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PHYSICAL RESEARCH OF METHODS

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Topic Chromatographic methods of analysis

Chromatography is used to analyze complex multicomponent mixtures. Chromatographic methods determine the qualitative and quantitative composition of organic substances, including volatile hydrocarbons and biological fluids. Pharmaceuticals, medicine, oil refining, chemical production and other industrial sectors use chromatographs to control the quality of raw materials and finished products, and also ensure compliance with environmental safety standards.

The widespread use of chromatographic methods of analysis is due to their diversity and specificity, which are revealed in this article:

- General information about chromatography
- Qualitative and quantitative analysis
- History of the method
- Classification of chromatographic methods of analysis
- Methods for moving sample in stationary phase
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- Liquid --liquid chromatographic method
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GENERAL INFORMATION ABOUT CHROMATOGRAPHY

Chromatographic methods of analysis are based on cyclic acts of sorption -and desorption occurring between the mobile phase (eluent) with a dissolved sample and a stationary sorbent. The components of complex mixtures have different sorbability, and passing along the stationary phase, they are absorbed at different rates and in

different quantities. Subsequent study of the results and their comparison with the standard makes it possible to establish the exact composition of the reagent.

In the traditional method, a material with a developed surface is used as a stationary phase, and a flow of inert gas or liquid acts as the eluent. Filtration of the eluent through a layer of sorbent triggers multiple repetitions of sorption and desorption, which distinguishes chromatographic methods of analysis from other analytical techniques and determines their effectiveness.

QUALITATIVE AND QUANTITATIVE ANALYSIS

Chromatographic methods of analysis establish the qualitative and quantitative composition of a substance. In qualitative testing, a sample is identified by its chromatogram, comparing the obtained parameters with reference values stored in a data library.

The quantitative method of analysis is based on measuring peaks that form depending on the concentration of impurities. The laboratory assistant examines the chromatogram using one of the following methods:

- Absolute calibration method. The dependence of the peak parameters on the concentration of different substances is determined experimentally. Then graphs and tables are compiled, with which the chromatogram is subsequently compared. Due to its simplicity and high accuracy, the method is the main one for identifying microimpurities.
- Internal normalization method. The sum of the selected peak parameters (for example, their height or area) is taken as 100%. Next, the ratio of the height of the individual peak under study to the total value is calculated, thereby determining the mass fraction of a specific component in the sample.
- Internal standard method. A standard substance for which the calibration curve is known in advance is introduced into the mixture. Then the peaks of the studied components are compared with the peaks of the “standard”. The method is used in the case of studying compositions with a variable but known amount of analyzed components.

Methods are constantly being refined and improved, which makes it possible to obtain more accurate data when analyzing complex mixtures and to level out noise in chromatograms.

HISTORY OF THE METHOD

Chromatography was first described by the Russian scientist Mikhail Tsvet, who studied the structure of chlorophyll. The botanist theorized that the green pigment was composed of several separate components and needed a method that would allow the substance to be separated into its components. To do this, he passed the chlorophyll extract through a glass column filled with crushed chalk. After washing the sorbent with ether, the scientist obtained several zones of different colors, which made it possible to confirm the multicomponent composition of the sample. The developed method was called chromatography.

Color described the principle of chromatography as follows: the substance in the mobile phase constantly reacts with new areas of the adsorbent and is partially absorbed, but at the same time the adsorbed components are “washed out” with fresh portions of the incoming eluent. That is, the scientist discovered only one method of interaction of separated components: molecular adsorption.

Because -of this, the botanist mistakenly assumed that the main condition for carrying out chromatographic analysis is the difference in the adsorbability of individual components. However, in modern chromatography, in addition to molecular adsorption, other physicochemical phenomena are also used to study complex mixtures. As a result, a variety of chromatographic methods have emerged, and a generally accepted classification has been developed to distinguish between them.

CLASSIFICATION OF CHROMATOGRAPHIC ANALYSIS METHODS

Chromatographic methods are divided into several groups depending on the parameters being compared. According to the aggregative state of the phases, chromatographic methods of analysis are divided into :

- Gas-liquid. The mobile phase is a flow of inert gas that passes through the liquid sorbent.
- Gas adsorption. A sample in a gaseous state is passed through a solid substance, on the surface of which adsorption occurs.
- Liquid --liquid. Liquid media are used as eluent and stationary phase.
- Liquid -adsorption. The reagent is supplied along with the solvent and passes through the solid porous material.
- Liquid -gel. In this method, the stationary phase is a gel-like substance.

The second classification concerns the design of chromatographic equipment. Most methods use a column chromatograph : adsorption is carried out in columns filled with a stationary phase. But sometimes plane chromatography is used, which uses a thin section of sorbent or special paper. Also recently, the capillary chromatographic method, in which separation occurs in a liquid film, and field chromatography, which requires the creation of additional magnetic, centrifugal or other forces for analysis, have become widespread.

Chromatographic methods of analysis differ in the characteristics of the interaction between the eluent and the adsorbent. According to separation mechanisms, chromatography is divided into :

- adsorption - based on the difference in the adsorbability of the sample components;
- distributive - occurs due to different solubilities of substances in the phases;
- ion exchange - carried out due to the achievement of ion exchange equilibrium constants;
- penetrating - based on the difference in the shapes and sizes of molecules;
- sedimentary - occurs due to the precipitation of insoluble compounds;
- adsorption -complexing - is carried out due to the formation of coordination compounds of different strengths on the surface of the stationary phase.

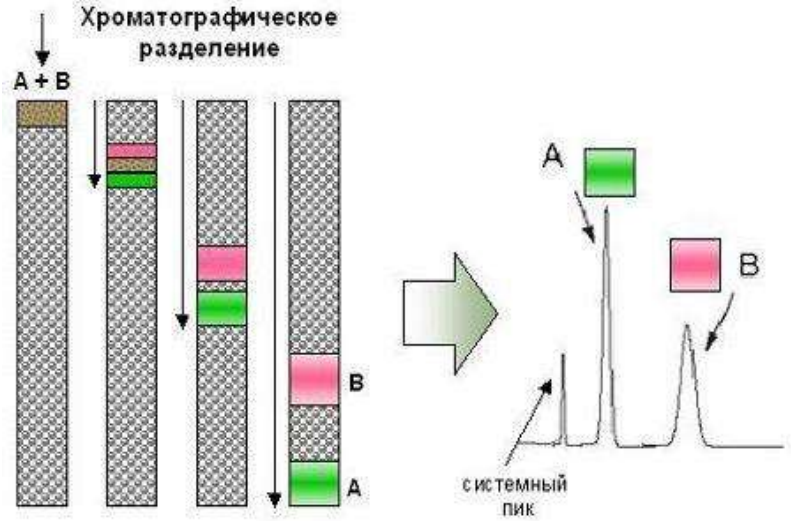
The following classification divides chromatographic analysis methods into three groups according to the methods of moving absorbed components along the adsorption layer. There are developing (or eluent), frontal and displacement methods. Let's take a closer look at them.

METHODS FOR SAMPLE MOVEMENT IN A STATIONARY PHASE

The simplest chromatographic analysis methods include frontal , in which the role of the eluent is minimized. Let us assume that the sample is a Solv solvent, which

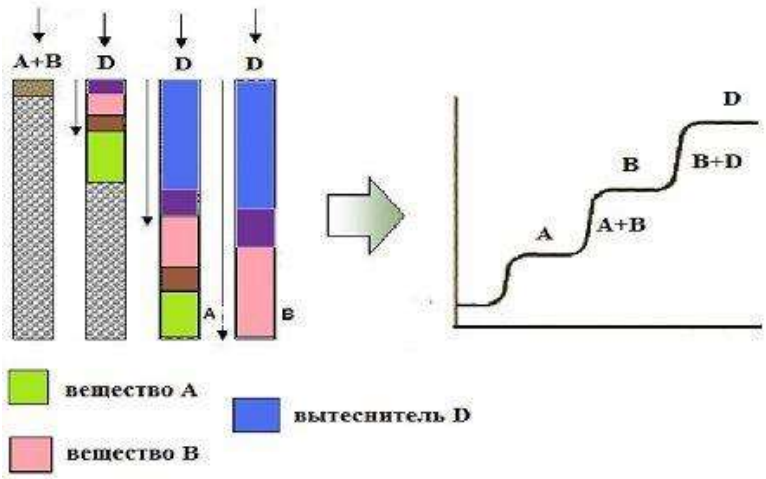
contains two components: A and B. The analyte is passed through a sorption column in a continuous flow. After passing through the chromatography equipment, the concentration of A and B in the output solution is measured and the initial volume of Solv is taken into account. Based on the data obtained, a dependence graph is constructed, which is the output curve (chromatogram).

Due -to the absorption of components A and B by the stationary phase, a solvent will first flow from the column, then a substance with a lower sorption coefficient (for example, A), and only then B. As a result, after some time, a solution with an unchanged composition (the same proportion Solv, A and B). This chromatographic method of analysis is used not only to study complex substances, but also to purify them from impurities, provided that they are absorbed better than the main elements of the reagent.



In laboratory tests, the development or eluent chromatographic method is most often used. The specialist adds a sample of the Solv reagent with components A and B dissolved in it to the column, after which he supplies the mobile phase under constant pressure. Under the influence of physical and -mechanical forces, the composition separates. The substance with better sorbability will occupy the upper part of the column, and the one with less sorbability will occupy the lower part. At the output of the equipment, component A will first appear, then pure Solv, then element B, which will be reflected in the chromatogram. Quantitative analysis is carried out by measuring the height and area of the peaks: the larger they are, the higher the concentration of the substance being studied in the composition.

The main advantage of the eluent chromatographic method is the ability to separate complex multicomponent reagents. However, when studying the chromatogram, it is necessary to take into account the decrease in the concentration of exiting solutions due -to dilution with the mobile phase.



The third method is repressive. It involves the use of a displacer (drug D) that continuously acts on the Solv solution introduced into the chromatography column. The sorption coefficient D must be higher than that of any components of the analyzed sample. Thanks to this, the drug gradually displaces the substance with worse sorbability, which is recorded when the mixture leaves the column. The displacement method does not require the use of a -carrier gas, resulting in reduced research costs. However, it is worth remembering that the analysis of the obtained data is difficult due to the overlap of zones of different substances on top of each other, since they are not separated by a solvent zone.

GAS-LIQUID CHROMATOGRAPHY METHOD

In analytical chemistry, the gas-liquid chromatographic method is widely used. Thanks to the variety of liquid stationary phases used, it is possible to create optimal conditions for the identification of almost any substance contained in a small concentration in the test sample. This determines the versatility of the method. To do this, it is necessary to correctly configure the chromatographic equipment and select a stationary phase that meets the following parameters:

- high ability to dissolve the elements contained in the reagent - otherwise the sample quickly leaves the column and does not provide sufficient material for analysis;
- low volatility - during the study the phase should not evaporate, as this will complicate the reading of the chromatographic graph;
- chemical inertness - the adsorbent should not react with sample components or -carrier gas;
- minimum viscosity - otherwise diffusion will slow down.

Also important for the implementation of the method is the maximum separation ability of the components of a particular sample.

In addition to choosing the liquid medium in which the mixture will be separated into individual components, during the preparation of the chromatographic analysis it is necessary to select a stationary phase carrier. A solid and durable material is used as a carrier, on which the liquid forms a thin, uniform film. The most commonly used materials are silanized chromosorbate, fluorocarbon polymers, and high-quality glass beads. These media have the following advantages:

- easily and evenly wetted by the stationary phase;
- practically do not absorb liquid, that is, they do not interfere with the normal course of the reaction between liquid and gaseous media;
- do not respond to an increase in temperature in the working column.

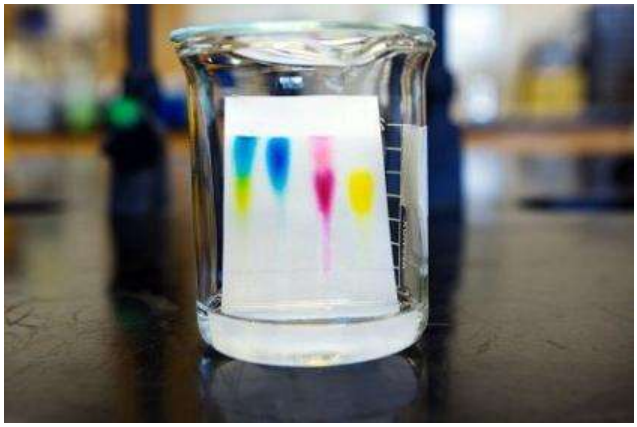
Chromatographic methods of analysis, based on the gas-liquid principle, are among the most modern , and are used when it is necessary to separate substances belonging to the same class. They are actively used in the chemical and oil and gas industries to control the quality of the resulting products. Among the key advantages of the gas-liquid analysis method are:

- expressiveness;
- maximum accuracy;
- full automation;
- low costs for sample preparation and research.

To use the method, it is necessary to select not only the liquid medium and its carrier, but also to resolve the issue of continuous supply of eluent. To minimize costs, a gas generator (for example, hydrogen) is connected to the chromatograph , which produces the required amount of the substance and is responsible for its uniform supply to the equipment.

LIQUID -LIQUID CHROMATOGRAPHIC METHOD

In terms of technology, -the liquid-liquid chromatography analysis method is similar to gas-liquid chromatography. A liquid medium is applied to the solid carrier, acting as a stationary phase. To prepare the sample, a solution, rather than an inert gas, is used.



The reagent being studied, together with the flow of liquid solvent, moves through the sorbent, on the surface of which the components are separated. Most often, a chromatograph column is filled with a stationary phase, but for some studies they resort to the thin-layer chromatography method, in which special paper is moistened with an adsorbent.

Separation is carried out by distributing substances between immiscible solutions. That is, the concentration of the same substance in the mobile and stationary phases will differ and depend on the distribution coefficient. The coefficient values are established empirically for each component, as a result of which liquid- -liquid chromatographic analysis methods make it possible to identify individual elements in a complex composition with high accuracy.

To successfully implement the method, it is necessary to correctly select immiscible phases. They are usually selected based on the experience of past analyses. The most commonly used are so-called “ternary systems”, which include two solvents that are immiscible with each other and a third liquid that is soluble in both phases. For example, this could be a system of immiscible heptanes and water, into which ethanol, which is highly soluble in both media, is introduced.

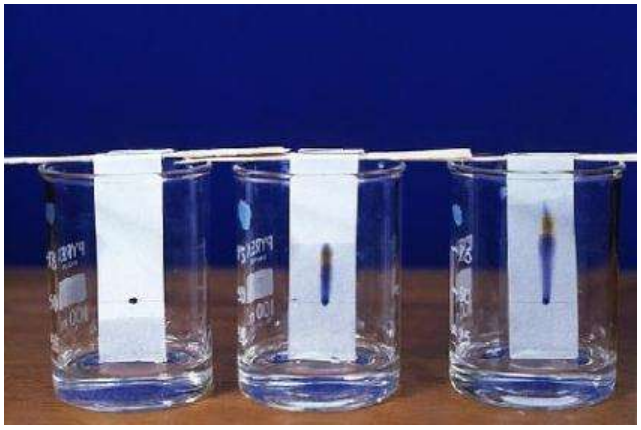
When choosing compositions for the mobile and stationary phases, it should be taken into account that their insolubility in each other is relative, and during the study the substances will interact (albeit in an insignificant amount), which affects the values shown by chromatographic methods of analysis. To minimize the error, one of two technologies is used: preliminary saturation of the mobile phase with the stationary phase or chemical fixation of the liquid on the sorbent.

The efficiency of the chromatographic analysis also depends on the choice of carrier for the stationary phase. The requirements for it are as follows:

- developed surface;
- chemical inertness;
- high fluid retention capacity;
- resistance to used solvents.

Most often, in liquid- -liquid chromatographic research methods, cellulose, fluoroplastic, silicate gels or polymers are selected as a carrier.

DISTRIBUTION PAPER CHROMATOGRAPHY METHOD



In addition to the above-described carriers that fill the columns, partition chromatographic methods of analysis can use special paper on which the components under study are separated. This method is rarely used on an industrial scale (compared to column chromatography), but is quite often used in analytical chemistry.

The technology for conducting paper chromatographic analysis involves calculating the coefficient Rf, which is the ratio of the displacement of the component zone to the displacement of the solution front. In theory, the coefficient depends only on the substance under study, solvent and paper parameters. However, in reality, when implementing the method, the coefficient is also influenced by the components present in the sample in micro concentrations and the technique used. As a result, a certain error arises that must be taken into account when interpreting the analysis.

Partition chromatographic analysis methods are sensitive to the characteristics of the paper used. It must meet the following criteria:

- chemical purity;
- neutrality;
- inertness towards reagents in the sample;
- homogeneity.

When selecting a material, the orientation of the fibers, the quality of the cellulose, and sorbability are also taken into account. The parameters determine the speed of movement of the solution and precipitation of the detected molecules.

There is one more nuance in the paper method - some substances can change the properties of the carrier from hydrophilic to hydrophobic, which will completely disrupt the course of the experiment. In this case, the chromatography paper is pre-impregnated with paraffin or vegetable oils.

SOLVENTS IN THE DISTRIBUTION METHOD

The chosen solvent has a great influence on the accuracy of chromatographic analysis methods. As a mobile phase, it is necessary to take a liquid that dissolves the detected components to a lesser extent than the stationary phase. If this condition is neglected, the method will not work: if the solubility is too high, the sample will pass along with the liquid without being adsorbed on the surface; if it is too low, it will remain on the initial line and will not give the gradation required for decoding.

If a water-soluble mixture is analyzed using the partition method, purified water is taken as the stationary phase, and any convenient organic solvent is taken as the mobile phase. The selected liquids should not be mixed or change their properties during the research process; their availability and non-toxicity for humans are important.

Partition chromatographic methods of analysis are based on the use of mixed phases: mixtures of alcohols with each other and organic acids, ammonia, aqueous solutions of phenol or cresol, and so on. By changing the concentration, saturation and proportions in the solution, it is possible to smoothly change the Rf coefficient, create optimal conditions for analysis, and obtain additional data when deciphering the chromatogram.

Like other chromatographic methods of analysis, paper chromatography determines both the qualitative and quantitative composition of the sample. In the first case, the specific color of spots on the chromatogram is studied and the numerical value of Rf for each detected reagent is analyzed.

To determine the quantitative composition of the mixture, the area of the formed spots and the intensity of their color are examined. The washing method is also used, in

which each color spot is treated with an extractant and then the amount of the washed substance is calculated.

THIN LAYER CHROMATOGRAPHIC METHOD

Chromatographic methods of analysis are distinguished by their informativeness, complexity, and relevance for solving practical industrial problems. One of the most common is the thin layer chromatography (TLC) method, developed by a group of scientists in 1938.

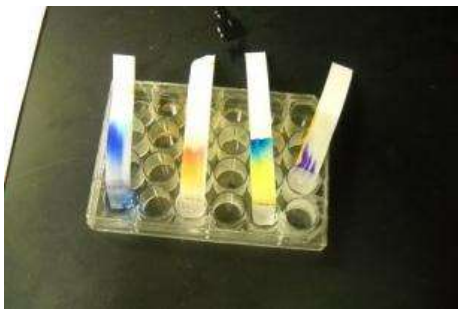
The solid phase is applied in a thin layer onto a specially prepared glass, metal or plastic plate. Then the laboratory assistant introduces the sample to be analyzed onto its edge and immerses the plate in a liquid solvent, which acts as a mobile phase. Under the action of capillary forces, the composition under study begins to move through the sorbent, separating into its components. Diffusion in a solid fixed layer occurs in two directions: longitudinal and transverse, which provides additional information for analysis.

The peculiarity of the chromatographic method is its relative simplicity of execution. To carry out the experiment you need:

- Plates for solid adsorbent. Typically, substrates are made of aluminum foil, polymer film or glass.
- Sorbent. Most often, this method uses sorbents made from silica gel, starch and cellulose.
- Solvent. The choice of mobile phase depends on the physicochemical -properties of the solid and the reagents being studied. As in the paper method, the use of multicomponent liquids is acceptable.

After finishing the work, before constructing a chromatographic graph, the plate is sprayed with a developing reagent or exposed to ultraviolet light. Then they begin to determine the components of the sample and their further study by any method convenient for the laboratory assistant.

QUALITATIVE AND QUANTITATIVE TLC ANALYSIS METHODS



For a qualitative study of a sample, one of the most reliable and revealing is the “witness method”. Together with the composition, individual substances (“witnesses”)—the supposed components of the mixture—are applied to the starting line. All liquids are affected by the same forces, so the coincidence of the Rf coefficient of one of the “witnesses” with the reagent component suggests the presence of this substance in the sample.

As for quantitative determinations in this method, they are performed directly on the plate or after removing the sorbent layer from it. In the first case, the area of the color spot is measured and the amount of the substance is calculated using a pre-prepared graph.

However, the spectrophotometric method is considered more indicative. The sorbent is removed from the plate and placed in special equipment, which shows the percentage of various components with high accuracy.

ION EXCHANGE CHROMATOGRAPHIC METHOD

The ion exchange chromatography method is based on the replacement of elementary particles included in the reagent with atoms contained in the ion exchanger. Therefore, the effectiveness of the analysis depends on the parameters of the equipment used. Modern ion exchangers have important advantages:

- High exchange capacity.
- Reproducible ion exchange properties.
- Resistant to acids and alkalis, and any strong oxidizing agents.

For their production, various polymer compounds are most often used: for example, polystyrene with a different set of functional groups, which determine the characteristic properties of the finished material.

The ion exchange chromatographic method is used primarily for the separation of elementary particles, after which it is possible to carry out a quantitative calculation of the analyzed components. This technology is used to detect a variety of anions in drinking and process water, processed products, food, pharmaceutical and chemical

raw materials. The most indicative method is for determining cations of alkali and alkaline earth metals, and substituted ammonium salts.

PROSPECTS FOR THE DEVELOPMENT OF CHROMATOGRAPHIC METHODS

Chromatographic methods of analysis are constantly being improved and modified. New technologies are emerging that make it possible to determine the components of a mixture in nanoconcentrations. Thanks to this, it is possible to improve the quality of finished products in various industries and minimize environmental risks by establishing strict control over the composition of wastewater.

However, the capabilities of chromatography are limited not only by the methods used, but also by the equipment used. It is important that chromatographs meet the following requirements:

- Simple sample preparation and administration.
- Get results quickly and easily interpret chromatographic graphs.
- Operating principle based on best practices.
- Maximum analysis accuracy.
- Leveling out errors arising from -the physicochemical properties of the mobile and stationary phases used.
- Minimum costs for commissioning equipment and its further maintenance.
- Possibility of analyzing raw materials or products without interrupting the main technological process.
- Determination of a wide range of compounds, including volatile hydrocarbons and other difficult-to-detect substances.
- Rapid training of personnel in methods of working with laboratory equipment.

Lecture 2

Topic Gas-liquid chromatography

Gas chromatography is a column chromatography technique in which the mobile phase is a gas moving through a column filled with a stationary phase.

Both gas adsorption and gas-liquid (mainly) chromatography are used.

The analysis is carried out using special devices - gas chromatographs.

The main components of a gas chromatograph: a source of mobile phase, a sample injection device, a column with a thermostat, a detector, a data collection and processing system. The required temperature conditions of the sample inlet device, column and detector are set in the appropriate thermostats.

Mobile phase

Nitrogen, helium or hydrogen are used as the mobile phase. These carrier gases can be supplied to the system either from cylinders or from gas generators, allowing the production of high purity gas. The gas passes through a gas flow regulation and stabilization unit, which makes it possible to measure its speed and pressure at the inlet to the chromatograph.

- Sample injection
- The most common method is to introduce a liquid sample (solution) into the evaporator using a syringe through a self-sealing membrane. However, the chromatograph can be equipped with a dispenser (including an automatic one) for introducing gaseous, liquid or solid substances.
- Blow and accumulate injection (purge and trap) is used to extract highly volatile components and accumulate them in a special adsorption trap (column), followed by rapid thermal desorption and introduction into a chromatographic column.
- A head-space preconcentration device allows you to increase the sensitivity of determining volatile compounds.
- Columns
- Three types of analytical columns are used: packed (packed), micropacked, and capillary.
- Packed columns (PCs) are made of metal (stainless steel, nickel, copper), glass, Teflon and other materials. To separate unstable compounds (catalytically decomposing upon contact with a metal surface), glass or Teflon columns are used. The shape of NCs are straight , U-shaped, W-shaped and spiral. The internal diameter of the NC is from 2 to 4 mm, and the length is from 1 to 4–5 m. The internal diameter of micropacked columns is 0.5–1 mm and the length is from 0.5 to 3 m.
- Capillary columns are made of quartz and have a spiral shape. According to their characteristics (internal diameter, d), they are divided into capillary (d = 0.2–0.3 mm, length from 5 to 100 m), narrow capillary (d = 0.05–0.2 mm, length from 5 up to 100 m), capillary wide diameter (d = 0.3–0.8 mm, length from 10 to 60 m) and polycapillary (d = 0.04 mm, length 0.2 or 1 m).
- In packed and micropacked columns, the sorbent packing inside the tube should be dense and uniform, without voids. The denser and more uniform the packing, the less peak smearing and the greater the column efficiency.
- In capillary columns, a layer of sorbent is applied to the inner surface of the capillary in the form of a layer of liquid stationary phase or in the form of an adsorbent layer with a thickness of 0.1 to 5.0 μm, the role of which is most often

played by a polymer film. Depending on the characteristics of the capillary columns and the concentration of the analyzed compounds in the sample, the sample is introduced into the column with or without splitting.

