixture.
11. **Selective reagents and reactions**allow the detection of multiple substances or ions.
12. **Group reagents and reactions**allow the detection of ions of a specific analytical group.
13. **The sensitivity of analytical reactions determines the possibility of detecting a substance (ions, molecules) in an extremely dilute solution.**
14. **Detection limit (opening minimum (in μg)**is the smallest mass (in

mcg) of the analyte that can be unambiguously revealed by a given analytical reaction in the minimum volume of an extremely dilute solution.

15. **Limit concentration Clim (Cmin)**– the lowest concentration at which the analyte can be detected in the solution of a given analytical reaction, expressed in g/ml.
16. **Limit dilution Vlim**– the maximum volume of solution in which one gram of a given substance (ion) can be unambiguously detected. The maximum dilution is expressed in units of ml/g.

Quantitative principles:

Measuring the amount of product of a chemical reaction

Measuring the volume of reagent consumed in a chemical reaction.

Measurement physical properties of determining substances or products of their replacement.

Right– absolute error, i.e. the difference between the arithmetic mean and the real value.

Systematic error– due to inaccuracy of equipment and measuring utensils.

Random errors – sharp difference result from set

Reproducibility – deviation individual measurements from the

Confidence interval– closeness of the arithmetic mean value to the true value.

Titrant– working solution with which the test solution is titrated.

Standard solution– a solution of a setting substance with a precise concentration, with which the titrant solution titer is established.

Normalization factor– the ratio of the true equimolar concentration to the theoretical (deciequimolar ~ 0.1 g*eq/l).

Fixanal- an ampoule with a precise amount of a substance, which, when dissolved in a liter volumetric flask, produces a standard solution.

Alkalimetry– titration of acids or acidic solutions salts alkali solutions.

Acidimetry– titration of alkalis or basic salts with acid solutions

Indicators – substances capable of changing their color in a narrow pH range, above and below which the indicator has sharply different colors.

pH interval changes in the color of the indicator - a period of time pH above which the indicator has sharply different colors.

pTInd – titration index – pH value numerically equal to the pK of the indicator at which the color of the indicator changes, which corresponds to the end point of titration (C.T.T)

Acid-Base Titration Curve – graphical dependence of the pH of the titrated solution (ordinate) on the amount of

added titrant (abscissa).

Titration jump – a sharp change in pH near t.e.

Redoximetry indicators(redoxtitration) - substances that sharply change color due to the formation of chromophore groups at a certain value of the equilibrium redox potential of the titrated solution.

Specific indicator– an indicator that sharply changes color due to the specific interaction of a titrant with an oxidizing or reducing agent.

Redox titration curve- curve of the dependence of the equilibrium redox potential of the titrated solution along the ordinate on the volume of the added titrant of the oxidizing agent (or reducing agent) along the abscissa.

Titration jump on the redoximetric titration curve- this is a sharp and significant change in the value of the equilibrium potential on the titration curve.

Permanganatometry– determination of reducing agents by a direct, indicator-free titration method, a titrated solution of potassium permanganate.

Permanganometric titration condition.

Sulfuric acid medium pH≈1-2.

Temperature – room temperature (exception – when titrating H2CrO4, heating is required at the beginning of titration).

The CTT is recorded without an indicator, with the appearance of a light pink color in the titrated solution.

Water oxidability– the number of milligram equivalents of reducing agents contained in 1 dm 3 of test water.

Based on the degree of oxidation, water quality is divided into:

Precipitation titration– titration of a solution of the analyte with a titrant and a precipitant to form a precipitate.

Argentometry– titration of halides with silver nitrate.

Thiocyanatometry– titration of silver nitrate with ammonium thiocyanate.

Mercurometry– titration of halogens with a solution of mercury (II) nitrate

Curve offensive titration – sharp change indicatorth

Jump in the precipitation titration curve– a sharp change in the concentration of the titrated ion near the equivalence point.