- Column temperature programming systems improve resolution and reduce analysis time.
- Detectors
  - The most important characteristics of detectors are sensitivity, linear dynamic range (the range of concentrations of the analyte, in which a linear dependence of the detector signal on concentration is observed) and selectivity.
- The most commonly used is a flame ionization detector (FID). This is due to its high sensitivity to most organic compounds and an extremely wide linear dynamic range (6–7 orders of magnitude), which is extremely important when carrying out quantitative analyses. Other types of detectors are also used - thermal conductivity detector (katarometer), thermionic detector (TID), electron capture detector (ECD), mass spectrometric. Depending on the specific task, other types of detectors can be used - flame photometric , photoionization, Fourier-infrared, etc.
- sensitivity of TID in relation to nitrogen- and phosphorus-containing compounds are higher than FID sensitivity by approximately 2 and 3 orders of magnitude, respectively.
- ECD is a highly selective detector, sensitive to compounds containing halogens, sulfur, phosphorus, nitrates, and oxygen.
- stationary phases
- In gas adsorption chromatography, inorganic (silica gel - Sferosil, Porasil, Silichrome, etc.; graphitized thermal carbon black - Carbopak S and B, Karbosiv, Karbosphere; molecular sieves - sodium and calcium aluminosilicates) and porous polymer sorbents are used as sorbents (adsorbents).
- In gas-liquid chromatography, the stationary phase (sorbent) is a liquid deposited on a solid carrier. The carrier is a relatively inert adsorbent with a low specific surface area, on which the stationary phase must be retained in the form of a film of uniform thickness. The carrier must be mechanically strong, have a spherical shape and a macroporous structure if possible. Mineral and polymer carriers are used. Most mineral carriers are processed diatomaceous earth. Typically, carriers with particle sizes in the ranges of 125 to 150 μm or 150 to 180 μm are used.
- Stationary phases are usually high-boiling liquids. They differ in the temperature limit of use (low temperature - up to 100 °WITH ; medium temperature – up to 200 °C; high temperature – up to 350 °C) and polarity. All stationary phases are divided into 4 groups - nonpolar, weakly polar, moderately polar and highly polar.
- In terms of chemical composition, stationary phases for the most part belong to the following classes: aliphatic and aromatic hydrocarbons; phthalates and phosphates; ethers, esters, polyesters; polyglycols; siloxanes with non-polar, medium-polar and polar radicals; nitriles and nitrile esters. Grafted stationary phases, which are chemically deposited almost monolayer films, have also been

developed. Such sorbents are called bondapaks. They are characterized by high heat resistance, greater inertness, and provide higher column efficiency compared to other sorbents.

- Methodology
- The description of the method must indicate: detector type, column type (packed or capillary), column material and dimensions, sorbent (solid carrier type and its characteristics, stationary liquid phase and its quantity), sample introduction method and its parameters, evaporator temperature, column and detector, carrier gas and its flow rate.

Liquid-liquid chromatography is essentially close to gas-liquid chromatography. A film of the liquid phase is also applied to the solid carrier and a liquid solution is passed through a column filled with sorbent. This type of chromatography is called liquid-liquid partition chromatography. The liquid deposited on the carrier is called stationary liquid phase , and the solvent moving through the carrier is called the mobile liquid phase. Liquid-liquid chromatography is carried out in a column (column version) or on paper (paper chromatography).

The separation of a mixture of substances in liquid-liquid chromatography is based on the difference in the distribution coefficients of the substance between immiscible solvents.

Ternary systems consisting of two immiscible solvents and a third, soluble in both phases, are widely used in liquid-liquid chromatography. Such systems make it possible to obtain a set of immiscible phases of varying selectivity. Although solvents that do not mix with each other are chosen as the mobile and stationary phases, some mutual solubility is still observed in many systems. To prevent the processes of mutual dissolution of liquids during chromatography, the mobile phase is pre-saturated with the stationary phase.

To maintain a constant composition of the phases, the method of chemical fixation of the stationary phase on the sorbent is also used. In this case, the interaction of the solvent with the OH – ^{groups} on the surface of the carrier is used. Adsorbents with a liquid phase fixed on their surface are produced by industry.

In liquid chromatography, columns of short length are most often used - from 3 to 25 cm. The internal diameter of the columns ranges from 1 to 4.6 mm. Column efficiency is related to the viscosity, diffusion coefficient, and other physical properties of the liquids. The stationary phase carrier must have a sufficiently developed surface, be chemically inert, firmly hold the liquid phase on its surface and not dissolve in the solvents used. Substances of various chemical natures are used as carriers: hydrophilic carriers (silica gel, cellulose, etc.), hydrophobic carriers (fluoroplastic, Teflon and other polymers).

In addition to the usual media used to fill columns, partition chromatography uses a specific media (chromatographic paper), and the technique is called partition chromatography on paper, or partition paper chromatography .

Chromatographic paper must be chemically pure, neutral, inert with respect to the components of the solution and the mobile solvent, and uniform in density. Properties such as the structure of cellulose molecules in paper, sorbability, fiber orientation and other process characteristics that affect the speed of solvent movement are also important.

When choosing paper as a stationary phase, it is necessary to take into account that some organic substances turn hydrophilic paper into hydrophobic one. To do this, it can be impregnated with solutions of various hydrophobic substances: paraffin, vegetable oil, etc.

In the selected solvents, the sample components must have different solubilities, otherwise separation will not occur at all. In the solvent, which is the mobile phase, the solubility of each component should be less than in the stationary phase solvent, but still be quite noticeable. This limitation is due to the fact that if the solubility of a substance is very high, the substance will move along with the solvent front, and if the solubility is low, the substance will remain on the initial line.

To separate water-soluble substances, an organic solvent is usually chosen as the mobile phase, and water as the stationary phase. Solvents of the mobile and stationary phases should not be mixed, the composition of the solvent should not change during the chromatography process, solvents should be easily removed from paper, accessible and non-toxic to humans. Individual solvents are used relatively rarely in partition chromatography. More often, mixtures of substances are used for this purpose, for example, butyl or amyl alcohol with methyl or ethyl alcohol, saturated aqueous solutions of phenol, cresol, mixtures of butyl alcohol with acetic acid, ammonia, etc.

The qualitative composition of a sample when using the paper partition chromatography method can be determined by the specific color of individual spots on the chromatogram or by the numerical value of the distribution coefficient each component.

Quantitative determinations in partition chromatography are performed using chromatographic characteristics (spot area on the chromatogram and intensity of its color) or by the washout method. In the latter case, the chromatogram is cut into separate parts according to the number of spots, each spot is treated with an appropriate extractant and the amount of extracted substance is determined by any suitable method (photometric, polarographic, etc.).

High performance liquid chromatography , or high performance liquid chromatography (HPLC) , is a computerized method that allows the determination of active substances and their ratios to parts per million accuracy.

The nature of the eluent has a major influence on the retention and selectivity of HPLC separations. For each mixture to be separated, in addition to the adsorbent, it is necessary to select an eluent of a certain nature and composition in order to achieve the optimal degree of separation: complete separation in the shortest possible time.

For the selected sorbent (based on the geometry of grains, pores and surface chemistry), all the main quantities that determine the degree of separation depend on the nature and composition of the eluent: system selectivity, adsorbent, eluent, analyte capacity factors, column efficiency. The nature of the eluent affects the operation of detecting systems.

An HPLC eluent must provide sufficiently high selectivity in an acceptable time; be low-viscosity to provide low flow resistance and high efficiency; dissolve analytes; be cheap, accessible and safe to operate.

The eluent should not react chemically with either the analyzed substances or the adsorbent, contain highly absorbable impurities, in particular, water and other polar substances when separated on polar adsorbents, and be recorded by a detector.

N-alkanes (pentane, hexane, heptane) are used as eluents, both in pure form and with the addition of various polar substances (methanol, ethanol, isopropanol, ethers and esters, chloroform and other polar substances). Water-alcohol mixtures are also used, and in some cases non-aqueous mixtures based on acetonitrile and tetrahydrofuran are also used. Deuterated compounds (CD_3CN, D_2O) are used as eluents in HPLC with Fourier transform IR spectrophotometer .

In HPLC, adsorbents of different geometric structures are used (with different specific surface area, different pore diameter, pore volume and different distribution of pores over effective diameters). For liquid adsorption chromatography, the total surface area of the adsorbent is important. However, both in gas chromatography and in liquid chromatography, selectivity at the same specific surface area may depend on the pore size of the adsorbent.

A fairly wide range of adsorbents has been developed and produced for HPLC; more than 50 companies produce about 200 items. The most commonly used adsorbents are silica gels - 75%, polymers (polymethacrylates, polystyrene divinylbenzenes, polyethylene glycols, celluloses, etc.) - 20%, porous carbon adsorbents based on graphitized carbon black, zirconium oxide, hydroapatites - 4%, aluminum oxide - 1%, as well as ion exchangers, bentons, adsorbents with a layer of liquid crystals, etc.

Polymer sorbents are used for the separation and determination of sugars in food and drinks. For analytical and preparative separations of peptides and proteins, hydrophilic polymeric materials such as polydextrins are used. Size exclusion chromatography uses porous polymers with wide pores. Size exclusion chromatography with organic eluents is called gel permeation chromatography and is used to separate polymers. Size

exclusion chromatography with aqueous eluents (gel filtration chromatography) is used to separate biomolecules.

A modern liquid chromatograph includes the following systems and devices: an eluent preparation and supply system, which includes an eluent reservoir and a pump, a sample injection system, chromatographic columns, column and detector thermostats, detectors and fraction collectors. In addition, an integrator or computer can be attached to it.

HPLC uses dozens of types of detection systems, both universal and selective, which must have a low detection limit determined by the ratio of noise level to sensitivity, a wide linear range, stability of readings, and low inertia (constant over time).

In analytical practice, the most widely used are photometric, spectrophotometric, fluorescent, refractometric , electrochemical, and mass spectrometric detectors. The choice of chromatograph model is determined by the analytical task. The following liquid chromatographs are produced: simple, universal, automated, preparative, special for molecular sieve chromatography, for ion chromatography, microcolumn and capillary, chromatographs on chips.

A type of liquid chromatography based on the exchange of solution ions for solid phase ions is ion exchange chromatography with conductometric detection. The method is widely used to solve biochemical problems in scientific research. For practical purposes, ion exchange chromatography is used to analyze amino acids. Currently, an automatic amino acid analyzer is used for this purpose, which allows analyzing a mixture of amino acids from protein hydrolysates.

The method of thin layer (planar) chromatography (TLC) , which is now widely used, was developed by N. A. Izmailov and M. S. Schreiber in 1938.

The TLC method is a simple, cheap, on-line chromatography method for the analysis of all classes of compounds. In the TLC method, a stationary solid phase is deposited in a thin layer on a plate. A sample of the liquid to be analyzed is applied to the starting line 2–3 cm from the edge of the plate, and the edge of the plate is immersed in a solvent, which acts as the mobile phase of liquid adsorption chromatography. Under the action of capillary forces, the solvent moves along the sorbent layer and transfers the components of the mixture at different speeds, which leads to their separation. Diffusion in a thin layer occurs in the longitudinal and transverse directions, so the process should be considered as two-dimensional.

For separation, glass, metal, porous ceramic and plastic plates of size 100 are used. $\times$ 100 mm and other plates with a uniform layer of adsorbent 50–300 microns thick. The fraction of adsorbent grains can be in the range of 3–15 μm. Glass plates are used, on the surface of which layers of adsorbent are sintered (such plates can be reused), as well as glass fiber-based plates (Instant thin-layer chromatography).

The main adsorbents for TLC plates are silica gel, aluminum oxide, microcrystalline cellulose, cellulose triacetate for the separation of metal complexes, as well as inorganic ion exchangers, chitosan. For preparative chromatography, plates with varying thickness of the adsorption layer are used. According to the adsorption activity, the plates are divided into polar, non-polar and medium polarity. To increase detection sensitivity, fluorescent substances (fluorescein, pyrene, etc.) are added to some plates.

In addition to plates, TLC uses rods (150×0.9 mm) made of steel, copper or quartz. After the mixture is separated and dried, the rods are passed at a constant speed through the flame of a flame ionization detector. These rods can be used multiple times (up to 100 times).

Qualitative analysis by TLC. The most common approach to qualitative analysis is based on mobility values . Chromatographic mobility is a sensitive characteristic of a substance , but it significantly depends on the determination conditions. If standard conditions are met, reproducible mobility values are obtained, which can be used for analytical purposes when compared with tabulated values, if they are obtained under the same experimental conditions.

The most reliable is the witness method , when individual substances corresponding to the expected components of the mixture are applied to the starting line next to the sample. In practice, a standard substance (witness) in the same solvent is applied to the starting line along with the analyzed sample and chromatographed under the same conditions.

Quantitative analysis by TLC. Quantitative determinations in TLC can be made directly on the plate or after removing the substance from the plate. In a direct determination, the spot area is measured using one method or another on a plate (for example, using millimeter tracing paper) and the amount of the substance is found using a pre-constructed calibration graph.

The most accurate method is considered to be one in which the substance, after separation, is removed from the plate and analyzed by spectrophotometric or other method. Removal of the substance from the plate is usually done mechanically, although sometimes washing with a suitable solvent is used.

The main advantages of TLC include: simultaneous separation of several samples (up to 20 or more), the possibility of two-dimensional separation, the ability to observe the entire separation process, high productivity; full analysis (at the start you can check the remaining sample), speed of separation; low cost, small amount of eluent, possibility of a wide choice of color reactions, possibility of using selective and specific detectors.

The disadvantages of TLC are that TLC plates are open systems, so some unstable compounds (sensitive to oxygen, moisture, etc.) may decompose; in the simplest versions of TLC, quantitative analysis is difficult, and in these cases we can talk about

a semi-quantitative method; In terms of separation efficiency, the TLC method is significantly inferior to high-performance liquid chromatography.

Historically, in TLC, quantitative measurements were made through visual observations. In recent years, sophisticated but expensive detection systems have been created: densitometry, mass spectrometry for TLC, radio scanning of isotopes, TLC-IR, laser scanning for fluorescence measurements. Scanning stains with UV scanners allows detection at the nanogram level. Fluorescent scanners allow detection limits to be reached at the picogram level in the most favorable cases.

The TLC method is used by State Sanitary and Epidemiological Supervision centers, standardization and metrology centers, environmental centers, analytical laboratories for food quality control, laboratories of plant protection stations, veterinary laboratories, agricultural chemical service laboratories, etc.

When analyzing food products Using the above methods the following problems can be solved:

· determination of the chemical nature of substances that determine the characteristic aroma of fresh products;

· monitoring the condition of products during processing and storage;

·objective assessment of indicators characterizing the quality of raw materials and finished products made from them;

·identification and elimination of causes causing undesirable changes in products during their manufacturing process;

· establishing the fact of product falsification, etc.

GC and HPLC methods are used to identify and determine volatile substances that are involved in the formation of taste and aroma of many foods or are responsible for their spoilage. For example, volatile fatty acids characteristic of high-quality meat are determined, or acids that are formed when the normal fermentation process of sauerkraut changes and cause foreign shades of its odor. The methods are used to determine nicotine, nitrosamine (in fish and smoked meats), food additives (dyes, preservatives, antioxidants), environmental pollutants (pesticides, aflatoxins, drug residues, vitamins), etc.

GC and HPLC methods are very valuable in establishing the facts of falsification of consumer goods. Thus, yellow dye in pasta can create the impression of a high cost of the product. The presence of such a dye can be confirmed by HPLC. Determination of anthocyanins and glycosides, which are responsible for the color of wine, allows us to identify the naturalness of the wine. Counterfeit cognac can also be detected using GC.

The HPLC method is used to identify and determine non-protein nitrogen, for example, urea, which is added when falsifying protein products in order to increase nitrogenous substances. The detection of the amino acid hydroxyproline, which is present mainly in connective tissue proteins, i.e., in cheap raw materials, makes it possible to identify the fact of replacing complete meat protein. Fats determined by triglyceride composition by GC can provide information on the amount of fat and extraneous fat additions. By determining the fatty acid composition, we can conclude that cocoa butter is replaced with hydrofat in chocolate, etc.

Currently, some types of chromatography are used not as independent methods of analysis, but as methods of preliminary research or as methods for preparing a sample for subsequent determination by other methods, including chromatography.

Thus, when determining amino acids in the hydrolyzate of meat or blood proteins using the method of biological chemistry, preliminary purification of the hydrolyzate is carried out on columns with ion exchangers. The same is done when determining volatile bases and free fatty acids in meat and fish.

The TLC method is used to determine the presence of organochlorine pesticides in the test sample, the quantitative determination of which is then carried out by GLC.

Lecture 3. Classification of molecular spectroscopic analysis methods

One of the main questions of chemistry is what is a substance and who is its molecule?

With the development of physical research methods and the development of science, the importance of the physical chemistry course increases. The main objective of this course is to develop students' thinking skills, a deep understanding of the current state of this science and to promote the creation of skills for the practical application of acquired theoretical knowledge. Physical chemistry uses theoretical and applied methods of physics and chemistry, as well as its own methods, and conducts multifaceted studies of chemical reactions and physical processes interacting with them.

The great discoveries of the late 19th century proved the complexity of atomic formation and made a major contribution to the development of physical chemistry. These include the discovery of the electron by Perrin (1895) and Thomson (1897), the discovery of X-rays (1895) and Becquerel (1896). In addition, one can cite as an example Planck's quantum tabulation of light (1900), the presence of Lebedev's radiation pressure, as well as the fact that Pere Curie and Marie Curie (Skladovskaya) study radioactivity (1889).

By the beginning of the 20th century, physical chemistry emerged as a science that studies the formation of matter, chemical thermodynamics, solutions, chemical kinetics and electrochemistry. With the use of new theoretical methods, studies of the structure of atoms, molecules and crystals came to the fore.

Proof of the dynamic development of physical chemistry even today can be considered the fact that the Nobel Prize laureates were: for research on energy-8, carried out on extremely high-speed chemical reactions by shifting the equilibrium under the influence of a weak impulse (M. Eigen and R. Norrish, 1967); to describe their successive relationships (L. Onsager, 1968); for theoretical and experimental studies of macromolecules in the field of physical chemistry (P. Flory, 1977); for his contribution to thermodynamics and especially to the theory of dissipative systems (I. Prigozhin, 1977); research on the molecular basis of biological energy transport (P. Mitchell, 1978); for the development of the theory of mechanisms of chemical reactions (K. Fukui, R. Hoffman, 1981); for studying the mechanisms of reactions with electronic transitions in metal complexes (G. Taube, 1983); for the application of the scaling concept to the thermodynamics of polymer systems (De Jen, 1987); to clarify the three-dimensional structure of the photosynthetic reaction center (J. Deisenhofer, R. Huber, H. Michel, 1988); for his contribution to the development of the methodology of NMR spectroscopy with high magnetic field voltage (R. Ernst, 1991); for the discovery of fullerene (H. Croteau, 1996); for the development of a method for calculating quantum chemistry (A. Zewail, 1999); for the development of the NMR spectroscopy method for determining the three-dimensional string of biological macromolecules in solutions (K. Vyukhrich, 2002); for the opening of channels, water supply systems in household membranes (P.Egr, 2002); for structural and mechanical studies of ion channels (R. MacKinnon, 2003); for research in the field of chemical processes occurring on solid surfaces (G. Ertl, 2007).

Physical chemistry is an independent science, which has its own research methods and is the theoretical basis of chemical and technological sciences. Physical chemistry is of great importance in production, as it requires perfect knowledge of its mechanism in the implementation of chemical processes

Academicians founded in our republic: O.S. Sadykov, T.F.Oripov, professors: Kh.Aslonov, V.B.Leontev, Yu.Toshpulatov, M.R.Yagudaev, A.M.Rashkes and a number of other scientists made significant contributions and published scientific articles.

The subject “Methods of Physical Research” has been taught as a general course for more than 35 years in the chemistry departments of universities, and advice on teaching methods for this subject was carried out on the initiative of Moscow State University in 1988 and 1989 at Kuban State University. The main goal of the Council was to familiarize students with the methodological work carried out at universities, modern tools and practical teaching methods for a deeper mastery of this science by students .

Young specialists in the field of chemistry must have sufficient knowledge of modern physical methods, which requires a perfect textbook in the Uzbek language. So far there are several textbooks and monographs written in Russian and translated from a foreign language into Russian.

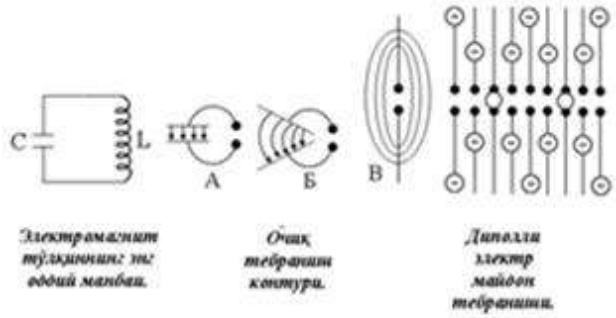
This literature is written in complex language, in of which more attention is paid to the theories of physical methods, the possibilities of application in practice are poorly covered, which creates difficulties for students to master science.

The first textbook in Uzbek language - “Physical methods of research in chemistry” was written by T.K. Yunusov and S.A. Auelbekov in 1992. It briefly describes mainly abstract, infrared, NMR and mass spectroscopy; other methods are not reflected in the text of the manual. It briefly describes mainly abstract, infrared, NMR and mass spectroscopy; other methods are not reflected in the text of the manual.

In the 60s of the 19th century, the English scientist Maxwell created a unified theory of electrical and magnetic phenomena. This theory is caused by experimental results known at that time, called Maxwell's theory of electromagnetic field. Maxwell's theory is based on the following two important ideas, reflecting the relationship between electric and magnetic fields. 1. A changing magnetic field over time creates an alternating electric field. 2. A changing electric field over time will create an alternating magnetic field.

Electromagnetic wave scale. Spectrum parameters. In fact, the source of electromagnetic waves can be any electrical oscillation circuit or conductor in which an alternating electric current flows. To excite electromagnetic waves, it is necessary to create an alternating electric field (shock current) or, accordingly, a changing magnetic field in space. The ability of a source to radiate is determined by its shape, size and oscillation frequency.

In order for the radiation to be noticeable, the variable electrical space must be large. Therefore, to create electromagnetic waves, closed oscillation circuits cannot be used, since an electric field and a magnetic field inside the inductance track will be located between the capacitor coatings. To shorten the wavelength, it is necessary to reduce the cost of inductance and capacitance. In this regard, Gers in his experiments examined the shield area and the surface of the capacitor coatings.



As a result, two rod (wire) circuits were formed, separated by a gap between flashes. If in an agar, a closed oscillation circuit, the electric field is located between the capacitor coatings, then in an open oscillation circuit, an alternating electric field occupies the space around the circuit and increases the intensity of electromagnetic radiation. If opposite charges are introduced at the ends of a two-rod oscillation circuit, electric field lines are formed around the rod. Dependent charges form a current in the exhaust conductor, which, in turn, will create an electric field around the conductor. The picture shows the location of charges relating to 1/8 of the entire period. Judging by the figure, this, in turn, represents an oscillation of the dipole electric field. If counter charges collide between the vibrators, they neutralize each other and the ends of the electric power lines are disconnected from the charges. The separated electric field lines begin to spread along all sides of the vibrator. Gers was able to create

electromagnetic waves with a frequency of 100 MHz through such a vibrator. The wavelength of these waves is approximately 3 m. By further reducing the thickness and length of the rods, P. N. Lesedov created electromagnetic waves λ= 6 ÷4 mm .
Electromagnetic waves with a wavelength of m 3 0.1 ÷10 are used for radio communication and image transmission (long, medium, short, ultrasonic and decimeter radio waves). Electromagnetic waves with a wavelength of 10-8 ÷10 -4 m, consisting of optical waves of three groups: infrared, eye-shaped and ultraviolet rays.
Finally, short-duration rays consist of x-rays and gamma rays, which have an input nature of matter.

Two methods are most widely used in chemistry:

1. X-ray structural analysis, which allows you to determine the coordinates of atoms in the three-dimensional space of crystalline substances from the simplest compounds such as NaCl to complex proteins.

2. Gas electron diffraction, which is used to determine the geometry of free molecules in gases, that is, molecules that are not influenced by neighboring molecules, as is the case in crystals.

Comparison of data from both methods for the same substances makes it possible to evaluate the influence of the crystal field on the molecule.

Optical methods

Optical methods study the propagation, scattering and absorption of light in matter. The physical quantities that are measured represent the following series:

1) n - refractive index: n = c / u, where c is the speed of light in a vacuum, u is the speed of light in matter;

2) a is the angle of rotation of the plane of polarization of linearly polarized light when passing through an optically active substance, which rotates the plane of polarization of the incident linearly polarized light;

3) r - depolarization coefficient, that is, the ratio of the intensity scattered at an angle of 90? light with polarization perpendicular to the plane of incident linearly polarized light I^ to the intensity of scattered light with parallel polarization I|| , that is, r = I^ / I|| .

4) - Kerr effect, where n|| and n^ are the refractive indices for linearly polarized rays propagating along the electric field E|| and perpendicular to this field, respectively;

5) a(B) - Faraday effect, where a(B) is the dependence of the angle of rotation of the plane of polarization of light on the magnitude of the magnetic field B;

6) e(l) - molar light absorption coefficient as a function of l, etc.; this parameter is also determined in spectroscopic methods.

The results of optical methods are used to identify substances, identify the mutual influence of atoms in a molecule, calculate the polarizability of molecules, assign frequencies in vibrational analysis, study the effect of a solvent on the system under study, etc.

Mass spectrometry and electron spectroscopy

This group of methods differs from the previous ones in that as a result of the interaction of any incident radiation or particle flux on a substance, the fluxes of other particles are measured. Thus, in mass spectrometry, the incident flow can be a flow of electrons, ultraviolet radiation, a flow of charged atoms or molecules, that is, ions that generate flows of molecular ions of the substance being studied or fragment ions resulting from the decay of a molecular ion according to the scheme

or

where I0 is the electron flow e, electromagnetic radiation hn, charged argon atoms Ar+, charged simpler molecules R+, inhomogeneous electric field E , etc. In mass spectrometry, ion currents I(M+) , or I(M-), etc. are measured.

The mass spectrometry method is used to determine molecular masses, identify substances, establish the chemical structure of substances, study the heats of evaporation and reactions, the mechanisms of chemical reactions, measure ionization potentials and energies of breaking chemical bonds.

In the methods of X-ray electron spectroscopy (XES) and optical electron spectroscopy (photoelectron spectroscopy, FES), the incident radiation I0 is X-ray or ultraviolet radiation. However, unlike mass spectrometry, they measure the energy of the flow of electrons ejected from a molecule or substance, that is, they measure I(E el).

X-ray radiation removes electrons from the inner shells of atoms of substances. Therefore, the XPS method makes it possible to determine the binding energy of the internal electrons of the skeletons of atoms in a molecule and substance. The FES method is used to determine successive ionization potentials from the valence shell of atoms in a molecule. Both of these methods make it possible to identify substances and study the patterns of influence of atoms in the immediate environment on the binding energy of electrons in atoms in different orbitals.

Dielcometry and magnetochemistry

Depending on the magnitude of the electric dipole moments or magnetic characteristics of substances, external electric and, accordingly, magnetic fields change

the behavior of the substance in these fields compared to its behavior in the absence of a field.

Measurements of dielectric constant e make it possible to determine the value of the electric dipole moment m, which characterizes the polarity of molecules. In addition, the value of m is a source of structural information when using additive design schemes.

Magnetochemical studies make it possible to estimate the number of unpaired electrons in the atoms of a substance based on the degree of paramagnetism (paramagnetic substances are drawn into a magnetic field). Diamagnets are pushed out by a magnetic field and the degree of this push-out is determined by the electronic structure of the molecules and matter. Particularly indicative is the difference in the molar diamagnetic susceptibilities cd parallel and perpendicular to the plane of the molecules of benzene, naphthalene and other aromatic hydrocarbons. This proves the existence of electronic currents in the planes of aromatic molecules.

INTEGRATION OF VARIOUS PHYSICAL METHODS

Physical quantities obtained by various physical methods provide not only a more complete description of the physical state of substances, but also a more complete description of the chemical structure of substances. Thus, if X-ray diffraction studies did not allow us to determine the coordinates of light hydrogen atoms, then the NMR method (meaning proton resonance) complements the picture of the chemical structure of the substance.

X-ray diffraction and neutron diffraction complement each other in that in x-ray diffraction studies they determine the complete distribution of the electron density of crystalline substances, and in neutron diffraction studies - the position of the nuclei of the atoms of such substances. By jointly processing X-ray and neutron diffraction data, the distribution of electron density in chemical bonds is found. This is achieved by subtracting the electron density of atomic cores, the positions of which are calculated from neutron diffraction data, from the total electron density of the atoms of the substance.

The geometric parameters of molecules of substances in the gas phase are determined more reliably and completely if data from gas electron diffraction, microwave spectroscopy, vibrational spectroscopy and the results of quantum chemical calculations are used simultaneously.

Only the joint use of these listed methods allows us to solve the problem. Thus, the structures of many compounds were determined: acrolein CH2=CH-CH=O, 1,1-difluoroethylene F2C=CH2, phosphabenzene C5H5P, arsabenzene C5H5As, etc.

The polarizability of molecules is generally expressed by three numbers, which characterize the different polarization of molecules in three directions of three-

dimensional space. Thus, the chlorobenzene molecule has three so-called main values for polarizability: the largest along the ring and the smallest in the perpendicular direction. However, in order to experimentally determine these values, it is necessary to jointly process data on refractive index measurements, study the Kerr effect, and find the electric dipole moment.

The list of such examples can be continued.

CONCLUSION

The article examines a very complex issue about the use of physical research methods in chemistry. The presented material is presented with the aim of showing that the combination of physics and chemistry helps to more deeply understand natural phenomena and, in particular, chemical phenomena. In connection with the solution of physical problems, very complex mathematical problems arise, since the processing of experiments, direct and inverse problems of physical methods require the use of mathematical theory and computational methods.

In connection with such complex problems in the use of physical methods, specialization of scientists takes place. As in medicine, which is a very clear example, specialists work in relatively narrow fields that require very deep knowledge and experimental skills. Almost every physical method is an area of specialization. However, both the physicist and the chemist must have an understanding of the capabilities of the various methods. A chemist must formulate the problem correctly. The physicist must not only solve it, but also know how his results compare with other methods.

Very often a chemist and a physicist, as well as a mathematician, are represented in one person. First, a chemist poses a problem, and then works as a physicist and mathematician to solve it.

General ideas about physical research methods can be found in books, textbooks and collections, such as, for example, [4 - 8]. Unfortunately, the material in this literature goes beyond the scope of the school curriculum. But if you have a strong interest in the subject, it will be very useful. This material will contribute to greater contacts between chemists, physicists and mathematicians at school and to better development of educational programs.

One more important circumstance should be noted. Due to the complexity and high cost of equipment and the different capabilities of the methods, the distribution and breadth of use of physical methods varies significantly . The most widely used methods are vibrational spectroscopy, mass spectrometry, ultraviolet spectroscopy and nuclear magnetic resonance. More limited use in chemical research includes methods of microwave spectroscopy, nuclear gamma resonance, nuclear quadrupole resonance, gas electron diffraction, photoelectron spectroscopy, etc.

In such a difficult situation, the cooperation of scientists helps, which allows them to solve emerging problems.

Another article will give the results of using physical methods in chemistry.

LITERATURE

1. Chemical encyclopedic dictionary. M.: Soviet Encyclopedia, 1983.

2. Physical encyclopedic dictionary. M.: Soviet Encyclopedia, 1983.

3. Gordon A., Ford R. The Chemist's Companion. M.: Mir, 1976.

4. Afanasyev V.A., Zaikov G.E. Physical methods in chemistry. M.: Nauka, 1984. (Series "History of Science and Technology").

5. Drago R. Physical methods in chemistry. T. 1, 2. M.: Mir, 1981.

6. Vilkov L.V., Pentin Yu.A. Physical research methods in chemistry. Structural methods and optical spectroscopy. M: Higher School, 1987.

7. Vilkov L.V., Pentin Yu.A. Physical research methods in chemistry. Resonance and electro-optical methods. M.: Higher School, 1989.

8. Journal of the All-Union Chemical Society named after. DI. Mendeleev. 1985. T. 30. N 2.

The issue is dedicated to new methods and instruments for chemical analyzes and research.

Lecture 4

Subject : Application of IR spectroscopy to identify functional groups and characteristic components.

Plan

1. Types and methods of spectroscopy
2. Infrared spectroscopy
3. Mass spectrometry
4. Mössbauer spectroscopy
5. Microwave spectroscopy
6. Molecular electron spectroscopy
7. Optical spectroscopy in the visible wavelength range
8. X-ray spectroscopy
9. Terahertz spectroscopy

Classification of spectroscopy methods

Electromagnetic radiation, when interacting with a substance, can cause processes of various physical natures in it, which are used in methods of chemical analysis. The general nature of these processes depends on the photon energy. Consequently, to classify analysis methods, it is advisable to divide the entire energy range of electromagnetic quanta into regions corresponding to a particular physical process. Table 1.1 shows the main areas of electromagnetic radiation used in chemical analysis, the wavelength ranges that characterize the area of radiation and the nature of the corresponding processes.

1. For analytical purposes, spectroscopic methods using electromagnetic radiation in the optical range are of greatest importance. These methods are divided into optical atomic and optical molecular spectroscopy . This section will discuss an analysis method based on measuring light absorption — molecular absorption spectroscopy.
2. The method of molecular absorption spectroscopy in the UV and visible regions of the spectrum is usually called spectrophotometry. Depending on the type of absorption spectral devices, photometric and spectrophotometric methods are distinguished. Their comparative characteristics are given in table. 1.2.

Table 1.1. Energy regions of electromagnetic radiation, corresponding methods of analysis and processes underlying them

Area (method)	Wavelength	Process
Gamma radiation (nuclear physics)	10^{-4}–10^{-1} nm	Nuclear reactions
X-ray	10^{-1}–10^{1} nm	Changing states of internal electrons
Optical UV	200–400 nm	Changing states of valence electrons
visible	400–750 nm	
infrared (IR, KR)	10^{3}–10^{6} nm	Change of vibrational states
Microwave	10^{-3}–10^{-1} m	Changing rotational states
Radio frequency (NMR, ESR)	10^{-1}–10^{1} m	Changing spins of nuclei and electrons

3. Table 1.2. Photometric methods of analysis

Method,	Device type	Working spectrum area, nm	Monochromatization method	Recorded signals
Photometry	Photometer (photocolorimeter)	Visible 400–750	Light filter	Optical density (A) and transmittance (T) in the wavelength range corresponding to the passband of the filter
Spectrophotometry	Spectrophotometer	UV and visible 100–750	Monochromator or polychromator	Optical density (A) and transmittance (T) at a fixed wavelength; electronic absorption spectra in the form of curves A = f(λ), A = f(ν), T = f(λ), T = f(ν)

4. Both methods are combined into one group of photometric methods of analysis. When the determination is carried out in the visible part of the spectrum, the term photocolorimetry (from Latin color - color) is often used , since we are dealing with colored solutions.

Laws of absorption of electromagnetic radiation

The basic principles and laws of radiation absorption are valid for all regions of the spectrum - from X-rays to radio emission. Quantitatively, the absorption of radiation by a system is described by the laws of Bouguer – Lambert – Beer and additivity.

Bouguer–Lambert–Beer law

When radiation passes through a solution of a light-absorbing substance, the radiation flux is weakened. The decrease in intensity depends on the concentration of the absorbing substance and the length of the path traversed by the flow. This dependence is expressed by the Bouguer–Lambert–Beer law. To take into account the loss of light passing through a solution due to reflection and scattering, the intensities of light passing through the test solution and the solvent are compared. With the same layer thickness in cuvettes made of the same material containing the same solvent, reflection losses and light scattering will be approximately the same for both light beams, and the decrease in intensity will depend on the concentration of the substance.

Let us denote the intensity of the incident light flux as I_o, I is the intensity of the light flux passing through the solution. The value of I/I_o is called transmission and is denoted by T ($0 \le T \le 1$).

T taken with the opposite sign is called optical density A :

$$A = -\lg T = -\lg \frac{I}{I_0} = \lg \frac{I_0}{I}$$

For an absolutely transparent solution A = 0, for an absolutely opaque solution – $A \to \infty$.

The decrease in radiation intensity as it passes through a solution obeys the Bouguer–Lambert–Beer law:

$$\frac{I}{I_0} = 10^{-\varepsilon l C} \quad \text{or} \quad -\lg T = A = \varepsilon l C$$

where ε is the molar absorption coefficient, l is the thickness of the absorbing layer, cm ; C – solution concentration, mol/l.

The physical meaning of the molar absorption coefficient becomes clear if we take l = 1 cm , C = 1 mol/l, then A = ε. Consequently, the molar absorption coefficient is equal to the optical density of a one-molar solution with a layer thickness of 1 cm. The molar absorption coefficient is an individual characteristic of a substance; it depends on the nature of the substance and the wavelength and does not depend on the concentration and length of the cuvette. Since the dimension of the quantity ε is unambiguously specified l/mol .s m, it is usually not indicated, but a numerical value is given. The value ε reflects the substance's ability to absorb light; the maximum possible value ε is $\approx 10^{5.}$

The concentration of solutions of substances with unknown molar masses is usually expressed in mass fractions (%). In this case, the absorption coefficient is called the

specific absorption coefficient and is designated by the symbol $E_{1cm}^{1\%}$. The latter is numerically equal to the optical density of a 1% solution at l = 1 cm. In another way of expressing the concentration of a solution (for example, g/ml or others), the absorption coefficient is denoted by the symbols a or k and the dimension is indicated.

Limitations and conditions of applicability of the Bouguer–Lambert–Beer law

Deviations from the linear relationship between optical density and concentration are encountered quite often. The main reasons for this phenomenon are as follows.

1. Beer's law is valid for dilute solutions. At high concentrations (>0.01 M), the average distance between particles of the absorbing substance decreases to such an extent that each particle affects the charge distribution of neighboring particles, which in turn can change the ability of the particles to absorb radiation of a given wavelength.

The coefficient εin equation (1.3) depends on the refractive index of the medium. An increase in the concentration of the solution leads to a significant change in the refractive index n and a deviation from Beer's law (the refractive indices of dilute solutions and the solvent differ insignificantly).

2. The law is valid for monochromatic radiation. Strictly speaking, equation (1.3) should be written as:

$$A_\lambda = \varepsilon_\lambda l C$$

The index λindicates that the values of A and εrelate to monochromatic light with wavelength λ. The non-monochromaticity of the light flux is associated with the imperfection of optical instruments. Deviation from Beer's law is less noticeable if the wavelength does not fall in a part of the spectrum with a sharp change in optical density. In practice, they tend to measure A at maximum light absorption.

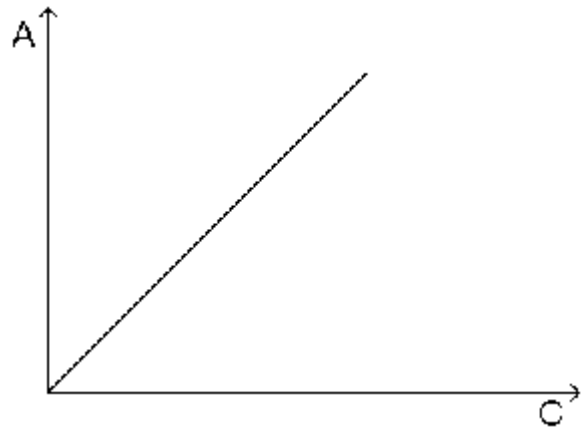
3. The temperature during measurements should remain constant at least within a few degrees.

4.The beam of light must be parallel.

5. Equation (1.3) is observed for systems in which only one type of substance particle absorbs, i.e. there is no chemical interaction. If, when the concentration changes, the nature of these particles changes, due, for example, to acid-base interaction, polymerization, dissociation, etc., then the dependence A = f (C) will not be linear, since the molar absorption coefficient of the newly formed and initial particles will not be the same.

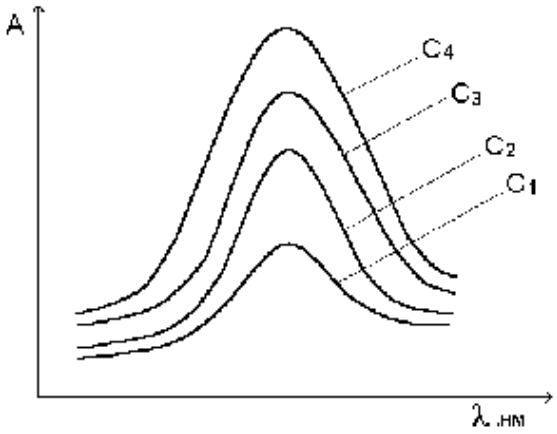
Constraints 1 and 2 are true, the rest are called apparent; limitations (3–5) depend on the experimental conditions and are associated with instrumental reasons. The last of the limitations is due to chemical reasons.

When Beer's law is satisfied, the graph of the dependence of optical density on concentration is a straight line passing through the origin of coordinates (Fig. 1.1.a), and the function $A_\lambda = f(\lambda)$ has the same form regardless of the layer thickness and solution concentration, and the position of the absorption maximum is preserved (Fig. 1.1.b).



A)

b)



Rice. 1.1. a) dependence of the optical density of a substance on concentration subject to the basic law of light absorption) . b) light absorption curve of the same substance subject to the Bouguer–Lambert–Beer law. $C_1 < C_2 < C_3 < C_4$.

Additivity law

Optical density is an extensive property of a substance. The absorption of light by any substance does not depend on the presence of other substances in the solution, and the optical density of a mixture of substances is equal to the sum of the optical densities of

each of them. This is true provided that each substance obeys the Bouguer–Lambert–Beer law and in the absence of chemical interaction between them. So, for a mixture of m substances at the same wavelength we have:

$$A = A_1 + A_2 + \cdots + A_m$$

or:

$$A_\lambda = l(\varepsilon_{\lambda,1}C_1 + \varepsilon_{\lambda,2}C_2 + \cdots + \varepsilon_{\lambda,m}C_m)$$

The principle of additivity (summing) of optical densities is widely used in analytical chemistry.

Lecture 5

Topic : Vibrations of oxygen-containing compounds.

When radiation passes through a transparent layer of liquid (solid or gas), selective absorption of radiation with certain frequencies occurs. Electromagnetic energy in this case is transferred to the atoms or molecules of the substance and transfers the absorbing particles from the normal, or ground, state to the excited one . The totality of all absorbed frequencies constitutes the absorption spectrum of a molecule (molecular absorption spectrum). The absorption of electromagnetic radiation by substance M can be represented as a two-stage process, the first stage of which is expressed as follows:

$M + h\nu \rightarrow M^*$,

where M^* is a volume or molecule in an excited state. The residence time in the excited state is short (10^{-9}–10^{-8} s) , then the particles return to their original state. In absorption methods, excitation energy is converted into heat (second stage of the process):

$M^* \rightarrow M + heat$

It is important to keep in mind that the lifetime of M^* particles is usually so short that their concentration at any time under normal conditions is negligible. Moreover, the amount of heat generated is imperceptible. As a result, irradiation of the system during its study is accompanied by minimal destruction, which is an advantage of absorption methods.

Spectra of atoms in the UV, visible and near -IR regions arise during transitions of valence electrons from one energy state to another; each transition corresponds to a spectral line of a certain frequency. The spectra of atoms consist of a large number of discrete spectral lines.

The spectra of molecules are much more complex, since they are caused not only by the movement of electrons, but also by the vibrations of atomic nuclei and the rotation of the molecule as a whole. Therefore, in any stationary state, the energy of a molecule consists of electronic, vibrational and rotational energies:

$$E = E_{эл} + E_{кол} + E_{вр}$$

The largest contribution to the total energy comes from the energy of electronic transitions, the smallest contribution from the rotational energy of molecules:

$E_{vr} / E_{count} / E_{el} = 1 / 10^{2} / 10^{3}$

Just like an atom, a molecule can only exist in certain energy states called energy levels (orbitals). Each electronic state corresponds to vibrational levels, and each vibrational level corresponds to rotational levels. When receiving energy from the outside, the molecule moves from one energy level to another.

When the electron energy changes (60–150 kJ/mol), the vibrational and rotational energies of the molecule simultaneously change, and electronic-vibrational-rotational transitions are observed instead of electronic ones. Since their number is very large, the electronic-vibrational-rotational spectrum, usually called electronic, takes the form of broad overlapping bands in the UV, visible and near-IR regions.

Depending on the composition of the molecules and the conditions for measuring the spectra (gas or condensed phase, type of solvent, temperature), the bands in the electronic spectra can be smooth or characterized by better or worse pronounced vibrational and rotational structures (Fig. 1.2.). In cases where fine structure appears, we speak of allowed spectra.

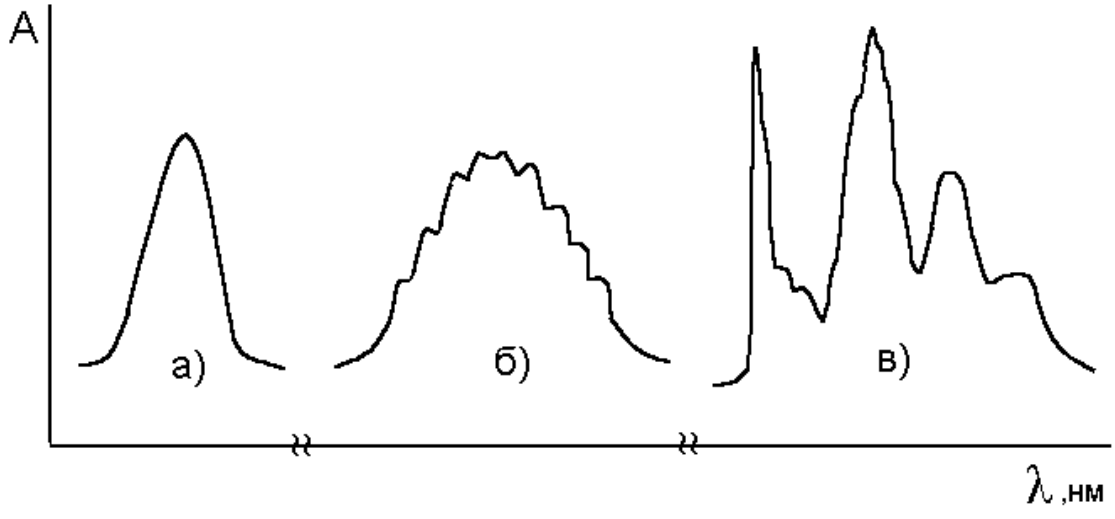


Fig.1.2. Electronic spectra of substances: a) smooth contour, vibrational structure does not appear; b) traces of a vibrational structure are visible on the contour of the band; c) absorption spectrum of anthracene vapor with a clear vibrational structure.

Electronic spectra

The action of visible and ultraviolet radiation leads to the excitation of valence electrons and the appearance in the spectrum of bands corresponding to electronic transitions between different energy levels in the molecule. The discrete energy states of a molecule can be described using the molecular orbital or valence bond method.

Electrons in a molecule can occupy different orbitals. The following molecular orbitals (MOs) are distinguished:

σ-binding, σ* - loosening, n - non-binding, π-binding, π* - loosening.

σ-bonds are found predominantly in molecules with single bonds, π-bonds - in molecules with double and triple bonds; examples of typical substances with n - orbitals are alcohols, organic sulfides and others, i.e. organic compounds with heteroatoms –N,O,S, halogens.

A diagram of the relative arrangement of energy levels corresponding to different MOs is shown in Fig. 1.3.

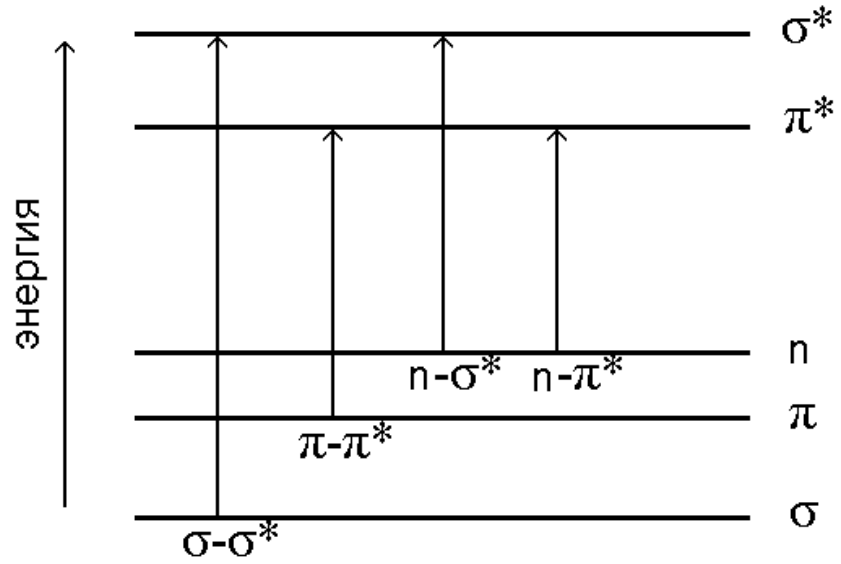


Fig.1.3. Diagram of electronic levels and energy of possible

electronic transitions.

Different electronic transitions require different energies, so the absorption bands are located at different wavelengths.

The greatest energy is required by the σ– σ* transition, associated with the excitation of internal electrons. It corresponds to absorption in the far ultraviolet region ($\lambda \leq 200$ nm , $E \geq 600$ kJ/mol). Such transitions are characteristic, for example, of saturated hydrocarbons. Obtaining a spectrum in this region is not easy because atmospheric

components are absorbed here; for this reason, single bond absorption is of little importance in analytical practice.

n– σ* transition is associated with lower energy costs; the bands associated with this transition are located in ordinary ultraviolet (λ~ 200 – 300 nm). Even less energy is required for the transition to antibonding π* orbitals . Transitions n – π* and π– π* occur in molecules of compounds with conjugated bonds and molecules of aromatic compounds. Functional groups such as ⟩C =O, ⟩C=C ⟨, –N=N–, –N=O, ⟩C=S, –C ≡N, –C ≡C– and many others always cause absorption in the visible and ultraviolet regions. They are called chromophore groups (literally, "color-bearing" groups). Substituents that increase the color intensity of a molecule are called auxochromes . As an example, we can name the following groups: –OH, –OR, $–NH_2$, –HR, $–NR_2$, –SH, $–CH_3$, –Cl, –Br, phenyl, etc.

Most transition metals that have an unfilled electronic d level exhibit chromophore properties. These metals are characterized by their characteristic feature of being in different valence states. The group of metals under consideration can give color reactions with colorless reagents that do not contain chromophore groups.

The same n– π* transition can explain, for example, the intense coloring of the MnO_4^- and CrO_4^{2-} ions (transition from the nonbonding orbital of oxygen). Since each substance is characterized by its own system of energy levels, the spectra of substances differ both in the number of bands and in their position on the wavelength scale.

Representation of absorption spectra

Electromagnetic radiation is absorbed selectively by substances: at some wavelengths, light absorption occurs intensely, and at others, light is not absorbed. Light quanta are intensively absorbed, the energy of which (h ν) is equal to the excitation energy of the particle.

A graphical representation of the distribution of absorbed energy over wavelengths is called an absorption spectrum .

of absorbed light energy is expressed in terms of T , A ,. εThe choice of one or another value is determined by the spectral region, the absorption value, the objectives of the study, etc. In the visible and UV regions of the spectrum, the coordinates A = f (λ) or ε= f (λ), are usually used.

lg ε= f (λ),

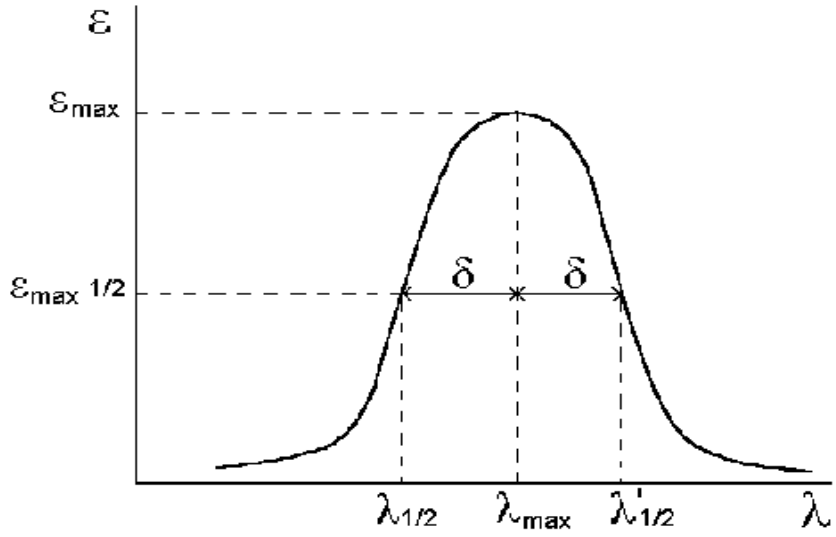
Main characteristics of the spectrum . The part of the spectrum in which intense absorption of radiation is observed is called absorption band . The following characteristics of the spectrum are of greatest interest for analysis: the number of

maxima (absorption bands), their position on the wavelength scale, the intensity of the absorption band, the width and shape of the band (Fig. 1.5).

Fig.1.5. Absorption band.

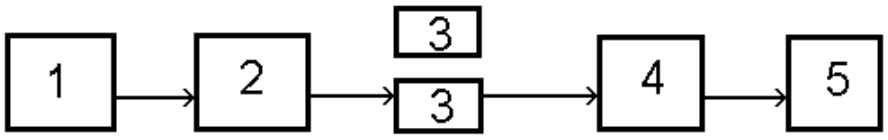
The absorption band width is usually characterized by the value δ, whereδ – half-width of the absorption band; it is measured at $\varepsilon = 1/2\ \varepsilon_{max}$. To characterize the intensity of bands in analytical practice, the value of the molar coefficient at the absorption maximum – ε_{max} is used.