Precipitation indicator– a substance whose solution forms a colored precipitate with the analyte at the equivalence point.

Metallochromic indicator - a substance or ion formed by an excess of the titrant of the precipitant, a product that has a color.

Adsorption indicators– special electrolytes, the anions of which, when

adsorbed on the micelle of the precipitate, become polarized and change color.

Optimal indicator concentration– such an indicator concentration at which it is triggered within the titration jump.

Complexometry -titrimetric determination of 2x, 3x charged metal ions with a solution of polydentate ligand complexone III (trilon B), forming strong but soluble complexes

Complexometric titration curve- graphical dependence of the concentration of the titrated ion on the volume of added Trilon B titrant.

Metallochromic indicator– an indicator that changes its color upon formation of a complex with the analyzed metal ion.

Interval (pM) of indicator color transition- the concentration range of the determined metal ion (pM), above and below which the metallochromic indicator has two different colors, corresponding to the free one and its complex with the metal.

A measure of the overall hardness of water- the number of milligrams - equivalents of calcium and magnesium contained in one liter of water.

Instrumental methodsanalysis I.M.A. - methods of analysis carried out using measuring devices.

Direct method I.M.A.- a physical method of quantitative determination directly from the measured physical property of the analyzed solution.

Indirect IMA method- physics - a chemical method of quantitative determination, in which the dependence of a physical property on the composition of the analyzed solution is measured.

Instrument calibration- checking the readings of the analytical instrument using a standard (substance, solution) sample

Standard sample- a substance or material that has a constant composition and properties.

Detector- part of an analytical instrument where the intensity of a measured physical property is recorded.

A selector is a part of an analytical device that selects a signal with certain parameters from the general flow of signals.

Converter- a vessel with an analyzed substance (solution), where the signal passing through it is converted.

Detector recorder- part of an analytical instrument where the detector signal is converted into an electrical signal and induced by a galvanometer.

Optical methods- measurement of the optical properties of substances or their solutions.

Emission methods- measuring the intensity of light emission and analyzing substances.

Absorption methods- measurement of light absorption by the analyzed substance (solution).

Chromatographic methods- separation of a mixture depending on the different means of its components to the mobile and stationary phase.

Electrochemical methods- measurement of electrochemical parameters of solutions.

Calibration graph- graph of the dependence of the physical property on the concentration of a series of standard solutions.

Comparison method- comparison of the physical properties of the analyzed solution with the physical properties of the standard solution.

Additive Method- change in the increase in the physical property of the analyzed solution when a certain amount of a standard solution is added to it.

Analytical Factors Method- Calculation of the concentration of the analyzed solution by dividing the value of the measured physical property of the substance by its analytical factor, i.e. molar or specific coefficient.

Molecular adsorption methods- measurement of absorption of ultraviolet, visible, infrared and radio frequency rays by the molecules of the analyzed substance.

Absorption spectrum- envelope curve of the dependence of the light absorption value (optical density-A or absorption coefficient along the ordinate axis) on the wavelength of the beam passing through the analyzed solution (along the abscissa axis)

Atomic absorption analysis. The method is based on measuring the absorption of monochromatic radiation (i.e., a beam with a certain wavelength) by atoms of the element being determined in the gas phase after atomization of the substance.

Emission spectral analysis. The method is based on measuring the intensity of light emitted by a substance (most often atoms or ions) when it is energetically excited, for example, in the plasma of an electric discharge.

Flame photometry. Based on the use of flame as a source of energy excitation of radiation.

Molecular absorption analysis. The method is based on measuring light absorption by molecules or ions of the substance being studied. This method is most widely used in analytical chemistry.

Luminescent method. The method is based on measuring the intensity of luminescence radiation, i.e. emission of rays by a substance under the influence of various types of excitation.

Spectral analysis using Raman effect(Raman effect). Based on the measurement of radiation intensity during the phenomenon of Raman scattering of light.