Strict individuality and constancy εfor each substance at a given wavelength allows for qualitative and quantitative determinations by the spectrophotometric method.



Obviously, the higher ε_{max} and the smaller the bandwidth, the higher the sensitivity of determining a given substance.

Equipment in absorption spectroscopy Block diagram of devices



With all the variety of schemes and design features of absorption spectroscopy devices, each of them has several main components (Fig. 1.6).

Fig.1.6. Block diagram of instruments for measuring radiation absorption. 1 – radiation source; 2 – monochromator; 3 – cuvettes with the test solution and solvent; 4 – radiation receiver; 5 – measuring or recording device.

Monochromatic radiation, separated from polychromatic radiation , passes through the sample. The ratio of the intensities of the incident and transmitted radiation fluxes through the cell is measured by a radiation receiver. The device can be made in a two-beam version, when the radiation flow simultaneously passes through cuvettes with the test solution and solvent (or a specially selected reference solution); The devices are often made according to a single-beam scheme, when the radiation flow passes alternately through cuvettes with a reference solution and a test solution.

Radiation sources

The radiation sources used in spectrophotometry are continuous spectrum emitters: tungsten incandescent lamps, gas-filled lamps (hydrogen, mercury).

In an incandescent lamp, a luminous tungsten filament produces light over a wide spectral range, however, glass transmits light with wavelengths of 350–1000 nm, i.e. near ultraviolet, visible light and near infrared radiation . In hydrogen (deuterium, xenon) lamps, gas glows during discharge; Continuous radiation appears in the region of 200–350 nm.

Monochromatization of radiation

Working with a narrow radiation band has the following advantages: 1) the probability of the absorbing system obeying Beer's law increases (see Section 1.2), 2) the selectivity and sensitivity of determination increase.

Devices for isolating part of the radiation are based on the use of various optical phenomena: interference, diffraction, light absorption, dispersion. It is impossible to isolate absolutely monochromatic radiation; in practice, a more or less narrow range of wavelengths is obtained; This is achieved using non-dispersive (filters) and dispersive (monochromators) methods.

In the visible part of the spectrum Light filters are commonly used and come in several types . And absorption filters are colored glasses or glass plates, between which a dye suspended in gelatin is placed. The former are usually more thermally stable. Absorption filters transmit radiation from a limited range of wavelengths (30 nm or more) and absorb radiation from all others. The characteristics of interference filters are much better; the effective transmission width usually does not exceed 5–10 nm. To further narrow the passbands, a system of two sequential interference filters is used. When marking filters, indicate the wavelength at maximum transmission and the bandwidth.

A monochromator is a device that decomposes radiation into its constituent waves of different lengths. All monochromators consist of a dispersing device and an associated system of lenses, mirrors, input and output slits. Prisms and diffraction gratings serve as dispersing elements. The bandwidth of monochromators reaches 1.5 nm.

Cuvettes

The samples to be tested are placed in transparent vessels with flat parallel walls - cuvettes.

Radiation receivers

Photocells are mainly used as radiation receivers in absorption devices . To receive signals in the visible and UV regions, photocells with an external photoelectric effect are usually used: antimony-cesium (180–650 nm) and oxygen-cesium (600–1100 nm). When measuring low intensity radiation, photomultiplier tubes are used .

The industry produces various absorption spectroscopy instruments: colorimeters, photometers, photoelectrocolorimeters, spectrophotometers, etc., which use various combinations of radiation sources, monochromators and radiation receivers.

Application of spectrophotometry in analysis
Qualitative analysis of absorption spectra

Absorption spectroscopy can serve as one of the methods of qualitative analysis. For the purposes of qualitative analysis, electronic absorption spectra are used much less often than vibrational ones, since absorption bands tend to broaden, which hides their fine structure. Spectra in the ultraviolet and visible regions are characteristic of more or less large structural elements in the molecule. The spectra of large, structurally similar molecules differ very little. They are usually represented by separate wide absorption bands, which are often superimposed on one another and overlap.

Compounds containing chromophore groups have characteristic absorption bands (see section 1.3.2). Spectral studies in this area often provide useful qualitative information about the presence or absence of certain functional groups, such as carbonyl, aromatic ring, nitro group or conjugated double bond. It should be kept in mind that identification is reliable if the chromophores in the molecule are isolated. In the presence of auxochromes and conjugation chains, identification becomes difficult.

Quantitative analysis using photometric methods

In photometric analysis, the amount of a substance is determined by the color intensity or light absorption of the colored compounds. A solution or object appears colored if it transmits or absorbs different wavelengths of visible light differently. In the visible region, the color of a solution is determined by the wavelength of radiation not absorbed by this solution. For example, a solution that absorbs radiation in the blue part of the spectrum (≈475 nm) is colored yellow, i.e., the blue color is complementary to the color of the solution. Table 1.3 provides such data for the entire visible radiation region.

Absorption spectroscopy, especially in the visible and UV regions, is one of the most common methods of quantitative analysis. Photometric methods are used to determine substances with their own absorption (organic substances with chromophore groups,

transition metals), as well as for the determination of non-absorbing substances.

When determining inorganic components to obtain colored compounds, reactions of formation (sometimes destruction) of complex compounds are most often used;

Oxidation-reduction reactions are used much less frequently. For photometric determination

Table 1.3. Visible colors

Observable color (color of solution)	Area of maximum absorption, nm	Additional color, (absorbed radiation)
Green-yellow	380–420	Violet
Yellow	420–440	Blue
Orange	440–470	Blue
Red	470–500	Bluish green
Purple	500–520	Green
Violet	520–550	Yellow-green
Blue	550–580	Yellow
Blue	580–620	Orange
Bluish green	620–680	Red
Green	680–780	Purple

organic components most often use reactions of synthesis of colored compounds. Such reactions are called photometric.

The main requirements for reactions boil down to the following: selective action of the reagent, high reaction rate, large value of the equilibrium constant, constancy of composition and stability of colored compounds during analysis. In this regard, the pH of the medium, reaction time, concentrations of reagents, and temperature are important .

Main stages of analysis in photometry

Before performing a photometric determination, it is necessary to select the analysis conditions. The following scheme can be recommended.

– transfer of the analyzed sample into solution and separation, if necessary, of interfering components;

– selection of the photometric form of the substance and carrying out chemical reactions to obtain a colored compound (if the substance being determined does not have intense intrinsic absorption)

– establishing the concentration range in which the basic law of light absorption is satisfied:

– measurement of the optical density of the test solution;

– calculation of the substance content in the analyzed sample and its metrological assessment.

Metrological characteristics of the method

Sensitivity is characterized by the angle of inclination of the calibration graph. The tangent of the slope is equal to the molar absorption coefficient. If we take the minimum value of optical density, measured with the required accuracy , $A_{min} = 0.01$, we can calculate the minimum detectable concentration:

$$C_{min} = \frac{0,01}{\varepsilon l}$$

At values$\varepsilon \approx 10^{5}$ detection sensitivity can be 10^{-7}–10^{-6} M.

Reproducibility . To obtain reproducible results, errors in optical density measurements must be taken into account. The measuring device of a photometric device usually has a constant measurement error in the transmittance value T over the entire scale ; the measurement error in the value A will not be the same, since A = – log T. The relative error in determining the concentration $\Delta C / C$ has a minimum value at T = 0.37 or optical density A = 0.435. To measure concentration with an error not exceeding twice the minimum, it is necessary to measure A in the range of 0.1–1.0. To reduce the random measurement error in the region of large and small values of A, there are special techniques, one of them is the differential analysis method.

Correctness . Systematic errors in photometry can arise due to deviations from Beer's law, due to the non-monochromatic nature of the light flux and chemical interactions in the measured system, as well as in the presence of impurities that absorb light in a given region of the spectrum. To reduce systematic error, there are special techniques, such as preparing a reference solution containing all components except the one being determined.

The accuracy of photometric methods depends on the individual characteristics of the photometric reaction, the characteristics of the device used and other factors. The usual relative error of photometric methods is 1–2%.

Analysis of single-component systems by photometric method

A method for comparing the optical densities of the standard and test compounds. To analyze a substance using this method, prepare a solution of the test substance and two or three standard solutions, then measure the optical densities of these solutions under

the same conditions (wavelength, thickness of the absorbing layer). The determination error will be smaller if the optical densities of the test and standard solutions have close values. To do this, first photometer the test solution, and then select the desired concentration of the standard solution. According to Beer's law, the optical densities of the test and standard solutions are equal:

$$A_x = \varepsilon_\lambda l C_x$$

$$A_{ст} = \varepsilon_\lambda l_{ст}$$

Dividing equation (1.9) by (1.10) and taking into account that optical densities are measured under the same conditions (λ= const, l =const) and the same light-absorbing particles in the solution (ε_λ=const), we obtain:

$$\frac{A_x}{A_{ст}} = \frac{}{ст}$$

where

$$C_x = C_{ст}\frac{A_x}{A_{ст}}$$

The comparison method is used for single analyzes and requires mandatory compliance with Beer's law.

Molar absorption coefficient method. When working using this method, the optical density of several standard solutions $A_{st\ is\ determined}$, and the molar absorption coefficient is calculated for each standard solution:

$$\varepsilon = \frac{A_{ст}}{l C_{ст}}$$

and the resulting value εis averaged. Since the molar light absorption coefficient does not depend on the thickness of the absorbing layer, measurements can be carried out in cells of different lengths. Then the optical density of the test solution $A_{x\ is\ measured}$ and the concentration $C_{x\ is\ calculated}$:

$$C_x = \frac{A_x}{\varepsilon l}$$

The method requires mandatory compliance with Beer's law at least in the area of concentrations being studied; used quite rarely.

Calibration graph method. In accordance with the Bouguer–Lambert–Beer law, the dependence of optical density on concentration must be linear and pass through the origin.

Prepare a series of standard solutions of different concentrations and measure the optical density under the same conditions. To increase the accuracy of determination, the number of points on the graph should be at least three or four. Then the optical density of the test solution $A_{x \text{ is determined}}$ and the corresponding concentration value $C_{x \text{ is found from the graph}}$ (Fig. 1.7).

The concentration range of standard solutions is selected so that the concentration of the test solution corresponds approximately to the middle of this range.

The method is the most common in photometry. The main limitations of the method are associated with the labor-intensive process of preparing standard solutions and the need to take into account the influence of foreign components in the test solution. Most often, the method is used for serial analyses.

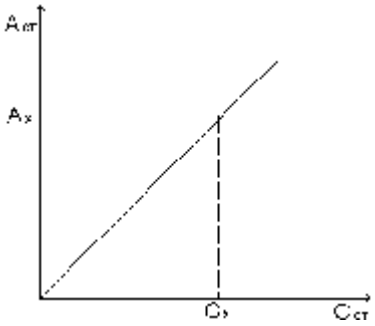


Fig.1.7. Calibration graph of dependence of optical

density versus concentration

Additive method. This method is used for the analysis of complex solutions, since it allows one to automatically take into account the influence of foreign components of the analyzed sample. First, measure the optical density of the test solution with an unknown concentration

$$A_x = \varepsilon l C_x$$

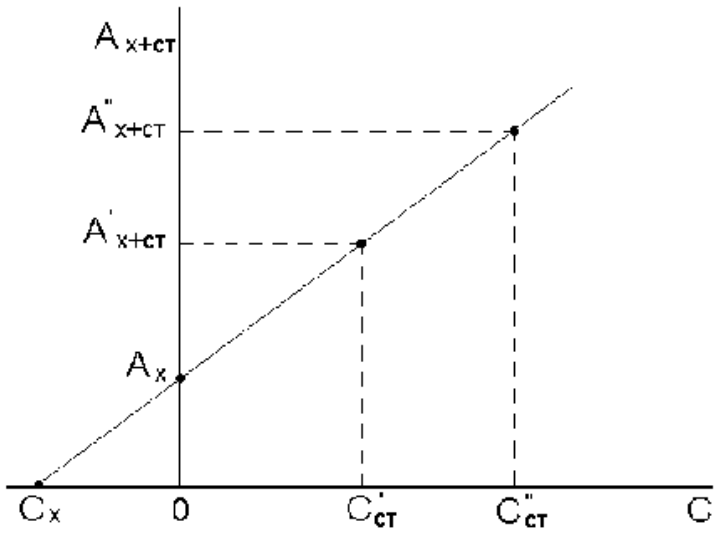
then a known amount of a standard solution of the component being determined (C_{st}) is added to the analyzed solution and the optical density $A_{x + st \text{ is measured}}$:

$$A_{x+ст} = \varepsilon l (C_x + C_{ст})$$

where

$$C_x = C_{ст} \frac{A_x}{A_{x+ст} - A_x}$$

To increase accuracy, the addition of a standard solution of the component being determined is done twice and the result obtained is averaged.



The concentration of the analyte in the addition method can be found graphically (Fig. 1.8).

Fig.1.8. Calibration chart for determining

concentration of the substance by additive method

Equation (1.16) shows that if you plot A_{x+st} as a function of C_{st}, you will get a straight line, the extrapolation of which to the intersection with the x-axis gives a segment equal to $-C_x$. Indeed, for $A_{x+st} = 0$, it follows from equation (1.16) that $-C_{st} = C_x$.

Method of differential photometry. In this method, the optical densities of the test and standard solutions are measured not in relation to a solvent or reference solution with zero absorption, but, in contrast to direct spectrophotometric methods, in relation to a solution with a known concentration of the analyte , CO .

Depending on the methods for measuring relative optical density, several variants of the method are distinguished.

1. High absorption method - the concentration of the reference solution is less than the concentration of the test solution a($C_o < C_x$). Prepare a series of standard solutions with concentrations C_1, C_2 KC $_n$ and photometer the standard and test solutions in relation to the reference solution with the concentration C_o. Relative optical density values A' represent the difference between the optical densities of the test (standard) solution and the reference solution:

$$A_x = A_x - A_o = \varepsilon l (C_x - C_o)$$

$$A_{ст} = A_{ст} - A_o = \varepsilon l (C_{ст} - C_o)$$

The concentration of the test solution is determined by calculation or using a calibration curve. The difference between the calibration graph and the usual one (Fig. 1.7) is that the concentration of the reference solution is taken as the starting point S_o.

In the calculation method, it is taken into account that the ratio of the optical densities of the test and standard solutions corresponds to the ratio of the difference between the concentrations of these solutions and the reference solution:

$$\frac{A_x}{A_{ст}} = \frac{C_x - C_o}{C_{ст} - C_o}$$

From here:

$$C_x = C_o + A_x \frac{C_{ст} - C_o}{A_{ст}}$$

or

$$C_x = C_o + FA_x$$

Where

$$F = \frac{C_{ст} - C_o}{A_{ст}}$$

F is called the conversion factor. In one series of measurements, F is a constant value.

The method is recommended for use in cases where the optical density of solutions is greater than unity.

2. Low absorption method. The concentration of the reference solution is greater than the concentration of the test solution a($C_o > C_x$). In this case, the reverse measurement procedure is used: the analyzed and standard solutions are conventionally taken as reference solutions and the optical density of the original reference solution is measured in relation to them. In the reverse order of measurement, the relative optical density A ′is equal to the difference in the optical densities of the test solution (standard) and the reference solution:

$$A_x = A_o - A_x$$

$$A_{ст} = A_o - A_{ст}$$

Concentration Cx is calculated using the formula :

$$C_x = C_o - FA_x$$

Where

$$F = \frac{C_o - C_{ст}}{A_{ст}}$$

The low absorption method is most often used for solutions with an optical density <of 0.1.

3. The method of two-way differentiation (method of extreme accuracy) combines both methods with direct and reverse order of measuring the optical density of solutions.

When working with this method, several standard solutions are prepared with concentrations lower than in the reference solution, and the same number of standard solutions with concentrations higher than in the reference solution.

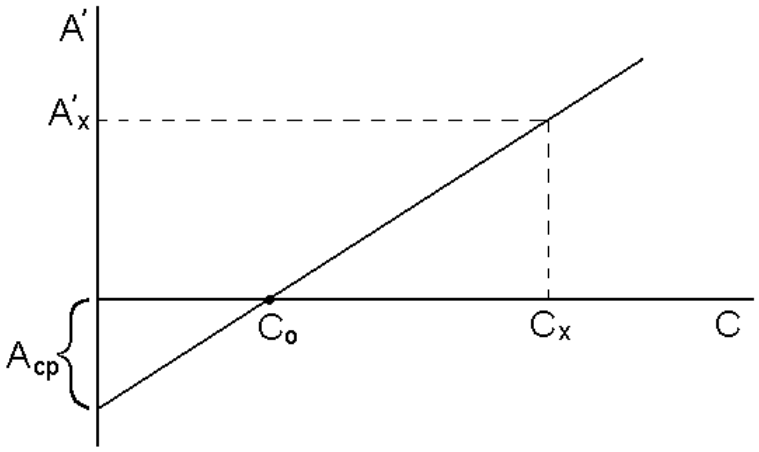


Fig.1.9. Calibration graph in the two-way method

differential photometry

If WITH >Co , use the direct measurement order; if C <Co , use the reverse measurement order, and the values of relative optical densities are taken with a minus sign (for pointer-type photometric devices with a scale). Modern photoelectrocolorimeters allow recording negative values of optical density, therefore they use a direct measurement order. In this case, the calibration graph does not pass through the origin of coordinates, but intersects the abscissa axis at the point corresponding to the concentration of the reference solution C_o (Fig. 1.9).

The concentration of the test solution can also be determined by calculation:

$$C_x = C_o + FA$$

As can be seen, at the concentration of the reference solution With $_o$ = 0, the differential method turns into the method of direct photometry.

Differential methods of analysis are used to determine large quantities of substances, to eliminate the interfering influence of foreign impurities and to eliminate the absorption of reagents. This method is also used in cases where, due to a high concentration, the Bouguer–Lambert–Beer law is violated, or when the optical density value exceeds the limits of the instrument scale, and further dilution of the solution is undesirable. The accuracy of determination when using the differential method increases.

Determination of a mixture of light-absorbing substances

The spectrophotometric method, in principle, allows the determination of several light-absorbing substances in one solution without prior separation. In the simplest case, substances absorb at different wavelengths, and analysis of the mixture is reduced to determining each component separately - the isolated absorption method. In the case

where the absorption spectra of the components of the mixture partially overlap each other, select the wavelength at which the maximum absorption of one component is observed, and the absorption of the other component is negligible.

If the spectra of substances overlap, then one of the methods based on the law of additivity is used for analysis. For example, for a mixture of substances A and B, you can write the Vierordt system of equations:

$$A_{\lambda_1} = l(\varepsilon_{A,\lambda_1} C_A + \varepsilon_{B,\lambda_1} C_B)$$

$$A_{\lambda_2} = l(\varepsilon_{A,\lambda_2} C_A + \varepsilon_{B,\lambda_2} C_B)$$

Solving this system of equations for l = 1 cm gives:

$$C_A = \frac{A_{\lambda_1}\varepsilon_{B,\lambda_1} - A_{\lambda_2}\varepsilon_{B,\lambda_1}}{\varepsilon_{A,\lambda_1}\varepsilon_{B,\lambda_2} - \varepsilon_{A,\lambda_2}\varepsilon_{B,\lambda_1}}$$

$$C_B = \frac{A_{\lambda_2}\varepsilon_{A,\lambda_1} - A_{\lambda_1}\varepsilon_{A,\lambda_2}}{\varepsilon_{A,\lambda_1}\varepsilon_{B,\lambda_2} - \varepsilon_{A,\lambda_2}\varepsilon_{B,\lambda_1}}$$

The wavelengths at which optical density measurements should be carried out are selected based on the absorption spectra of substances A and B. Good results are obtained, for example, by the maximum difference method. To do this, first take the absorption spectra of substances A and B (Fig. 1.10.a), and then plot the dependence of $\varepsilon_A - \varepsilon_B$ or $\varepsilon_B - \varepsilon_A$ on the wavelength and find the areas of maximum and minimum (Fig. 1.10.b).

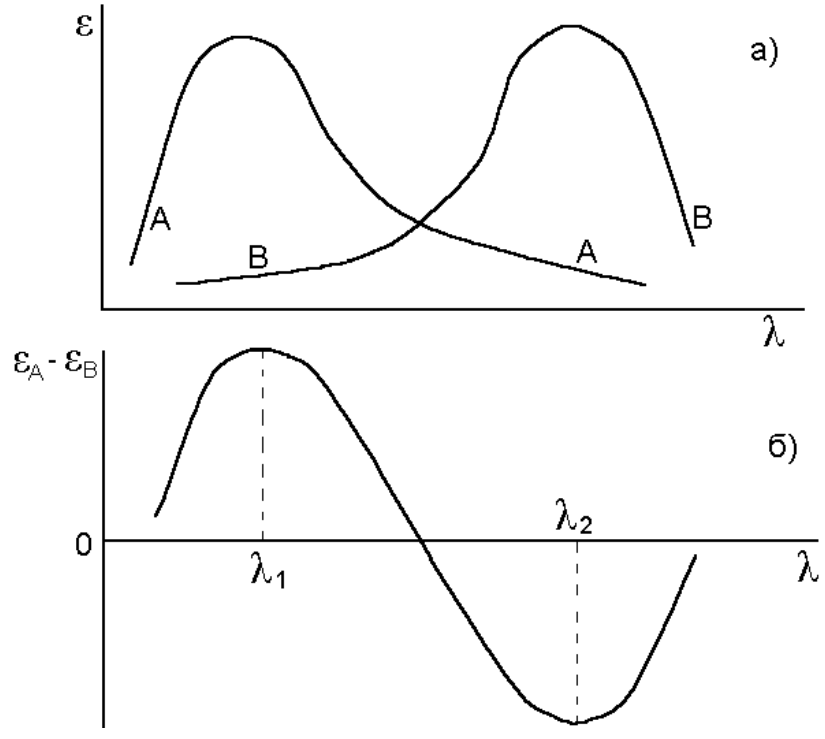


Fig.1.10. Absorption spectra of substances A and B (a)

and addiction $\varepsilon_A - \varepsilon_B$ on wavelength (b).

Molar light absorption coefficients are determined in advance, so the analysis is reduced to measuring optical density at two wavelengths. This analysis is practically impossible to carry out using photocolorimeters, so the quantitative determination of components is carried out using spectrophotometers.

The greater the difference in the values of ε_A and ε_B at the same wavelength, the higher the accuracy of determination. The accuracy of the analysis results depends on the ratio of the concentrations of the components. The determination error increases sharply with a decrease in the relative content of a component and with a large number of components being determined. If the number of components in the mixture is more than two, the number of terms in equations like (1.29–1.30) increases in proportion to the number of components and the number of equations increases accordingly. A necessary requirement is the subordination of the system components to Beer's laws and additivity.

Thus, for n components a system of n equations will be written , the optical densities must be measured at n wavelengths. Such systems of equations are solved using computer technology.

Other applications of molecular absorption spectroscopy

Photometric titration . Photometric and spectrophotometric measurements can be used to determine the end point of a titration. Photometric titration often provides more accurate results than the direct photometric method. The advantage of the photometric endpoint determination method over other methods is that experimental data are used at points sufficiently distant from the equivalence point. Therefore, there is no longer a condition associated with the completeness of the reaction, which is mandatory for methods in which a change is recorded near the equivalence point (for example, with potentiometric or visual titration with an indicator). For the same reason, more dilute solutions can be titrated; the presence of other absorbing substances can be neglected, since only the change in optical density is measured. Photometric titration applies to all types of reactions.

Study of equilibria in solutions . The characteristic absorption of light by particles in solutions opens up wide opportunities for the study of chemical systems. Determination of equilibrium constants by this method is based on the use of three laws: the law of mass action, the basic law of light absorption and the law of additivity of optical densities. The basis of this type of research is the assessment of changes in the optical characteristics of solutions as a result of a shift in chemical equilibrium under the influence of various factors. Spectrophotometric measurements make it possible to determine the number of absorbing components of a mixture, the composition of compounds formed in solutions, chemical equilibrium constants,

including dissociation constants of acids and bases and stability constants of complex compounds.

Lecture 6

Nuclear magnetic resonance (NMR) spectroscopy. Plan

Synthesis of organic matter of a given structure is the main task of synthetic chemists. However, proof of the structure and determination of the amount of the synthesized product is equally important. For these purposes, the following instrumental methods are most often used: electron or ultraviolet (UV) spectroscopy, infrared (IR) spectroscopy, nuclear magnetic resonance spectroscopy (NMR spectroscopy) and mass spectrometry. These methods can be used separately, although more often they are used in combination, complementing each other.

For objective reasons, this manual does not pretend to be a detailed examination of these methods, but at the same time it reflects their main provisions, and also includes some specific issues that are not discussed in traditional manuals on physical and chemical methods of analysis of organic substances. For a detailed introduction to the methods of IR spectroscopy , NMR spectroscopy, and mass spectrometry, we recommend the literature listed at the end of the manual.

Among the diverse physical methods that are used in studying the structure of organic molecules, the greatest interest is the interaction of matter with electromagnetic radiation in a wide frequency range, starting with radio waves and ending with γ- rays, i.e. across the entire electromagnetic spectrum. In this case, the energy of the molecules changes:

$$\Delta E = E_k - E_n$$

where ΔE is the change in the energy of the system;
E_k and E_n – energy of the system in the final and initial states.

If the energy of the final state is higher than the energy of the initial state ($E_k > E_n$), i.e. ΔE is positive, then this corresponds to the absorption of radiation and, conversely, with a negative value of ΔE (i.e. $E_k < E_n$) energy emission occurs. In the first case we are dealing with absorption spectra, in the second - with emission spectra.

The electromagnetic spectrum consists of several different "types" of radiation, which differ in their wavelengths (the distance between two adjacent wave crests) and their frequencies (the number of waves passing through a given point per unit time).

The speed of propagation of electromagnetic waves is a constant and is usually denoted as (s). The numerical value of this constant, i.e. the speed of light in vacuum is $3 \cdot 10^{10}$ cm/s. Although the speed of light is constant, its frequency and wavelength can vary. If frequency is expressed as the number of "oscillations" per second, or in hertz, then the following relationship between the speed of light, its frequency and wavelength is valid:

$$c = \lambda \nu$$

where c is the speed of light (3×10^{10} cm/s),
λ – wavelength [cm],
ν is the frequency (in cycles per second [s^{-1}], or in hertz [Hz]).

From this equation it follows that there is an inverse relationship between frequency and wavelength:

As the radiation frequency increases, the wavelength decreases.

A given frequency of electromagnetic radiation corresponds to energy determined by the following equation:

$E = h \nu$
where h is Planck's constant, ($9.534 \cdot 10^{-14}$ kcal s/mol),
ν – frequency [Hz].

It follows that the energy of electromagnetic radiation is directly dependent on its frequency.

As the frequency of radiation increases, its energy increases.

As the wavelength of radiation increases, its energy decreases.

Radiations corresponding to different regions of the electromagnetic spectrum are characterized by different wavelengths (and frequencies). Therefore, these radiations must have different energies. Here are some notations and units used to describe electromagnetic radiation.

Wavelength (λ):
Å (angstrom); 1 Å = 10^{-10} m
μm (micrometer) (formerly called micron) 1 μm = 10^{-6} m = 10^{4} Å
nm (nanometer) (formerly called millimicron) 1nm = 10^{-9} m = 10Å.

Frequency (ν):
Hz (hertz) (formerly known as cycles per second)
cm^{-1} (wave number; equal to the reciprocal of the wavelength measured in centimeters, i.e., the number of waves that fit into 1 cm).

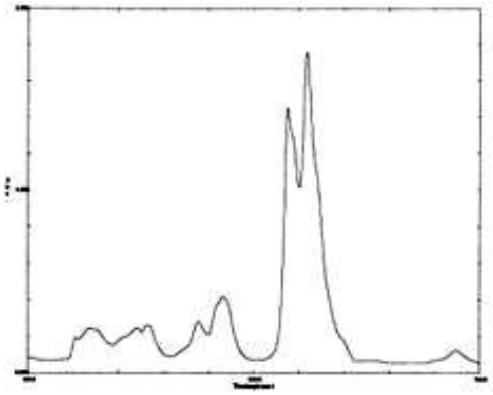
Transition energies between two energy levels are measured in electron volts (eV), calories (cal), or joules (J). Table 1.1. The main regions of the electromagnetic spectrum and the processes occurring with organic matter when absorbing or emitting radiation are shown.

Table 1.1
Electromagnetic spectrum [6]

Radiation	λ, cm	E, ev	Processes that occur during absorption or emission
γ-rays	$10^{-11} – 10^{-}$	$\sim 10^{7}$	γ -resonance spectroscopy)

	10^{8}		
X-rays	$10^{-8} – 10^{-6}$	$\sim 10^{5}$	Changes in the energy state of the inner electrons of atoms (X-ray spectroscopy)
Ultraviolet and visible	$10^{-6} – 10^{-4}$	~10	Change in the energy state of external electrons (electron spectroscopy)
Infrared	$10^{-4} – 10^{-2}$	$\sim 10^{-1}$	Vibration of atoms in a molecule (IR spectroscopy)
Microwave	$10^{-1} – 10$	$\sim 10^{-3}$	Vibration of atoms in a crystal lattice; change in rotational energy state
Radio waves	> 10	$\sim 10^{-6}$	Change in the energy state of nuclear and electron spins (NMR and EPR spectroscopy)

Chapter 1. Electron or UV spectroscopy



Electronic absorption spectra are observed as a result of the absorption of ultraviolet and visible radiation by a substance; in this case, a transition (excitation) of valence electrons occurs to higher energy levels. Based on the type of radiation absorbed, electron spectroscopy is often called ultraviolet-visible spectroscopy, or UV spectroscopy .

Of the entire spectrum of electromagnetic radiation, the human eye is able to perceive only its small “visible” part with wavelengths from 400 to 800 nm. The ultraviolet region of the spectrum extends from 1 to 400 nm, however, since components of the earth's atmosphere absorb radiation with wavelengths below 200 nm, the term "ultraviolet rays" usually refers to radiation with a wavelength of 200-400 nm (more correctly called "near ultraviolet region").

To study the spectral region from 1 to 200 nm, it is necessary to use vacuum devices (“vacuum ultraviolet radiation region”, “far ultraviolet region”).

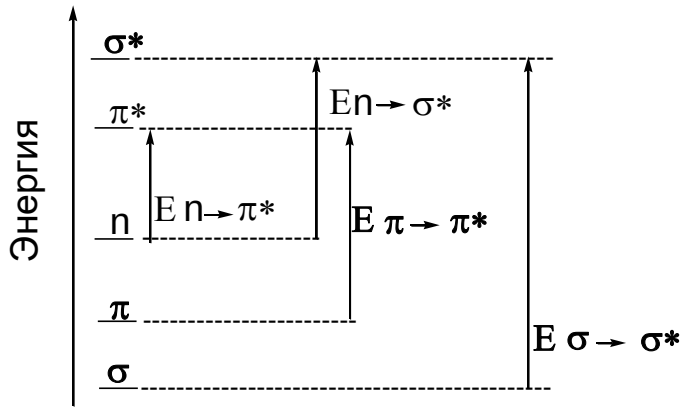
The terms “near and far regions” characterize the position in relation to the visible region of the electromagnetic spectrum. Solar radiation consists primarily of life-threatening “vacuum ultraviolet radiation,” so the absorption of radiation below 200 nm by the atmosphere preserves life on the Earth's surface.

1.1 Arousal and relaxation

When energy is absorbed in the ultraviolet region of the electromagnetic spectrum, electrons from bonding σorbitals π, as well as nonbonding orbitals (n - electrons), can move to various antibonding orbitals.

These are the transitions n →π*, π→π*, and n →σ*, where the first letter means the ground state, and the second means the excited state.

Transition σ→σ* requires more energy than those mentioned above, and such a transition can only be observed in the short-wavelength region of vacuum ultraviolet. The relative energies of all transitions are shown in Fig. 1.1.



Rice. 21.1. Relative energies of electronic transitions.

A molecule transferred to an excited electronic state can lose excess energy in any of the following ways.

1. Bond breaking: usually results in an irreversible chemical reaction.
2. Emission: Radiation is emitted at the same frequency as that absorbed.
3. Fluorescence: After excitation, emission is observed with a wavelength greater than the absorbed one. Fluorescence occurs quickly, often in less than 10^{-6} s after absorption.
4. Phosphorescence: Once excited, longer wavelength radiation is emitted than absorbed. The emission can continue for several hours after stimulation.
5. Non-radiative transitions: some molecules, having absorbed the energy of UV radiation , can lose this energy as a result of processes not accompanied by radiation.

The ability to absorb electromagnetic radiation is a common property of all molecules. Absorption is selective, i.e. Radiation of a certain wavelength by a given molecule is strongly absorbed, while radiation of other wavelengths is weakly absorbed or not absorbed at all.

The absorption region is called a band; the set of absorption bands of a given molecule is its absorption spectrum.

Beer-Booger-Lambert law

Ultraviolet-visible spectrophotometric measurements are most often made for solutions, although such measurements can also be made for pure substances in the vapor, liquid and solid states.

Spectrophotometric analysis by direct measurement of optical density can be carried out for organic substances that have only certain structural features (aromatic compounds, compounds with conjugated multiple bonds, compounds of a number of metals, etc.).

The amount of absorbed radiation is directly proportional to the number of molecules of the solute and therefore increases with increasing concentration and/or thickness of the sample layer (i.e., with the optical path length in the cuvette).

At any wavelength, the intensity of light leaving the solution ($_I$) is related to the intensity of light entering the solution (Io), a relationship called the Beer-Booger-Lambert law:

$$\lg (I_0 / I) = a\ b\ c$$

where a is the absorption coefficient, a constant that depends on the wavelength, but does not depend on the concentration;

b is the length of the optical path;

c is concentration.

With c expressed in moles per liter of solution and b in centimeters, a takes the value of the molar absorption coefficient (ε) (in old works the molar extinction coefficient)

If the concentration is expressed in grams per 100 ml of solution, then a takes the value of the specific absorption coefficient ($E^{1\%}_{1cm}$).

Thus:

Molar absorption coefficient (ε) is the optical density of a one-molar solution of a substance at a layer thickness of 1 см.

Specific absorption coefficient ($E^{1\%}_{1cm}$) is the optical density of a solution containing 1 гsubstances in 100 ml of solution at the same layer thickness.

The transition from the specific absorption rate to the molar one is carried out according to the formula:

$$\varepsilon = E^{1\%}_{1cm} \times M/10$$

where M is molecular weight

The magnitude of the molar absorption coefficient is proportional to the probability of a particular electronic transition.

For transitions with low probability this coefficient has an insignificant value (from 10 to 10^3), for transitions with high probability it is about 10^5.

The amount of radiation absorbed by a solution can be characterized by absorption (A) (in old works "optical density, D ") or transmission (T), which are related by the relations:

$A = \log (I_0 / I)$
$T = I/I_0$
$A = - \log T$

C Taking into account the above, the mathematical representation of the law of light transmission can be presented in the following form:

$A = \varepsilon bc$

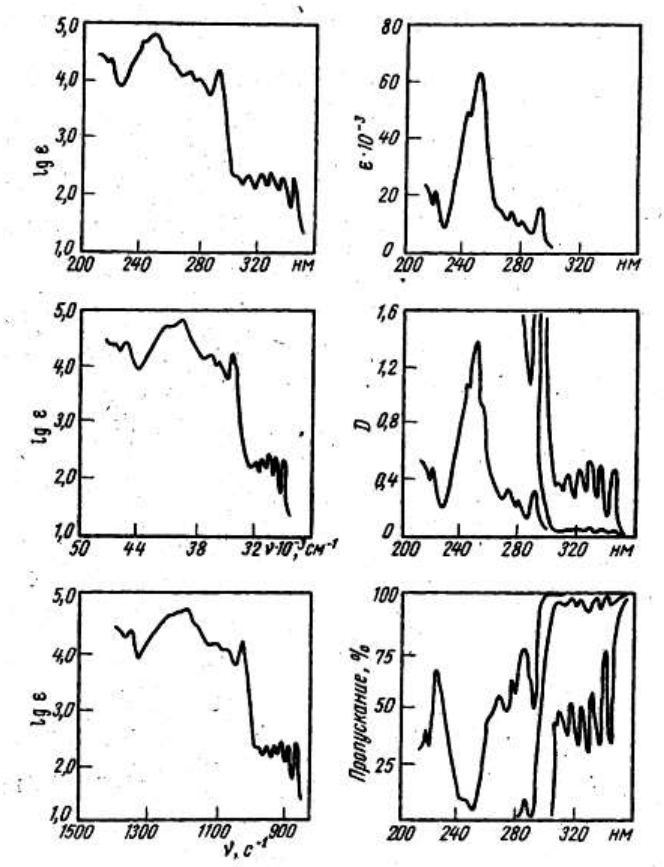
When describing the spectrum, only the positions of the absorption maxima are usually given, as well as the corresponding values ε.

Example:

λ_{max}^{hexane} = 235 nm (ε5400). The solvent is also indicated, since it can also affect λ, and on ε.

1.3 Methods for imaging electronic spectra

Electronic absorption spectra are recorded as dependence of absorption on wavelength (angstrom, nanometer) or frequency (cm^{-1}). The absorption value can be expressed by the percentage of absorption [$(I_0 - I)/ I_0 \times 100\%$], the percentage of transmission [$(I / I_0) \times 100\%$], optical density A ($A = \log I_0 / I$), molar absorption coefficient (ε) or its logarithm (log ε). The type of absorption spectrum depends on the choice of coordinates (Fig. 1.2.)



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Rice. 1.2. Electronic absorption spectrum of phenanthrene in various coordinates.

Let us present several important notes regarding the conditions for obtaining the working spectral curve A = f (λ). It was noted above that electronic spectra can be obtained for any state of aggregation of a substance. However, to solve a common structural problem, electron spectroscopy is usually used to record solutions of substances. Many solvents are suitable for spectrophotometric analysis in the UV region , including water, alcohols, chloroform, lower hydrocarbons, ethers, dilute solutions of ammonia, sodium hydroxide, hydrochloric or sulfuric acid. Solvents that do not contain impurities that absorb in this spectral region should be used; For spectrophotometry, special solvents are produced that guarantee the absence of impurities. Table 1.2 below shows the absorption regions of organic solvents most commonly used in UV spectroscopy .

Table 1.2

Absorption regions of solvents most commonly used in UV spectroscopy

Solvent	Absorption region, nm
acetonitrile	190
water	191
cyclohexane	195

hexane	195
methanol	201
ethanol	204
diethyl ether	215
methylene chloride	220
chloroform	237
carbon tetrachloride	257

To reduce the error in determining the optical density A, the concentration of the solution and the thickness of its layer are selected such that the optical density in the spectral region under study is in the range from 0.2 to 0.7.

Depending on the absorption capacity of the substance, this is usually achieved using concentrations of 0.01 to 0.00001% (layer thickness cuvettes 10 мм).

Electron spectroscopy – spectroscopy of low concentrations!

Thus, for a compound with a molecular weight of ~100 and having ε ~ 10000, the condition A = 0.5 (at b = 1 см) corresponds to a solution concentration of about 0.005 g/l. Considering that cuvettes are used for research, the volume of which, as a rule, does not exceed 5 ml, we obtain a value of about 0.025 mg for weighing a substance of such a volume of solution. Therefore, a solution is usually pre-prepared, the concentration of which is 10 - 100 times higher than the required concentration. Then, using pipettes and volumetric flasks, dilute to the required concentration. It should be remembered that:

Information about the concentration of the solution and the thickness of the cuvette should always accompany the spectrum A = f (λ) produced by the device.

Relationship between electronic spectra and structure of organic molecules. Chromophores and auxochromes

A simple functional group responsible for absorption with characteristic quantities εand λis called a chromophore.

It is usually assumed that the spectra of substances are similar if their molecules contain the same chromophores. If a molecule contains two chromophores separated by more than one single bond, the spectrum of the compound is the sum of the spectral characteristics of the individual chromophores. If, however, two chromophores are separated by only one single bond (i.e., the chromophores are in conjugation), the spectrum of the compound will no longer be the sum of the spectra of the individual chromophores. In this case, two simple groups form a new chromophore with new spectral characteristics.

Table 1.3
Main chromophoric groups

Chromophore	Transition type	λ_{max}	log(ε)

nitriles	n → π*	160	<1.0
alkynes	π → π*	170	3.0
alkenes	π → π*	175	3.0
alcohols	n → σ*	180	2.5
ethers	n → σ*	180	3.5
ketones	π → π*	180	3.0
	n → π*	280	1.5
aldehydes	π → π*	190	2.0
	n → π*	290	1.0
amines	n →σ*	190	3.5
acids	n → π*	205	1.5
esters	n → π*	205	1.5
amides	n → π*	210	1.5
thioalcohols	n → π*	210	3.0
nitro compounds	n → π*	271	<1.0
azo compounds	n → π*	340	<1.0

Functional groups that themselves do not absorb in near ultraviolet, but affect the behavior of the chromophore conjugated with it, are called auxochromes.

Auxochromes usually cause absorption to occur at longer wavelengths and with greater values of δ εthan is typically characteristic of the chromophore. Representatives of auxochromes are the groups - SH , - NH_2 and - OH .

When identifying the relationship between the spectrum and the structure of a molecule in electronic spectroscopy, it is considered advisable to monitor changes in spectral parameters during the transition from some original chromophore to a modified one by introducing the first additional chromophore or auxochromic group into the system. To characterize the spectral changes caused by structural modification, the following special terms were introduced:

hypsochromic shift (blue shift) - to shift absorption bands to the short wavelength region of the spectrum;

bathochromic shift (red shift) - to shift absorption bands to the long wavelength region;

hyperchromic effect - increased absorption intensity; hypochromic effect - decrease in absorption intensity.

Absorption bands in UV spectra can differ markedly in their parameters - position, intensity, structure. It was found that bands with similar characteristics correspond to a certain extent to related groups of chromophores. Such observations led to the classification of bands and the formulation of empirical criteria for the assignment of bands in the spectrum. In electronic spectra, at least four types of bands should be distinguished : K , R , B , E.

K-bands are associated with π → π * transitions in the conjugated chromophore system.

These bands have high intensity (ε > 10000). An increase in the number of multiple bonds in a conjugated system always leads to a bathochromic shift of the K-band and

is accompanied by a hyperchromic effect. In conjugated systems such as divinyl or styrene, the K-bands practically do not change their characteristics when replacing a non-polar solvent with a polar one, while in other conjugated systems, such as acrolein or nitrobenzene, the K-bands experience a bathochromic shift with a similar change in solvent. In many cases, K-bands have a solid contour, but there are bands with a fine structure (Table 1.4).

R bands are associated with n → π* transitions in an isolated chromophore such as a carbonyl group.

R -bands are characterized by weak intensity (ε < 100). These bands are characterized by a hypsochromic shift when replacing a nonpolar solvent with a polar one. The introduction of an n → π* chromophore into the conjugate position to the π → π * chromophore system leads to a bathochromic shift of the R band. On the contrary, the addition of a typical auxochrome (OH or NH2) to $_{\text{the}}$ n → π* chromophore causes a hypsochromic band shift. Sometimes R bands have a fine structure.

The B-band is often called the "benzene" band and is associated with one of the forbidden π → π * transitions in the aromatic ring.

The band is characterized by medium intensity (ε about 100 − 1000); as a rule, does not experience shear when replacing the solvent, and usually has a fine structure. In alkylbenzenes, the position of the B band is in the region near 260 nm. The introduction of a chromophore or auxochromic group into the benzene ring leads to a bathochromic shift of the B-band and an increase in its intensity. In this case, the fine structure of the strip may disappear.

E (E_1 and E_2) bands are also characteristic of aromatic systems.

For benzene itself, the symbols E_1 and E_2 indicate bands at 180 and 200 nm, respectively. The E_1 band, corresponding to the allowed π → π * transition of the benzene chromophore, falls into the near ultraviolet region only in polynuclear aromatic systems. This band is characterized by increased intensity.

The E_2 band is always observed in the spectra of substituted aromatic systems in the region of 200 - 230 nm. In intensity, it is usually inferior to the longer-wavelength K band, but in some substituted benzenes the ratio of the intensities of the E and K bands can be reversed.

B and E bands are always present in the spectra of aromatic compounds. The appearance of a K-band in the spectrum of substituted benzene along with these bands indicates the presence of a conjugated chromophore including a benzene ring.

Table 1.4 shows experimental data and electronic spectra for benzene and some of its monosubstitutes.

Table 1.4

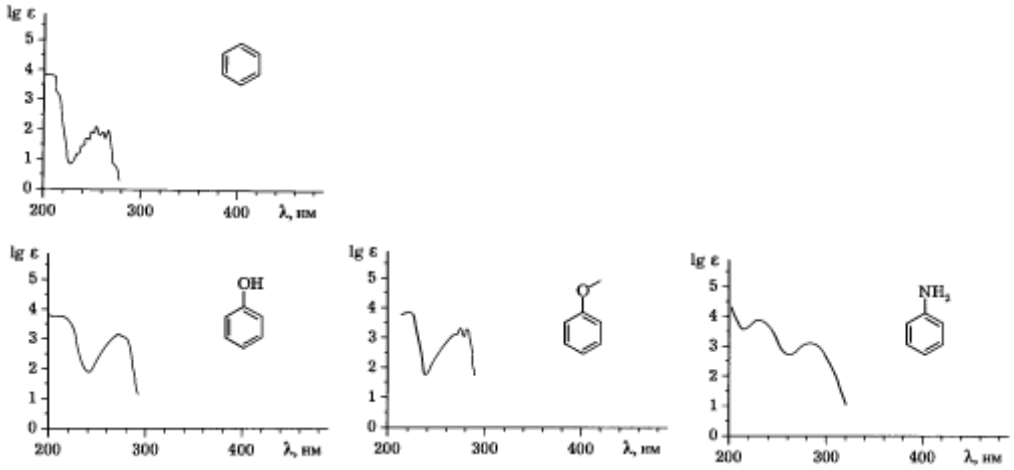
Absorption regions and type of spectrum of monosubstituted benzenes [2]

Deputy	E ε (> 30000)	K ε (~ 10000)	IN ε (~3 00)	R ε (~5 0)
	λ_{max} nm	λ_{max} nm	λ_{max} nm	λ_{max} nm
Electron-donating substituents (n – π -conjugation)				

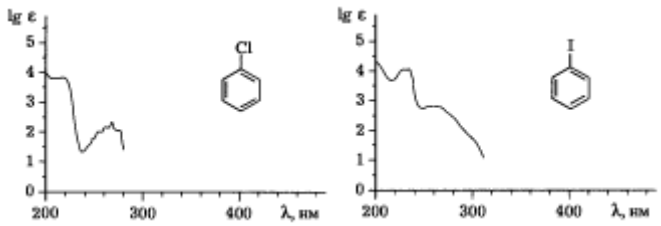
N	184	204	254	
-R	189	208	262	
-OH		211	270	

Continuation of Table 1.4

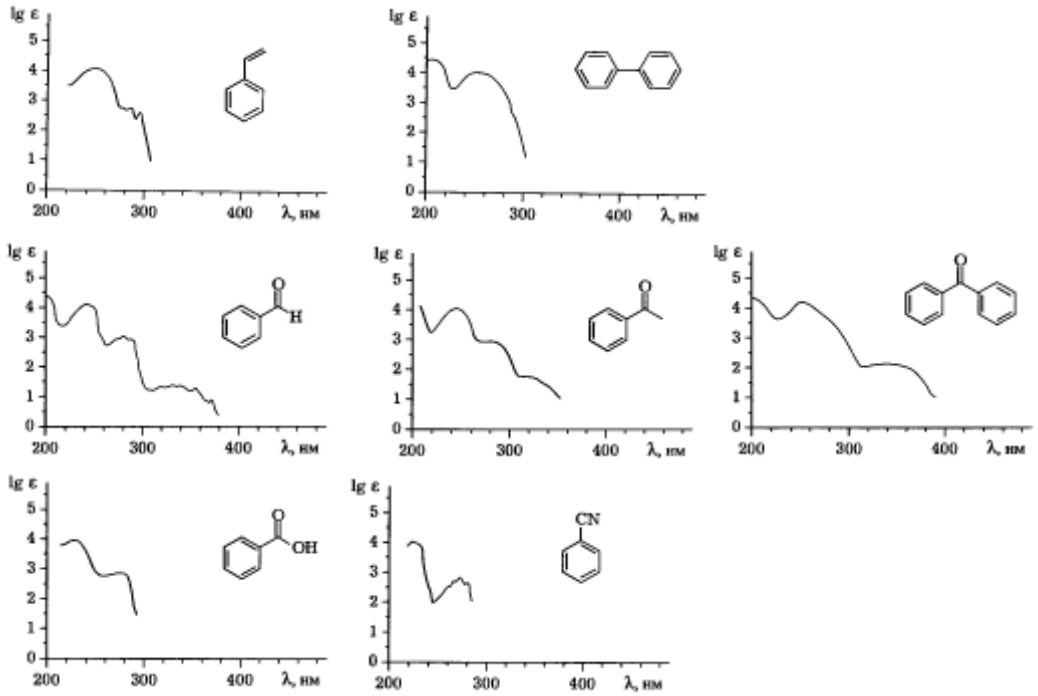
Deputy	E ε (> 30000)	K ε (~ 10000)	IN ε (~3 00)	R ε (~5 0)
	λ_{max} nm	λ_{max} nm	λ_{max} nm	λ_{max} nm
-OR		217	269	
$-NH_2$		230	280	



Deputy	E ε (> 30000)	K ε (~ 10000)	IN ε (~3 00)	R ε (~5 0)
	λ_{max} nm	λ_{max} nm	λ_{max} nm	λ_{max} nm
Electron-withdrawing substituents (n – π -conjugation)				
-F		204	254	
-Cl		210	257	
-Br		210	257	
-I		207	258	



Deputy	E ε (> 30000)	K ε (~ 10000)	IN ε (~3 00)	R ε (~5 0)
	λ_{max} nm	λ_{max} nm	λ_{max} nm	λ_{max} nm
Electron-withdrawing substituents (π – π -conjugation)				
-C=CH $_2$		248	282	
-CCH	202	248	278	
-C6H5 _ _ _		250		
-CHO		242	280	328
-C(O)R		238	276	320
-CO2H _ _		226	272	
-CN		224	271	
-NO $_2$		252	280	330



Currently, a large amount of experimental material has been accumulated in the field of structural analysis using UV spectroscopy . Based on this material, empirical rules have been developed that make it possible, without conducting an experiment, to calculate $\lambda_{the\ max}$ of many complex chromophores. For example, in the practice of structural analysis, the Woodward-Fizer empirical rules are used to estimate the position of the $\pi \rightarrow \pi^*$ transition band, the extended Woodward rule to estimate the position of the $\pi \rightarrow \pi^*$ transition band, and Scott's rule to estimate the K-band. These methods are described in detail in the specialized literature [2].

1.5 Application of UV spectroscopy for the quantitative determination of organic substances

Currently, electron spectroscopy has limited use for the structural analysis of organic compounds, because more important structural information is achieved using NM P- , IR spectroscopy and mass spectrometry.

A more important application of UV spectroscopy is quantitative analysis. The use of this method is effective both in the case of studying reaction kinetics and in determining impurities in a sample of organic matter. Compounds that absorb strongly in λthe UV region can often be detected even at low concentrations if they are present as impurities in samples of substances that have weak absorption in the $_{max}$ impurity region. A classic example is the determination of benzene, present in low concentration as an impurity in ethyl alcohol (see example 1).

To carry out a quantitative determination of a substance using the spectrophotometric method, it is necessary, based on the recorded spectrum, to measure the intensity of light absorption by this substance at a selected wavelength. However, this is possible only in cases where it is established that, in the range of possible concentrations, absorption obeys the basic law of light absorption. Theoretically, the concentration can be determined at any wavelength. At the same time, it should be emphasized that the minimum determination error is obtained at those wavelengths that meet the following requirements:

1) the selected band should be as free as possible from the overlap of absorption bands of other components of the analyzed system;

2) the selected band must have a sufficiently high absorption coefficient for an individual connection.

Such absorption bands are called analytical.

When analyzing, the maximum or minimum of the absorption band is used and measurements should not be made in areas of steep decline or rise of the curve .

In some cases, identification and quantification of substances by spectrophotometry requires comparison with chemical standard samples. To check the transmittance of the spectrophotometer scale, use a standard sample of potassium dichromate. Below are the permissible values of the optical density of a solution of a standard sample of potassium bichromate containing 60.06 mg in 1000 ml of sulfuric acid solution (0.005 mol/l), with a layer thickness of 10 mm:

Wavelength λ , nm	235	257	313	350
Optical density	0.748	0.748	0.292	0.640

Determination of the concentration of a substance in the analyzed solution is carried out using one of the following methods:

by molar or specific absorption coefficient;

according to the calibration schedule.

Determination of the concentration of a substance by molar absorption coefficient

The method is applicable only when the light absorption of the test solution at a given concentration strictly obeys the basic law of light absorption.

The determination is carried out according to the formula:

$C = A/\varepsilon$

where C is the concentration of the substance, mol/l;
A – optical density;
ε – molar absorption coefficient;
b is the optical path length (solution thickness).