Nephelometric analysis. Based on measuring the scattering of light by particles of a dispersed system.

Turbodimetric analysis. It is based on measuring the attenuation of radiation intensity as it passes through a dispersed medium.

Refractometric analysis. Based on measuring the optical angle of rotation of the plane of polarization of light by optically active substances.

Spectroscopy (spectrophotometry) in the UV region of the spectrum, i.e. in the near ultraviolet (UV) region - in the wavelength range 200-400 nm and in the visible region in the range 400-760 nm.

Infrared spectroscopy, studying a section of the electromagnetic spectrum in the range of 0.76-1000 m.km (1 μm = 10-6 m).

d) Based on the nature of energy transitions, the following spectra are distinguished:

Electronic: (mainly in the UV region) - arise when the energy of the electronic state of particles (atoms, ions, radicals, crystal molecules) changes.

Oscillatory. Covers the IR region. Vibrational spectra arise when the energy of the vibrational states of particles (two and polyatomic ions, molecules, as well as liquid and solid phases) changes.

Rotational spectra. Spectra of the IR region and Raman scattering of light arise when the energy of the rotational states of molecules of two and polyatomic ions and radicals changes.

Electrochemical methods based on measuring the electrical parameters of solutions.

Ohm's law - the current strength is directly proportional to the potential applied to the electrodes.

Faraday's law - the mass of the electrolysis product is directly proportional to the amount of electricity and the molar mass of the substance released during electrolysis and inversely proportional to the number of electrons given up (or received) during electrolysis.

Nernst's law (equation) - describes the dependence of the (conditional) equilibrium redox potential on the ratio of the molar concentration of the oxidized to the reduced form.

Direct electrochemical method - quantitative determination directly from the

measured value of any electrochemical parameter.

The indirect electrochemical method is the use of the dependence of the electrical parameter on the composition of the solution to establish the equivalence point.

Potentiometry is the measurement of potential difference between dissimilar electrodes.

Conductometry - measurement of specific electrical conductivity.

Polarography is the radiation of the current-voltage characteristics of the analyzed solution between homogeneous electrodes.

Amperometry - measurement of the dependence of the saturation current of the analyzed solution.

Coulometry is the measurement of quantity consumed for the electrochemical transformation of an analyte.

Potentiometry – measurement of the potential difference between electrodes immersed in an electrolyte solution.

A standard electrode is an electrode with a constant potential value.

Indicator electrode – an electrode whose potential is sensitive to the concentration of the ion being determined.

An ion selective electrode is an electrode whose potential is sensitive to only one ion in the mixture.

Potentiometric titration is the dependence of the electromotive force between the standard and indicator electrodes on the volume of added titrant.

Direct potentiometry - quantitative determination directly from the measured potential value.

Indirect potentiometry (potentiometric titration) - establishing the equivalence point based on the dependence of the potential on the volume of added titrant.

Chromatographic methods– based on selective absorption (adsorption) of mixture components by solid (or liquid) substances – adsorbents.

Rf value– main parameter t.s.kh. for qualitative analysis - the ratio of the distance (a) from the start to the center of the spot to the distance (c) - from the start to the front of the chromatogram.

Planimetry– calculation or measurement of the area of a chromatographic spot in the shape of an ellipse.

Densitometry– determination of the optical density of a chromatographic spot on a chromatogram.

Ion exchange chromatography– separation of mixture components as a result of ion exchange between ionogenic groups of the ion exchanger and the analyzed electrolyte.

Ionites– high molecular weight compounds containing ionic groups in the side chain.

Cationite– an ion exchanger that exchanges a proton for a cation.

Anion resin– an ion exchanger that exchanges hydroxyl ion for an acid anion.

Eluent– carrier gas (or liquid) – mobile phase moving relative to the sorbent. Eluate is a solution flowing from a chromatography column containing the analyte.

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