In quantitative determinations, it is more convenient to express the concentration as a percentage rather than as moles. In this regard, it is often not the molar coefficient that is used, but the specific coefficient - $E^{1\%}_{1cm}$.

The concentration of a substance in a solution, knowing the specific coefficient, is determined by the formula:

$c\ (\%) = (A / E^{1\%}_{1cm}) \times b$

Example 1.

Ethyl alcohol containing water can be dehydrated by distilling aqueous ethanol with benzene. Dehydrated ethyl alcohol is often used for the preparation of medicinal substances and therefore it is important that it is completely free of benzene. One method for determining residual benzene is to analyze the UV spectrum of a sample near 260 nm. At this wavelength, ethanol is transparent, and benzene has an absorption maximum at ε230.

Calculate the amount (g) of benzene in 100 лan ethanol solution if the following characteristics of the electronic spectrum of this solution are known: λ_{max} 260 nm, A = 0.0295, ε= 230, cuvette length 1 см.

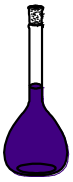
Solution . $A = \varepsilon bc$

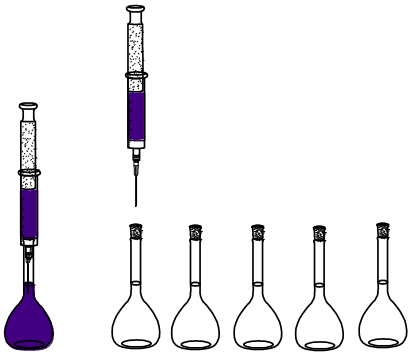
$c = A / \varepsilon b = 0.0295/230 \cdot 1 = 0.0001$ mol/l.

Then 100 лethanol contains 0.01 mol of benzene, which corresponds to 0.78 г.

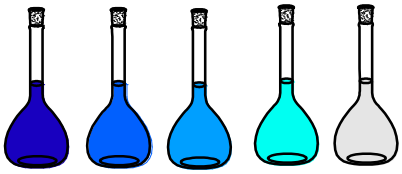
Even such a small amount can be determined using electron spectroscopy!

Determining the concentration of a substance using a calibration graph

1. Prepare a standard solution of the test substance. 

2. Prepare a series of standard solutions: 

Various volumes of the prepared standard solution are placed in volumetric flasks of equal volumes. The volume of the flasks is adjusted to the mark with the selected solvent.

3. Thus, they have a series of standard solutions of the test substance. 

It is necessary to prepare at least five solutions, the concentration of each must differ from the concentration of the previous solution by at least 30 - 50%.

4. Spectrophotometric measurements are carried out - the optical density of the prepared standard solutions is determined. The reference solution is the solvent used to prepare the series.

5. The obtained experimental data are entered into the table:

Experience no.	C, mol/ l	A
1		
n...		

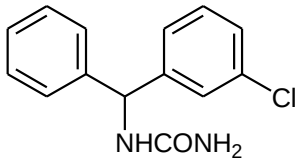
6. Construct a graph of concentration versus optical density. Currently, there are a large number of computer programs (for example, CurveExpert) that allow quantitative assessment of linear regression dependencies.

7. Determine the optical density of the test substance of unknown concentration.

Having an equation for the linear dependence of optical density on concentration of the type y = a + bx (in our case, y is optical density, x is concentration), we can determine the concentration of the solution under study.

Example 2.

Determine the concentration (mol/l) of the anticonvulsant drug “Galodif” in a solution whose optical density is 0.55.



galodif

a C = O bond in the Galodif structure causes the appearance of an absorption maximum in the electronic spectrum in the region of 320 − 340 nm (logε ≈2.5). To carry out quantitative studies, we prepared a series of standard Halodif solutions and determined the optical density of these solutions at a wavelength of 340 nm in a cuvette with a layer thickness 10 мм(table

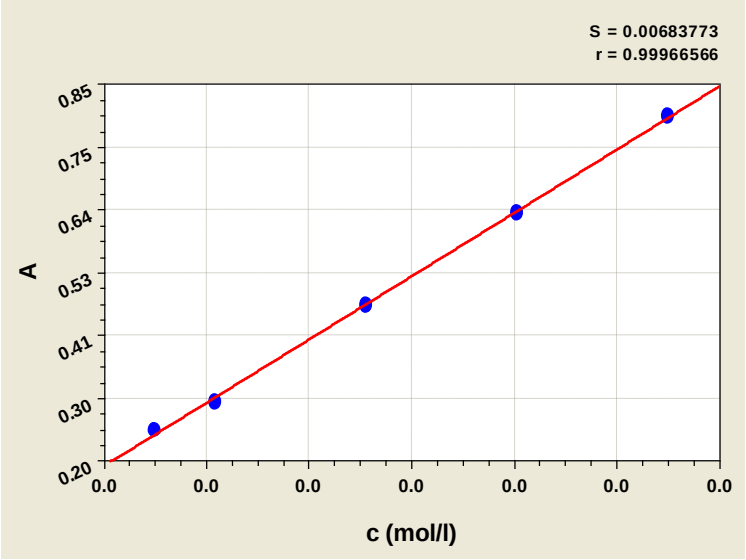
Table 1.5

Results of spectrophotometric measurements of a series of standard Galodif solutions at a wavelength of 340 nm in a cuvette with a layer thickness10 мм

Experience no.	C, mol/ l	A
1	0 .0006	0.2
2	0.0008	0.25
3	0.001	0.3
4	0.0015	0.47
5	0.002	0.63

Solution:

Using the data in table (1.5), we plot the dependence of optical density on concentration and obtain an equation for the linear dependence.



Y = a + b x

a = -0.021

b = 326.1

Thus, we get: A = -0.02 + 326.1 x C.

From here, the concentration is calculated:

C = (A+0.02)/ 326.1

We substitute the optical density value (0.55) into the resulting equation and calculate the concentration of the Galodif solution:

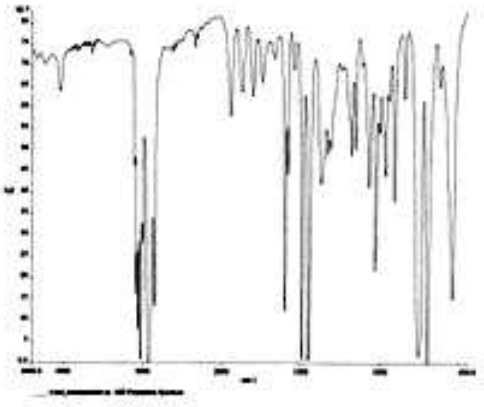
C = (0.55+0.02)/ 326.1 = 0.0017 (mol/l)

Questions for self-control

1. What region of the spectrum is called near and far ultraviolet?
2. What region of the spectrum is called the visible region?
3. Formulate the Beer-Bouguer-Lambert law.
4. What determines the value of the molar absorption coefficient?
5. Define chromophore, auxochrome.
6. What phenomenon is called bathochromic shift?
7. What phenomenon is called hypsochromic shift?
8. What are hyperchromic and hypochromic effects?
9. What types of bands can be observed in UV spectra ? Try to briefly formulate the main features of these bands.
10. What methods are used to spectrophotometrically determine the concentration of organic matter?

Lecture 7

Topic: Constants of the spin-spin effect.



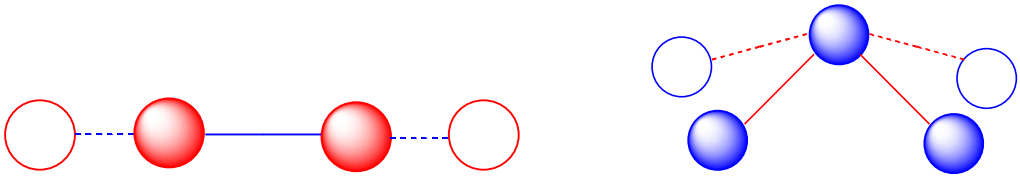
About the main provisions of the IR spectroscopy method

Infrared radiation is part of the electromagnetic radiation occupying the spectral region between the red end of the visible color (μm) and microwave radiation (μm) For the structural analysis of organic substances, infrared spectra are usually recorded in the frequency range 4000 − 400 cm $^{-1}$ (wavelengths from 2.5 to 20 μm). When recording a spectrum, the value of wave numbers in cm $^{-1}$ or microns is plotted on the abscissa axis on a linear scale, and the transmittance value T (in %) is plotted on the ordinate axis.

Absorption in the infrared region is characteristic of molecules whose dipole moments change when vibrational motions of nuclei are excited.

Vibrational movements of nuclei that lead to a change in bond length are called stretching vibrations (denoted by ν).

Oscillatory movements of nuclei, leading to changes in angles between bonds, are called deformation vibrations (denoted by □) (Fig. 2.1.).



(a) (b)

Rice. 2.1. Stretching ν (a) and deformation (b) vibrations of atoms

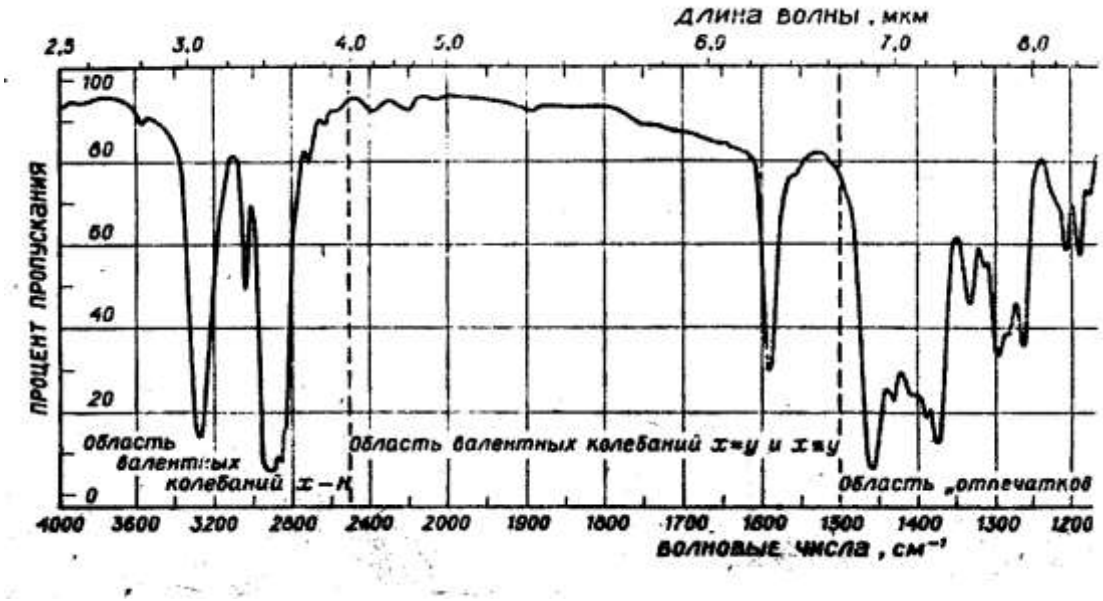
The energy of bending vibrations is significantly less than the energy of stretching vibrations, and bending vibrations are observed at long wavelengths (low wavenumbers). The frequency of stretching vibrations is related to the strength of the corresponding bonds. Triple bonds (absorption at 2300−2000 cm $^{-1}$) are stronger than double bonds (absorption at 1900−1500 cm $^{-1}$), which, in turn, are stronger than single ones (C-C, C- N , C-O bonds absorb at 1300 − 800 cm $^{-1}$) (Fig. 2.2.).

molar extinction coefficient (absorption intensity) in IR spectroscopy takes a value from 0 to 200. Its value is proportional to the square of the change in the dipole moment of the molecule caused by a given vibration. The most intense peaks in the IR spectrum are those corresponding to stretching vibrations. The intensities of the bands of the IR spectra according to the degree of transmission are divided into strong, medium, weak and are designated as:

With. – strong

Wed – average

sl. – weak



Rice. 2.2. IR spectrum of an organic substance indicating the region of stretching vibrations and the region of “fingerprints”

The use of infrared spectra for structural studies is based mainly on the use of characteristic absorption bands (bands associated with ν or vibrations of bonds of typical functional groups in molecules). The groups OH, NH_2, NO_2, C =O , C=N-, etc. have such characteristic absorption bands.

Identification of the test substance can be carried out by comparing the IR spectrum of the test substance with a similar spectrum of its standard sample or with its standard spectrum. The most important and reliably interpreted characteristic absorption bands are located in the short-wave (high-frequency) frequency range of the

fundamental vibrations of molecules from 4000 to 1500 cm $^{-1}$ (from 2.5 to 7 μm). This area is of paramount importance for structural analysis.

For low frequency interval 1350 −400 см $^{-1}$ is characterized by a specific set of bands , which is called the “fingerprint” area (Fig.2.2) .

The complete coincidence of the absorption bands in the IR spectra of the two substances indicates their identity.

Preparation of samples for recording IR spectra

Infrared spectra can be measured for gases, liquids and solids. To measure the spectra of gaseous substances, special gas cells are used.

Samples are prepared for recording infrared spectra using the following methods.

1. For solids

a) Pastes: thoroughly mix 10-20 mg of solid substance with 1 - 2 drops of immersion liquid (vaseline oil, polyfluorocarbon, hexachlorobutadiene, etc.), the prepared paste is squeezed between two plates of substances that do not absorb IR radiation (NaCl or KBr) and placed in a spectrophotometer for measurement.

b) Tablets in KBr: a sample of the solid (1 - 3 mg) is thoroughly mixed with spectrally pure bromide (150 - 200 mg) and the mixture is pressed.

2. For liquid substances

A thin film of liquid is clamped between plates of NaCl or KB r .

3. Solutions.

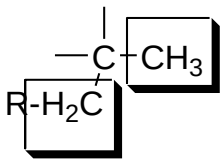
A solution of the test sample in an organic solvent that weakly absorbs in the IR region, for example CC l $_4$, CHCl $_3$.

2.3 The most important characteristic absorption bands in the region of the main frequencies of vibrations of bonds of organic molecules

Although IR spectroscopy is often used for the quantitative determination of organic matter (for example, in kinetic studies), the main application of this method is structural analysis. In this case, IR spectroscopy is indispensable for determining the functional groups of a molecule.

It is often difficult to represent many of the characteristic vibrations of complex functional groups as a set of simple stretching and bending vibrations. However, a practicing chemist must be familiar with the frequencies of typical functional groups and use them when analyzing the structure of a molecule. It must be borne in mind that the position of the absorption band of a particular functional group may change under the influence of other structural fragments of the molecules. More detailed information on the interpretation of IR spectra of individual classes of organic substances is well presented in the literature [2, 3, 6, 7].

In this manual we will focus on the issue of identifying the most important functional groups using IR spectroscopy .

Alkyl groups 

The most important for identifying alkyl fragments (CH_3, CH_2 groups) are absorption bands caused by stretching and bending vibrations of the CH bond.

Stretching vibrations of the C-H bond of alkyl fragments are found in the region of $3000 - 2840\ cm^{-1}$.

The following rule must be remembered:

Stretching vibrations of C_{sp3}-H bonds, as a rule, are observed below $3000\ cm^{-1}$, while stretching vibrations of C_{sp2}-H and C_{sp}-H bonds lie above $3000\ cm^{-1}$.

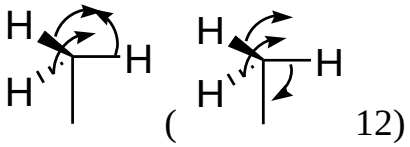
Stretching vibrations of methyl groups (CH_3) are observed in the form of two absorption bands at 2962 and 2872 cm^{-1}. The first is the result of an antisymmetric (as) stretching vibration, in which two C-H bonds of the methyl group are stretched, while the third is compressed (ν_{as} CH3).

The second band is due to symmetrical (s) stretching vibrations ($_{vs}$ CH_3), when all three C-H bonds are stretched or compressed in phase. The presence of several methyl groups leads to an increase in the intensity of the corresponding bands.

Stretching vibrations of methylene groups (CH2) are also observed in the form of two absorption bands (2962 and 2853 cm^{-1}) due to antisymmetric (ν_{as} CH_2) and symmetrical (ν_s CH_2) stretching vibrations.

Deformation vibrations of C-H bonds of alkyl fragments

The methyl group can exhibit two bending vibrations: a symmetric bending vibration (δ_s CH_3), appearing around 1375 cm^{-1}, and an antisymmetric bending vibration (δ_{as} CH_3) - in the region of 1450 cm^{-1} (Fig. 2.3)

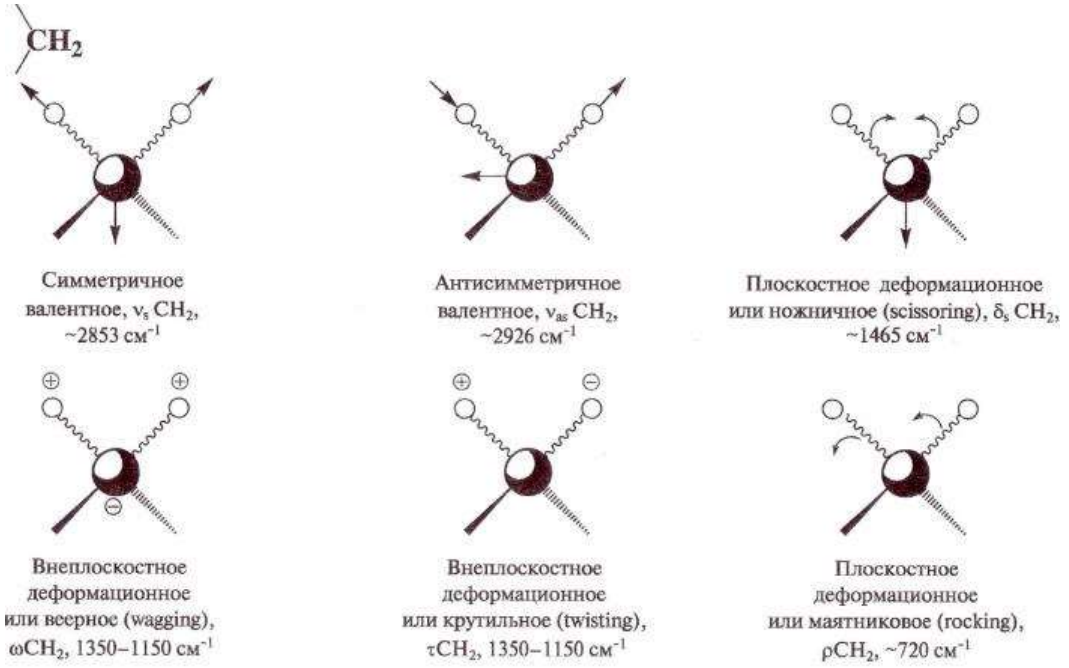


(12)

Rice. 2.3. Symmetrical (scissor) bending vibration in the methyl group (1); antisymmetric (pendulum) bending vibration in the methyl group (2)

Absorption at 1375 cm^{-1} is an important criterion for confirming the structure. It is absent in the spectra of compounds that do not contain a methyl group.

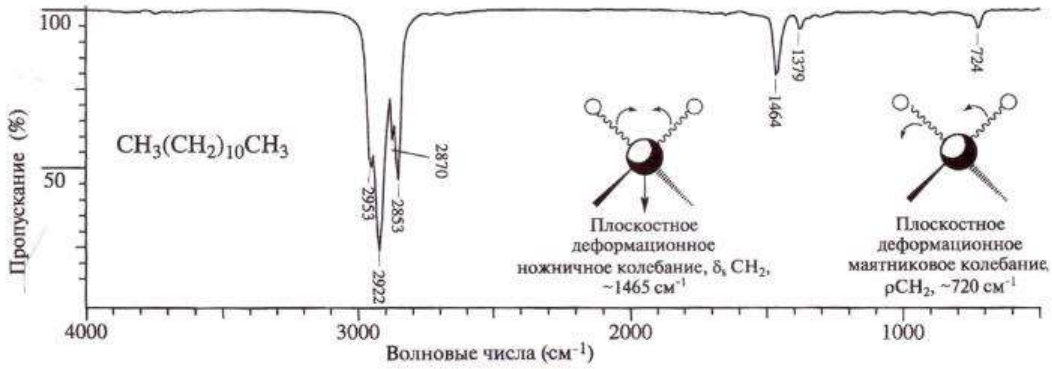
In the methylene group, four types of deformation vibrations are observed (scissor, fan, pendulum, torsional) (Fig. 2.4).



Rice. 2.4. Vibration modes of the $CH_{2\ group}$.

The "+" and "- " signs indicate the movement of atoms perpendicular to the plane of the page.

In this case, the most informative is absorption in the region of 1465 cm^{-1}, caused by scissor bending vibration ($\delta_s CH_2$) (Fig. 2.5).



Rice. 2.5. IR spectrum of dodecane.

Stretching vibrations C - H (cm^{-1}): 2953 ($\nu_{as} CH_3$), 2870 ($\nu_s CH_3$), 2922 ($_{vas} CH_2$), 2853 ($\nu_s CH_2$);

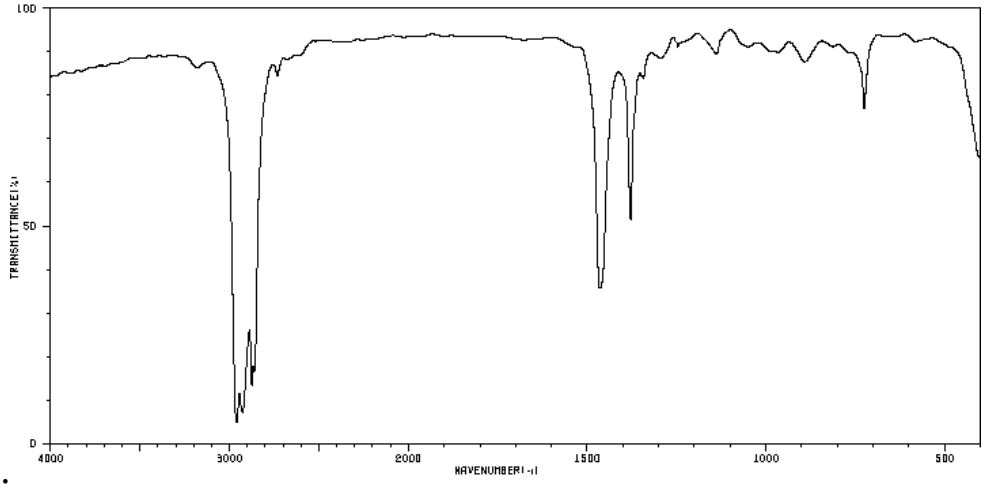
Deformation vibrations C - H (cm^{-1}): 1464 ($\delta_s CH_2$), 1450 ($\delta_{as} CH_3$), 1379 ($\delta_s CH_3$);

Pendulum vibration of the $CH_{2\ group}$: 724 cm^{-1} (p CH2).

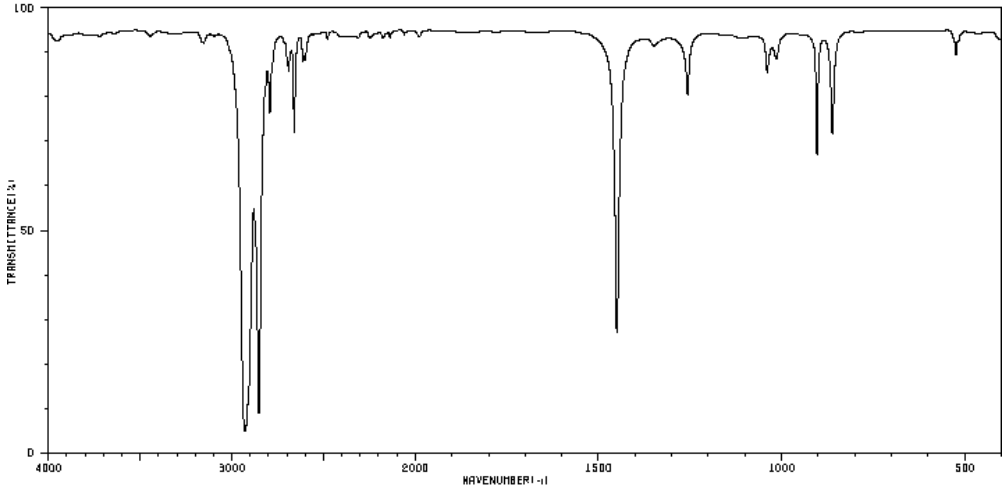
Exercise:

Below are the spectra of hexane, cyclohexane and methylcyclohexane. Analyze the range of stretching vibrations of the C-H bond. Explain the differences you found. Give an explanation for the fact that in the spectrum of hexane in the region of 1379 cm^{-1} there is a band of medium intensity, which is absent in the spectrum of

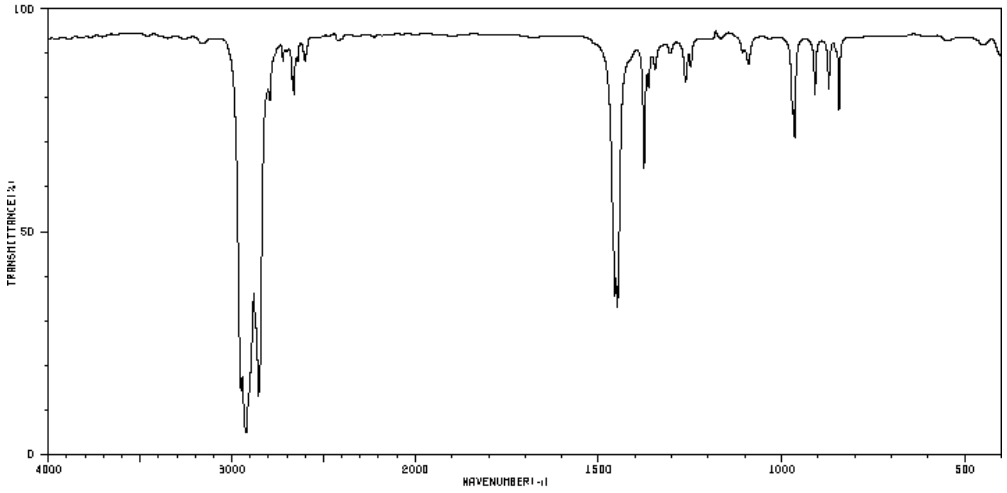
cyclohexane, but reappears in the spectrum of methylcyclohexane at a frequency of 1376 cm $^{-1}$.



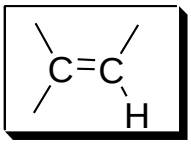
Rice. 2.6. IR spectrum of n-hexane, taken in a film of the substance.



Rice. 2.7. IR spectrum of cyclohexane, taken in a film of the substance.



Rice. 2.8. IR spectrum of methylcyclohexane, taken in a film of the substance

Ethenyl groups 

To identify ethenyl groups, stretching vibrations of C = C bonds in the region of 1650 ±20 cm $^{-1}$, as well as stretching and bending vibrations of = C-H bonds, are important.

Bond stretching vibrations (=C-H)

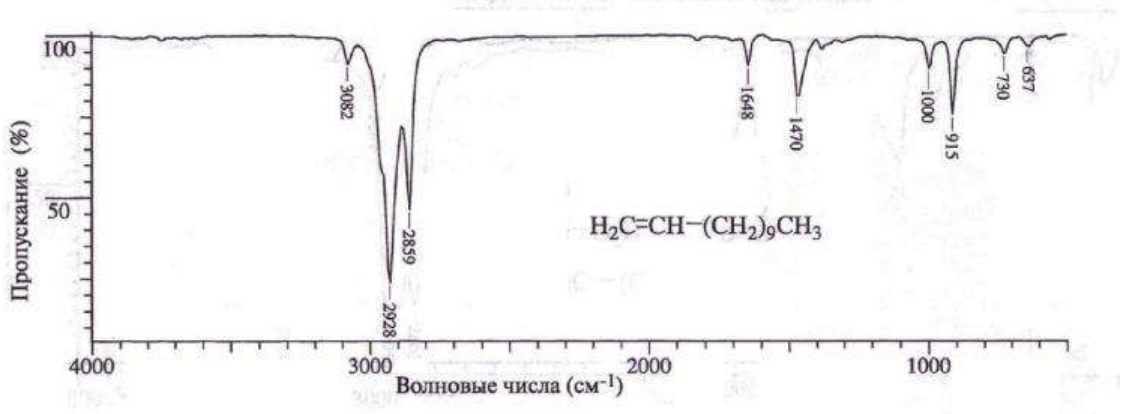
The frequency of stretching vibrations =C-H is observed at 3010 − 3095 cm $^{-1}$, and the value of ν is determined by the degree of substitution at the double bond.

Compounds containing the =CH R fragment in their structure are characterized by absorption ν = 3040 − 3010 cm $^{-1}$. For the =CH $_{2\ group}$, vibrations appear with a frequency of 3095 − 3075 cm $^{-1}$.

Bond vibrations (=C-H)

The most characteristic types of absorption of ethenyl groups are out-of-plane C-H vibrations in the region of 1000 − 650 cm $^{-1}$.

The most typical are the absorption bands of vinyl, vinylidene groups, as well as trans-disubstituted alkenes (Table 2.1). In Allene structures, a strong absorption band is observed, around 850 cm $^{-1,}$ related to the fan vibrations of the group (=CH $_2$).



Rice. 2.9. IR spectrum of dodecene-1.

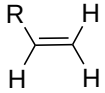
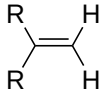
Stretching vibrations C = C and = C - H : 1648 cm $^{-1}$ and 3082 cm $^{-1}$;

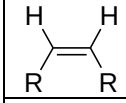
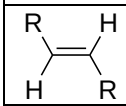
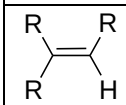
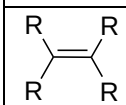
Out-of-plane deformation vibration C - H 1000 cm $^{-1}$, (in the alkene unit) 915 cm $^{-1}$;

Pendulum swing CH $_2$ 730 cm $^{-1}$.

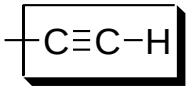
Table 2.1

Main absorption bands of alkenes in IR spectra , cm $^{-1}$

Type [a]	νS-N [b]	νC= C	δC=C-H out-of-plane
	> 3000	164 8 − 1638 Wed	CH 995 - 985s. CH $_2$ 915 − 905 s.
	> 3000	1658 − 1648 Wed.	895 − 885 p.

	> 3000	1662 − 1626 Wed.	730-665 p. − cf. _
	> 3000	1678 − 1668 Wed.	980 − 960 s.
	> 3000	1675 − 1665 Wed. − words	840 − 790 s.
	-	1670 words	

It should be noted that the R substituents may not be the same; Moreover, the higher the symmetry, the weaker the absorption intensity. The absorption bands corresponding to the stretching vibrations of the C-H bond have medium intensity.

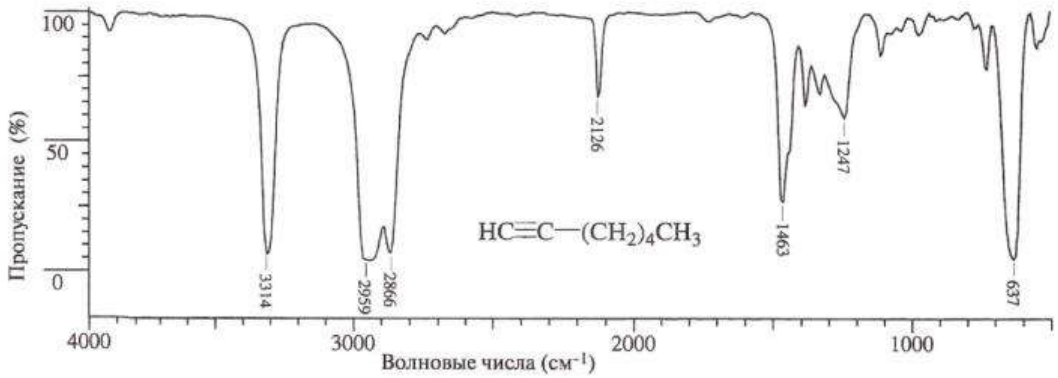
Acetylene groups 

The acetylene group is characterized by stretching vibrations of two types of bonds: C ≡C and C-H. In Fig. Figure 2.10 shows the IR spectrum of a typical terminal alkyne.

Stretching vibrations of the C ≡C bond are observed in the form of a weak absorption band in the region of 2260 − 2100 cm $^{-1}$. For acetylene itself and its symmetrically substituted compounds, C ≡–C stretching vibrations do not appear in the IR spectrum.

Stretching vibrations of C-H bonds in the spectra of monosubstituted alkynes appear in the region of 3333 − 3267 cm $^{-1}$ in the form of intense absorption bands.

Deformation vibrations of C-H bonds of terminal alkynes and their monosubstituted alkynes give a strong, broad absorption band in the region of 700 − 610 cm $^{-1}$.



Rice. 2.10. IR spectrum of heptin-1.

Stretching vibrations ≡C-H 3314 cm $^{-1}$;

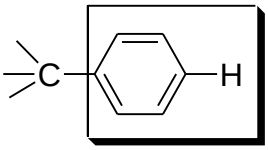
Stretching vibrations of alkyl CH: 2960 − 2860 cm $^{-1}$;

Stretching vibrations C ≡C 2126 cm $^{-1}$;

C-H vibrations: 1463 cm $^{-1}$ (δ_s CH $_2$), 1450 cm $^{-1}$ (δ_{as} CH $_2$);

Overtone of bending vibration δ_{as} ≡C-H 1247 cm $^{-1}$;

The main deformation vibration is ≡C-H 637 cm $^{-1}$.



Phenyl group

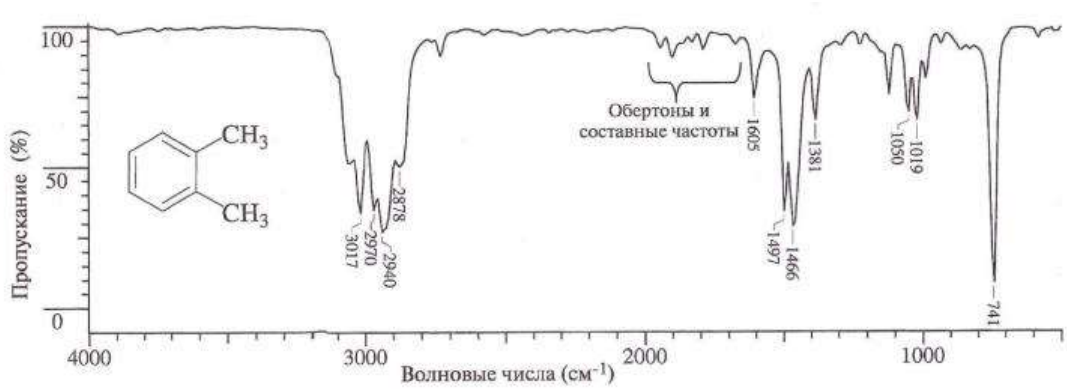
The phenyl group (benzene fragment) is characterized by four types of bond vibrations (Fig. 2.11):

C-H stretching vibrations are observed between 3100 and 3000 cm $^{-1}$. The bands of these vibrations are of medium intensity and usually represent a group of bands;

Out-of-plane deformation vibrations of C-H bonds in the ring appear in the form of intense absorption bands in the region of 900 − 675 cm $^{-1}$. These are the most informative absorption bands in the IR spectrum of aromatic compounds. Bands of planar vibrations appear in the region of 1300–1000 cm $^{-1}$.

Overtones or composite bands of C-H deformation vibrations appear in the region of 2000 − 1650 cm $^{-1}$ in the form of low-intensity absorption bands. The appearance of these bands characterizes the type of substitution in the aromatic ring.

Skeletal vibrations, including vibrations of the C-C cycle, absorb in the regions of 1600 - 1585 and 1500 - 1400 cm $^{-1}$. Skeletal vibration bands often appear as doublets depending on the nature of the substituents on the ring.



Rice. 2.11. IR spectrum of o-xylene .

Stretching vibrations of aromatic CH: 3017 cm $^{-1}$;

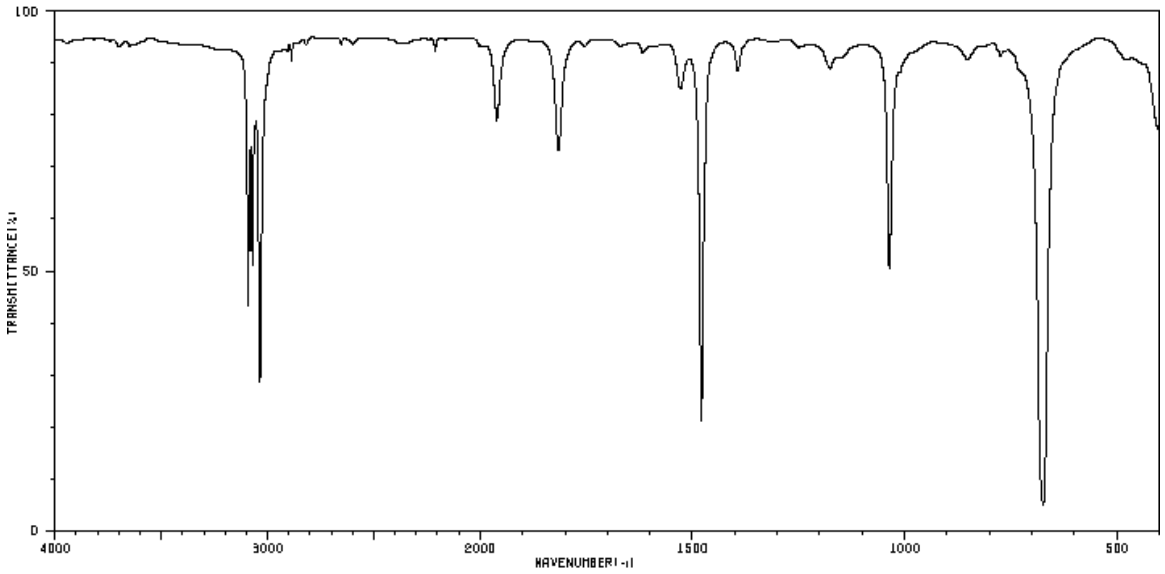
Stretching vibrations of methyl CH: 2970, 1940, 1878 cm $^{-1}$; Overtones: 2000 − 1667 cm $^{-1}$;

Stretching vibrations of the C-C ring: 1605, 1497, 1466 cm $^{-1}$;

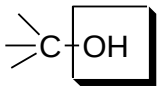
Planar deformation vibrations C-H: 1050, 1019 cm $^{-1}$; Out-of-plane deformation vibrations C-H: 741 cm-1.

Exercise

Analyze the IR spectrum of benzene below and explain the origin of the observed absorption bands.



Rice. 2.12. IR spectrum of benzene.

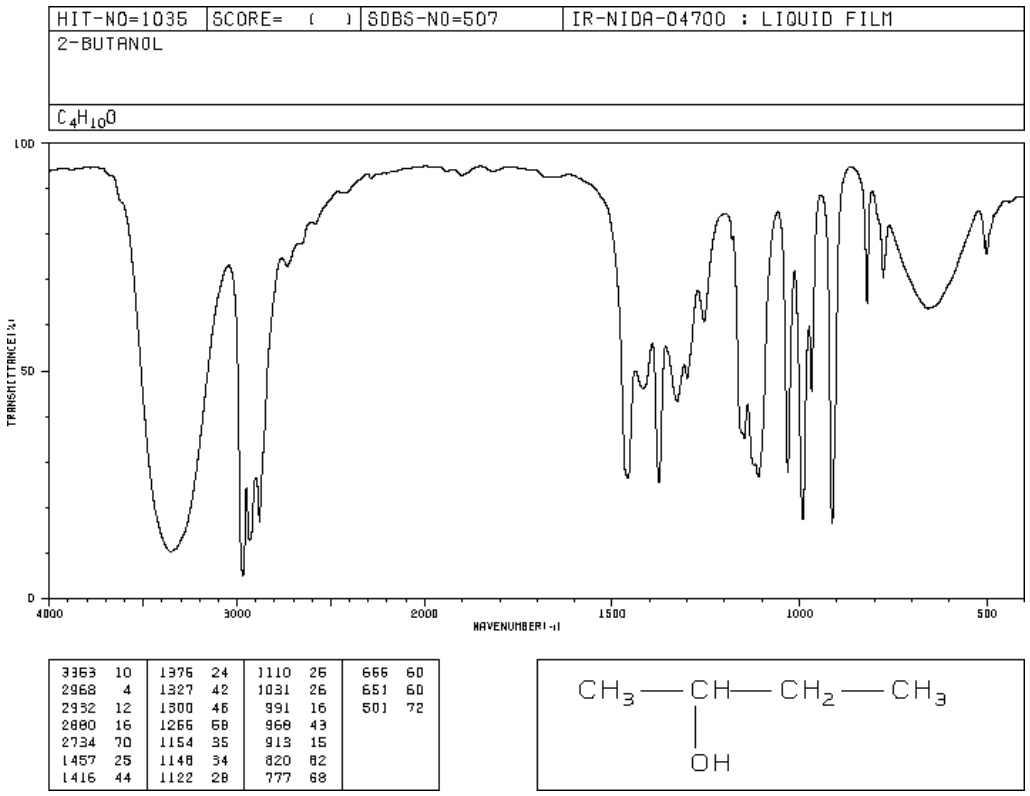
Hydroxyl group 

The introduction of a hydroxyl group into a molecule of an organic compound leads to the appearance of absorption bands associated with vibrations of the C-O and O-H bonds.

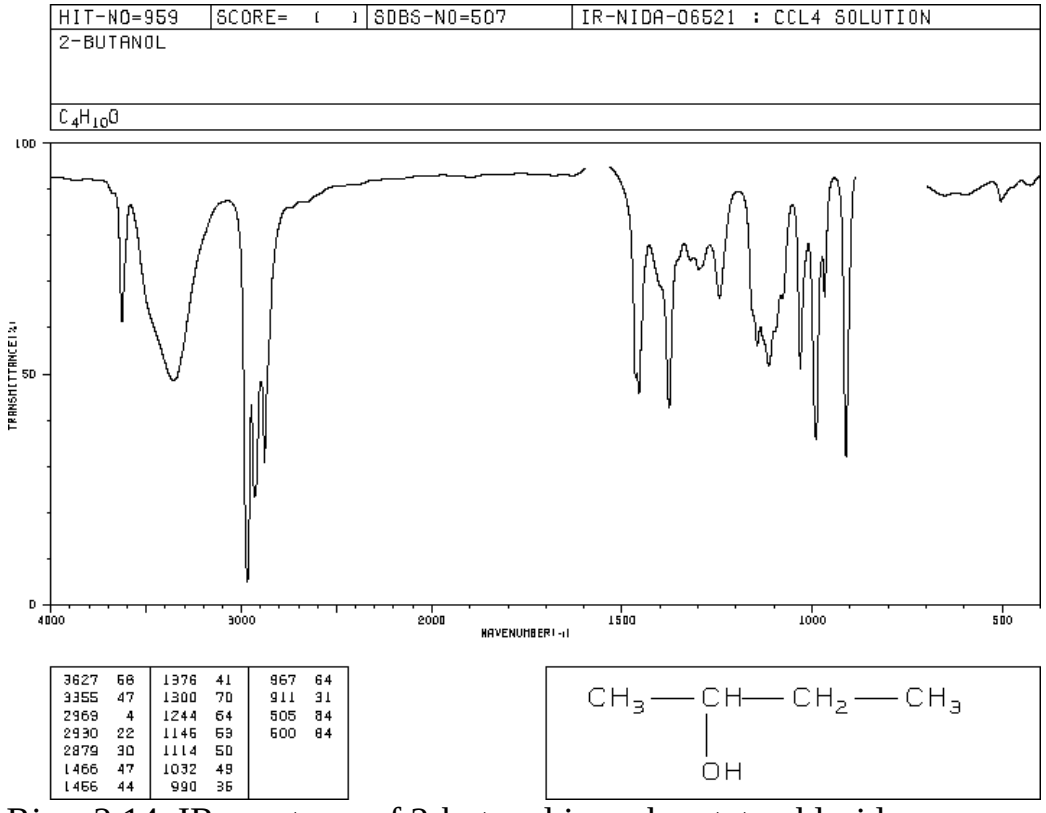
O-H stretching vibrations appear in a wide frequency range (3600 − 2500 cm $^{-1}$), which is associated with the ability of the hydroxyl group to form hydrogen bonds.

The free, unassociated hydroxyl group of alcohols and phenols has a narrow absorption band in the region of 3700 - 35840 cm $^{-1}$. This band is usually observed in dilute solutions of hydroxyl-containing compounds in inert solvents.

The possibility of the formation of intermolecular hydrogen bonds increases with the concentration of the solution, which causes the appearance of additional bands at lower frequencies (3550 − 3200 cm $^{-1}$) due to a decrease in the absorption intensity of the “free” hydroxyl group (Fig. 2.13, 2.14).



Rice. 2.13. IR spectrum of 2-butanol without solvent.



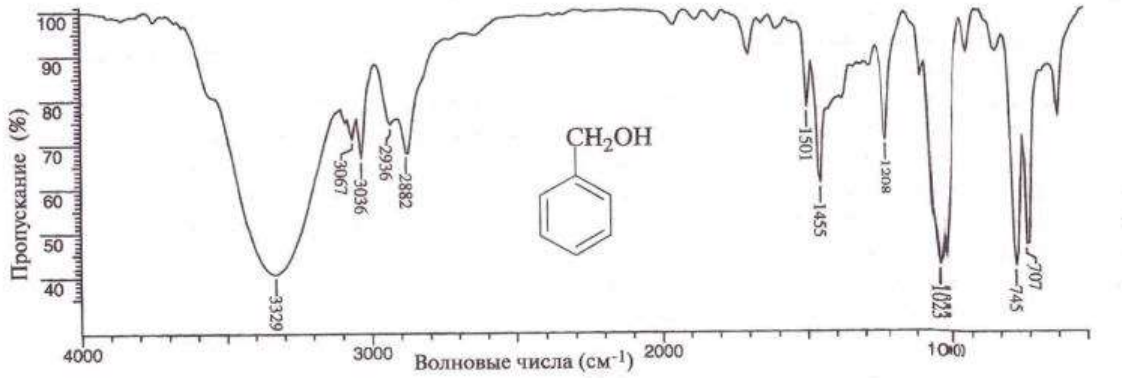
Rice. 2.14. IR spectrum of 2-butanol in carbon tetrachloride.

Stretching vibrations of the C-O bond in alcohols and phenols give a strong band in the region of 1260 − 1000 cm $^{-1}$. The shape of the absorption band becomes more complex when the carbon skeleton is branched and in the presence of a double bond, which is reflected in the frequency values at which absorption is observed.

Deformation vibrations of the O-H bond :

Planar deformation vibrations are observed in the region 1420 − 1330 cm $^{-1}$;

Out-of-plane deformation vibrations of the bound hydroxyl group - in the region of 769 - 650 cm $^{-1}$.



Rice. 2.15. IR spectrum of benzyl alcohol.

Stretching vibrations of the O-H group connected by a hydrogen bond: 3329 cm $^{-1}$;

C-H stretching vibrations: aromatic 3100-3000 cm-1, methylene 2940 - 2860 cm $^{-}$;

Overtones: 2000 − 1667 cm $^{-1}$;

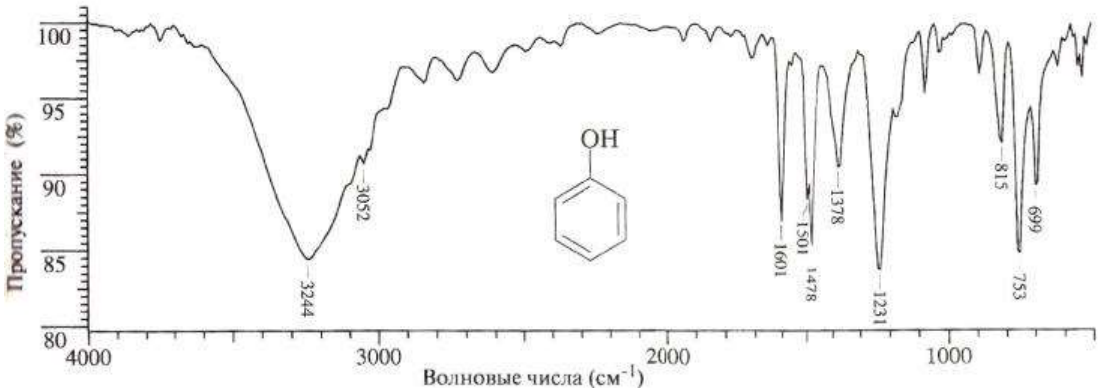
Stretching vibrations of the C-C aromatic ring: 1501, 1455 cm $^{-1}$, overlap with the scissor vibrations of CH_2 at about 1471 cm $^{-1}$;

Deformation vibrations O-H , enhanced by planar vibrations C-H: 1209 cm $^{-1}$;

C-O stretching vibrations of primary alcohol: 1023 cm $^{-1}$;

Out-of-plane vibrations of aromatic CH: 745 cm $^{-1}$;

Bending vibrations of the C-C aromatic ring: 707 cm $^{-1}$.



Rice. 2.16. IR spectrum of phenol (melt).

Wide band of stretching vibrations of O - H groups connected by intermolecular hydrogen bonds: 3244 cm $^{-1}$;

Stretching vibrations of aromatic C - H : 3052 cm $^{-1}$;

Overtones: 2000-1667 cm $^{-1}$;

Stretching vibrations of the C-C aromatic ring: 1601, 1501, 1478 cm $^{-1}$;

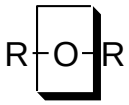
Planar deformation vibrations: O-H 1378 cm $^{-1}$;

Stretching vibrations C- O : 1231 cm $^{-1}$;

Out-of-plane deformation vibrations C - H : 815, 753 cm $^{-1}$;

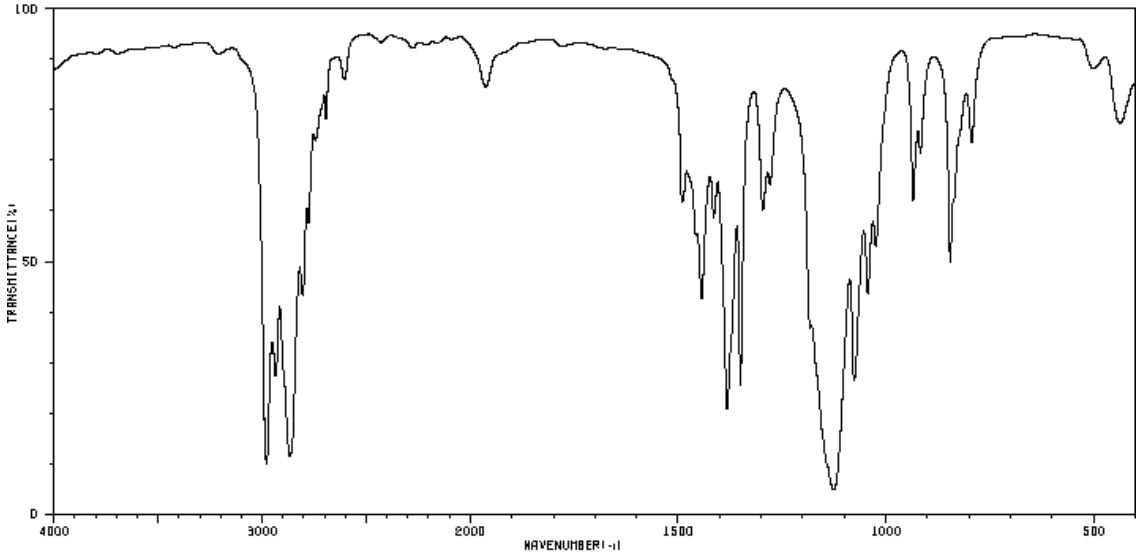
Out-of-plane deformation vibrations of the C-C aromatic ring: 699 cm $^{-1}$;

Wide band of out-of-plane deformation vibrations of the O - H group associated with a hydrogen bond: about 650 cm $^{-1}$.

Simple ether group 

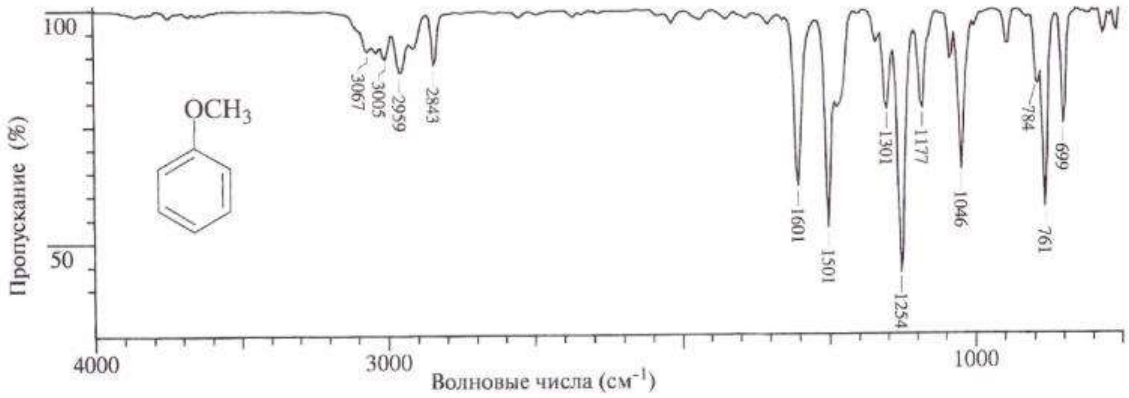
Stretching vibrations of the C-O-C bond cause the appearance of a characteristic absorption band, the position of which depends on the structure of the ether.

Alicyclic ethers: the most characteristic absorption band is in the region 1150 − 1085 cm $^{-1}$ (Fig. 2.17), caused by antisymmetric stretching vibrations of C-O-C. The band of symmetrical stretching vibrations is usually weak.



Rice. 2.17. IR spectrum of diethyl ether taken in a film of the substance.

Arilalkyl ethers: the band of the antisymmetric stretching vibration of C-O-C appears in the region of 1275 − 1200 cm $^{-1}$, the band of the symmetric stretching vibration is about 1075 − 1020 cm $^{-1}$ (Fig. 2.18)



Rice. 2.18. IR spectrum of anisole.

Stretching vibrations of aromatic CH: 3067, 3030, 3005 cm $^{-1}$; C-H stretching vibrations of the methyl group: 2950, 2843 cm $^{-1}$; Overtones: 2000-1667 cm $^{-1}$;

C-C stretching vibrations of the aromatic ring: 1601, 16501 cm $^{-1}$;
Antisymmetric stretching vibrations C-O-C: 1046 cm $^{-1}$;
Out-of-plane deformation vibrations C-H: 784, 761 cm $^{-1}$ Deformation vibrations C-C : 699 cm $^{-1}$

Carbonyl group C=O

Stretching vibrations of the C = O bond of aldehydes and ketones are characterized by intense absorption in the region of 1870 - 1540 cm $^{-1}$.

The position of the stretching vibration band of the C = O group is determined by many factors: structure, physical state, the presence of hydrogen bonds, etc. A typical absorption band is ν C =O of acetone at 1715 cm $^{-1}$ (Fig. 2.19).

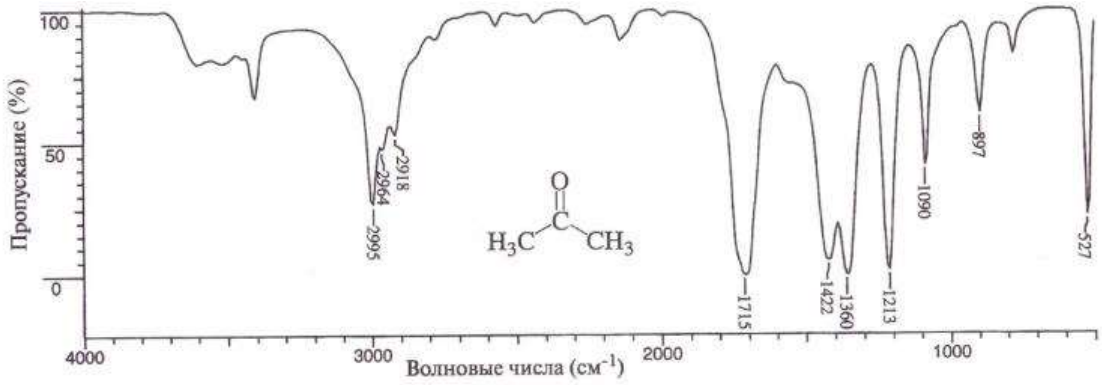


Fig.2.19. IR spectrum of acetone.

C-H stretching vibrations: methyl group ν_{as} 2995 cm $^{-1}$, ν_{s} 2918 cm $^{-1}$, methylene group ν_{as} 2964 cm $^{-1}$;
Stretching vibrations C = O: 1715 cm $^{-1}$;
Deformation vibrations of CH_3: δ_{as} 1422 cm $^{-1}$, δ_{s} 1360 cm $^{-1}$;
Stretching and bending vibrations C-CO-C: 1213 cm $^{-1}$.

In open-chain ketones, the absorption frequency of the carbonyl group is observed in the range 1725 - 1705 cm $^{-1}$.

In aldehydes, absorption is observed in the region of slightly higher frequencies:
aliphatic aldehydes - 1740 - 1720 cm $^{-1}$,
α,β-unsaturated and aromatic aldehydes - 1710 - 1685 cm $^{-1}$.

Stretching vibrations of the CH bond of the aldehyde group are observed in the region of 2830 − 2695 cm $^{-1}$, bending vibrations are around 1390 cm $^{-1}$. The spectrum of octanal shows all the features typical of aldehydes (Fig. 2.20).

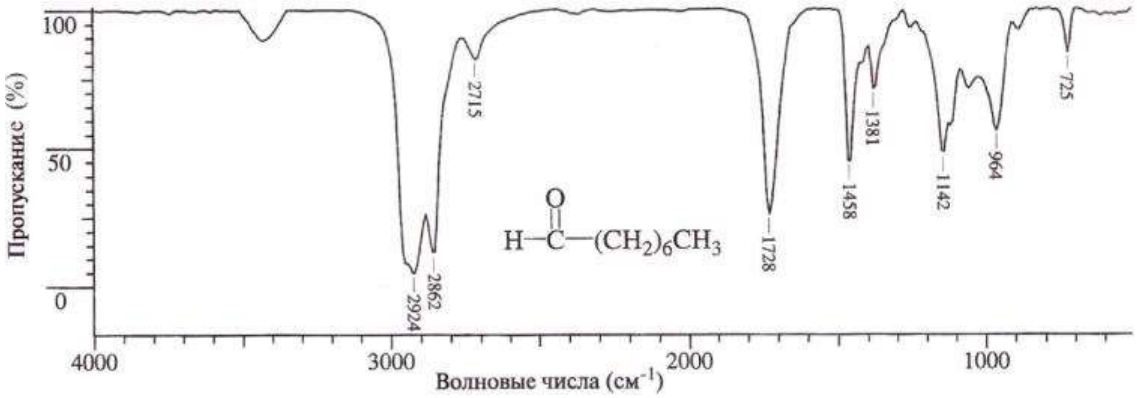
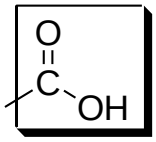


Fig.2.20. IR spectrum of octanal.

C-H stretching vibrations of the aliphatic part: 2980-2860 cm $^{-1}$; C-H stretching vibrations of the aldehyde group: 2715 cm $^{-1}$;

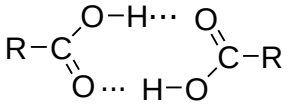
of the C = O stretching vibration in aldehyde: 1728 cm $^{-1}$;

Deformation vibrations of C-H aldehyde group: 1381 cm $^{-1}$.

Carboxyl group 

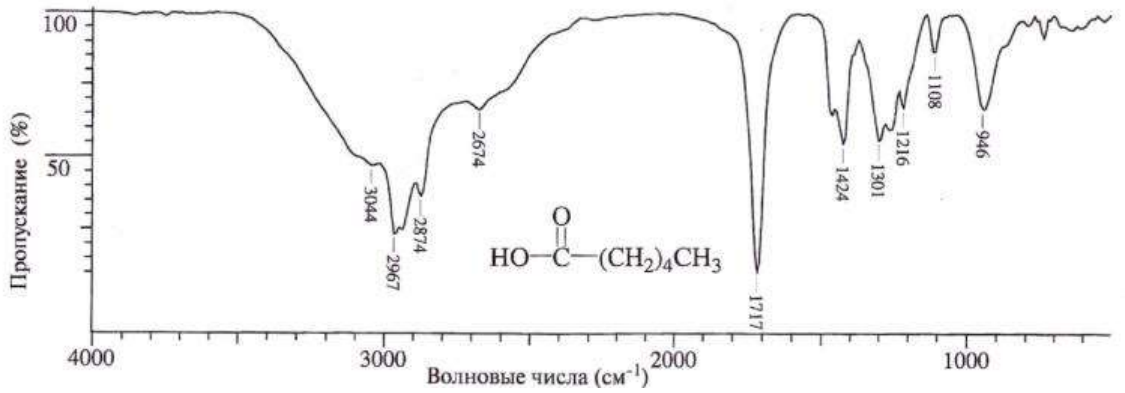
The carboxyl group is detected in the IR spectrum by stretching and bending vibrations of the O-H bond, stretching vibrations of the C = O bond and bending vibrations of the C-O bond.

Carboxylic acids, due to the formation of hydrogen bonds, predominantly exist in the form of dimers:



For this reason, stretching vibrations of the free hydroxyl group (about 3520 cm $^{-1}$) are observed only in very dilute solutions in non-polar solvents or the gas phase.

Dimers of carboxylic acids are characterized by a very wide intense band of stretching vibrations of the O-H bond in the region of 3300-2500 cm $^{-1}$ with a center of about 3000 cm $^{-1}$. The spectrum of a typical aliphatic carboxylic acid is shown in Fig. 2.21.



Rice. 2.21. IR spectrum of hexanoic acid.

O-H stretching vibrations : 3300-2500 cm $^{-1}$;

C-H stretching vibrations: 2967, 2874, 2855 cm $^{-1}$, overlap with a wide band of O-H stretching vibrations ;

Stretching vibration of the carboxyl group C = O, characteristic of the dimeric state: 1717 cm $^{-1}$;

Planar deformation vibration C-O-H: 1424 cm $^{-1}$;

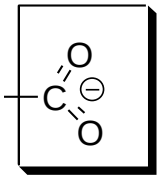
C-O stretching vibration in the dimer: 1301 cm $^{-1}$;

Out-of-plane deformation vibration O-H : 946 cm $^{-1}$.

the C =O stretching vibrations of the carboxyl group are more intense than the bands of the carbonyl stretching vibrations of ketones. Monomers of saturated aliphatic acids absorb about 1760 cm $^{-1}$. The formation of hydrogen bonds shifts absorption to lower frequencies (1720 − 1706 cm $^{-1}$). Unsaturated groups in conjugation with the carbonyl group of the acid slightly reduce the frequency of the absorption band (1710 − 1680 cm $^{-1}$). Electron-withdrawing groups in the α-position leads to an increase in the absorption frequency of C = O (by 10 − 20 cm $^{-1}$).

Deformation vibrations of the C-O and O-H bonds are absorbed in the region of 1320 - 1210 and 1440 - 1396, respectively. The absorption band of the C-O bending vibration is more intense; the band of C-O-H deformation vibrations has moderate intensity.

The characteristic band in the spectra of carboxylic acid dimers is observed in the region of about 920 cm $^{-1}$ and is due to out-of-plane bending vibrations of the O-H bond .

Carboxylate anion 

The carboxylate anion has two strongly interacting carbon-oxygen bonds with lengths intermediate between C =O and

S-O. The carboxylate ion gives two bands in the IR spectrum : a strong band of antisymmetric stretching vibrations in the region of 650-1550 cm $^{-1}$ and a weaker band of symmetric stretching vibrations around 1400 cm $^{-1}$.

The transformation of a carboxylic acid into a salt is used to identify it. The usual procedure involves reacting the acid of interest with a tertiary aliphatic amine (eg triethylamine) in chloroform. In the spectrum of the resulting salt, along with the "ammonium band" (2700-2200 cm $^{-1}$), two characteristic bands of the carboxyl group are visible; the band of O-H stretching vibrations , of course, disappears (Fig. 2.22).

Rice. 2.22. IR spectrum of ammonium benzoate.

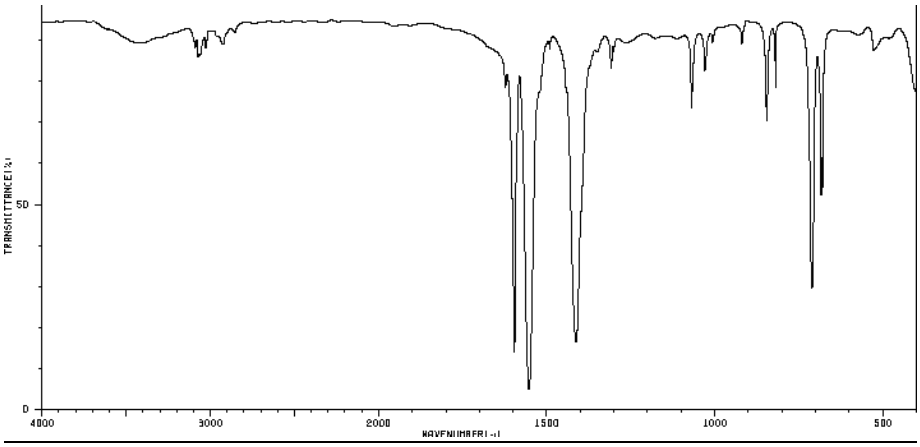
Stretching vibrations N - H and C-H: 3600-2500 cm $^{-1}$;

Stretching vibrations of the C-C ring: 1600 cm $^{-1}$;

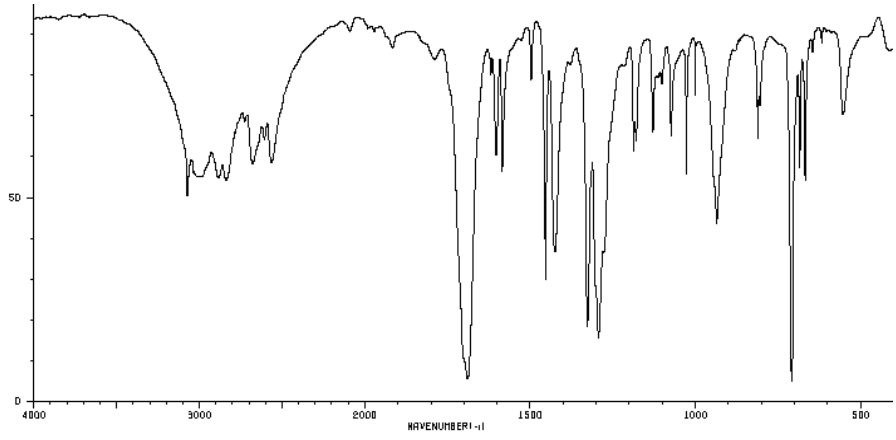
Antisymmetric stretching vibration of the carboxylate anion: 1500 cm $^{-1}$;
Symmetric stretching vibration of the carboxylate anion: 1385 cm $^{-1}$.

Exercise

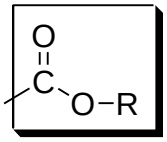
Which of the IR spectra below corresponds to benzoic acid and which to sodium benzoate?



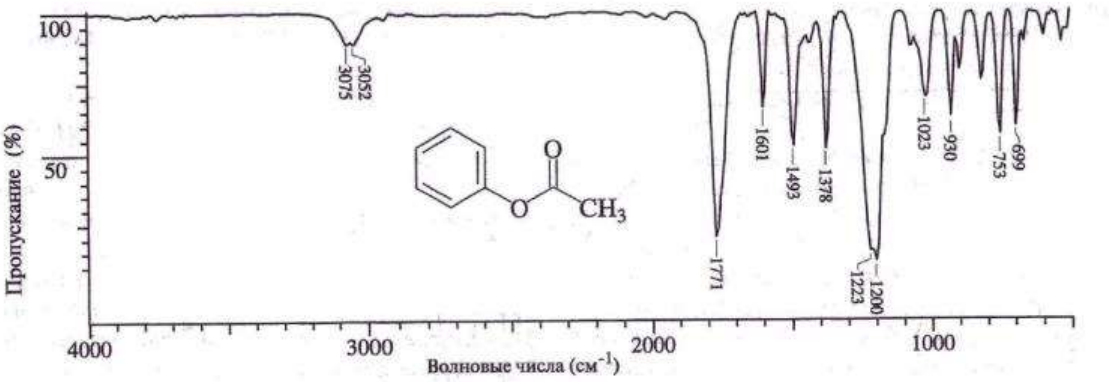
Rice. 2.23. IR spectrum of compound 1.



Rice. 2.24. IR spectrum of compound 2.

Ester group 

In the IR spectra of esters, two strong absorption bands are observed, related to the C =O and C-O stretching vibrations. Conjugation of an aryl or other unsaturated group with a carbonyl group lowers the frequency of C = O stretching vibrations (Fig. 2.25).



Rice. 2.25. IR spectrum of phenylacetate.

Stretching vibrations of aromatic CH: 3075, 3052 cm $^{-1}$;

Stretching vibration C = O: 1771 cm $^{-1}$, this frequency is higher than the frequency of stretching vibrations of the alkyl ester group (1740 cm $^{-1}$) due to the conjugation of the phenyl group with the oxygen atom of the phenolic fragment;

Stretching vibration of the C-C ring: 1601 cm $^{-1}$; δ_{as} CH_3 1493 cm $^{-1}$, δ_s CH_3 1378 cm $^{-1}$;

Stretching vibration of the acetate group C(=O)-O: 1223 cm $^{-1}$;

Antisymmetric stretching vibration O-C-C: 1200 cm $^{-1}$.

Stretching vibrations of the C=O bond of the ester group appear in the region of -1735 cm $^{-1}$:

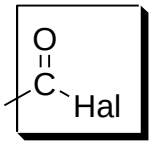
aliphatic esters (excluding formates) – 1750 − 1735 cm $^{-1}$;

formates, α,β-unsaturated esters and benzoates - 1730-1715 cm $^{-1}$;

C = O stretching vibration :

vinyl acetate - 1776 cm $^{-1}$, phenylacetate - 1771 cm $^{-1}$; ethyl ester of trichloroacetic acid - 1770 cm $^{-1}$.

The "stretching vibrations of the C-O bond " in esters actually consist of two interacting antisymmetric vibrations: C- C(=O)-O and O-C-C, with the former being much more important. These bands are observed in the region of 1300-1000 cm $^{-1}$, often called the “ether band” in the literature.

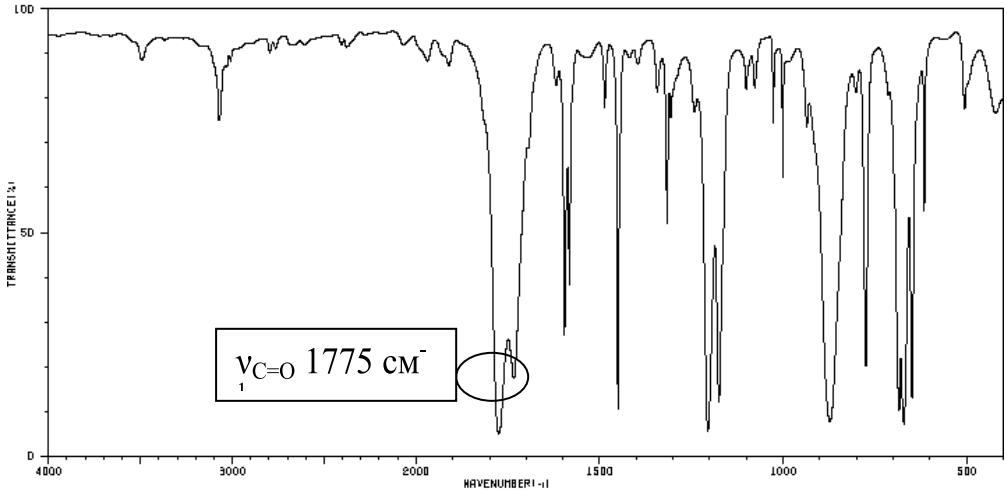
Anhydride group 

Acid halides are characterized by intense absorption in the region of C = O stretching vibrations at low frequencies (Table 2.2, Fig. 2.26).

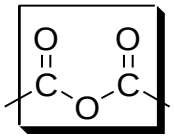
Table 2.2

C =O stretching vibrations in the acid halide group

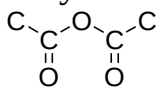
Hal	ν (C = O), cm $^{-1}$
Cl	1815 − 1785
F	~1869
Br	1812
For comparison	
OH (for monomer)	1760
OR	1750 − 1735
NH_2	1695 − 1650



Rice. 2.26. IR spectrum of benzoic acid chloride.

Anhydride group 

The anhydride group is found:

1. by two absorption bands in the region of C = O stretching vibrations (symmetric and antisymmetric vibrations) (Fig. 2.27).
2. by an intense absorption band in the region of stretching vibrations of the fragment 

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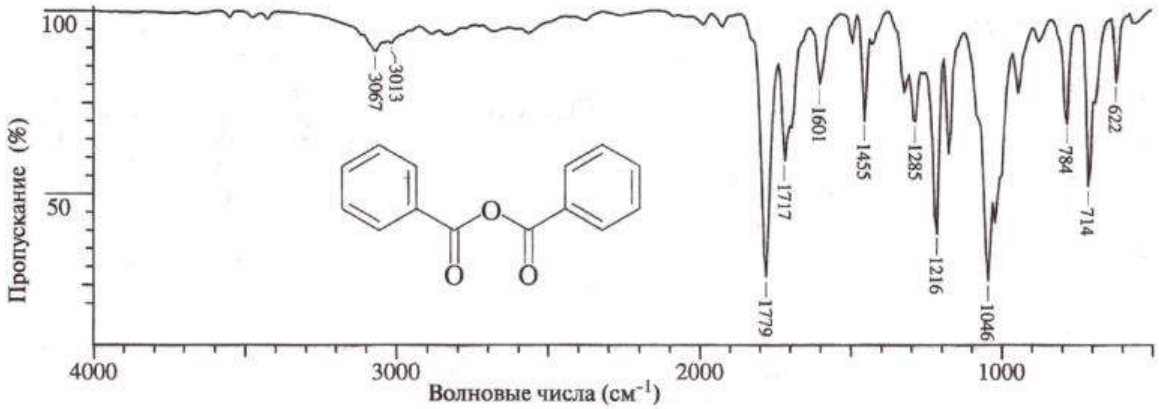


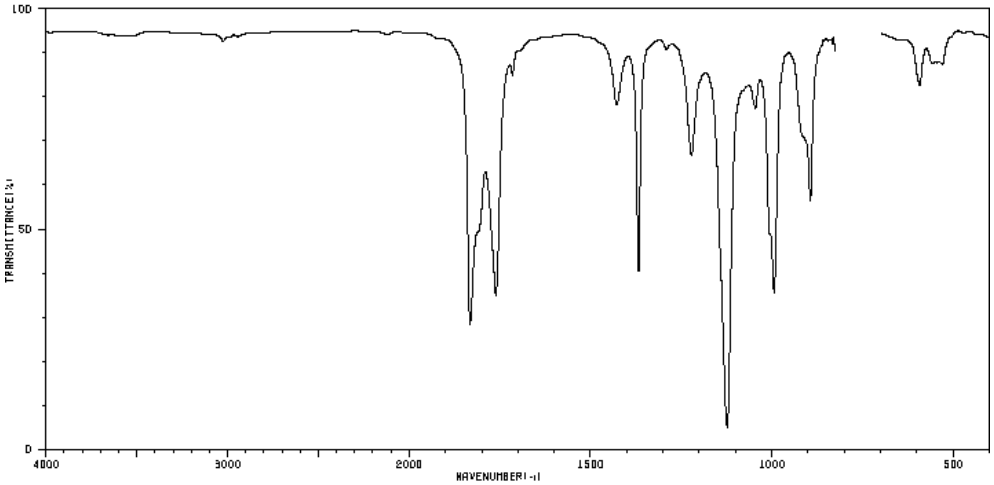
Rice. 2.27. IR spectrum of benzoic acid anhydride.

Stretching vibrations of aromatic CH: 3067, 3013 cm $^{-1}$;

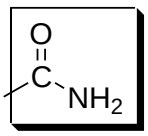
Interacting antisymmetric and symmetric stretching vibrations of C = O: 1779 and 1717 cm $^{-1}$, respectively;

Stretching vibration C-CO-O-CO-C: 1046 cm $^{-1}$.

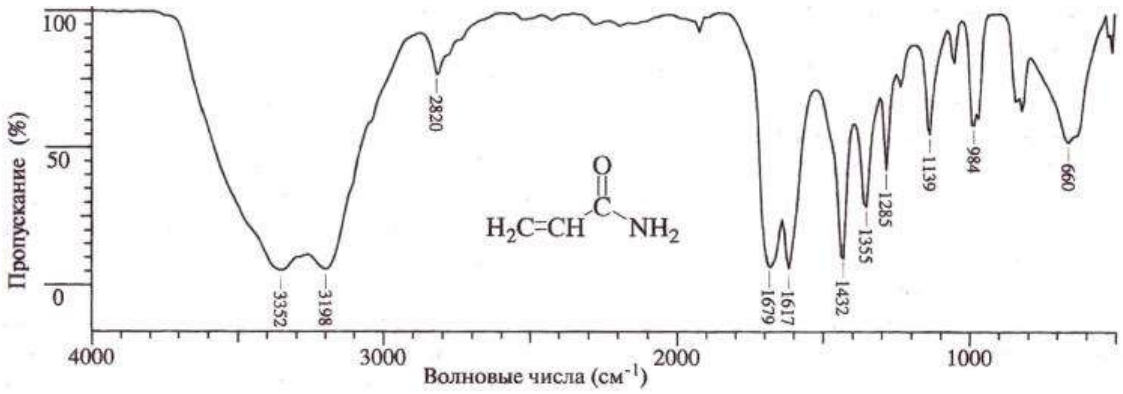
Non-conjugated anhydrides absorb about 1047 cm $^{-1}$, for example, acetic anhydride - 1125 cm $^{-1}$ (Fig. 2.28).



Rice. 2.28. IR spectrum of acetic anhydride taken in a $CCl_{4\ solution}$.

Amide group 

The amide group is characterized, first of all, by two absorption bands - stretching vibrations of the C = O bond ("Amide I " band and bending vibrations of the N - H bond ("Amide II "). Figure 2.29 shows the IR spectrum of acrylic acid amide.



Rice. 2.29. IR spectrum of acrylamide.

N - H stretching vibrations of the primary amide bound by hydrogen bonds: antisymmetric 3352 cm $^{-1}$, symmetric 3198 cm $^{-1}$;

the C =O stretching vibration and the first amide band: 1679 cm $^{-1}$;

Deformation vibration N - H (second amide band): 1617 cm $^{-1}$;

Stretching vibration C - N : 1432 cm $^{-1}$;

Wide band of deformation out-of-plane vibration N - H : 700-600 cm $^{-1}$.

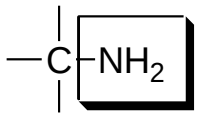
Stretching vibrations of the C = O bond ("Amide I " band) are observed in the region 1690 - 1630 cm $^{-1}$ in the spectra of dilute solutions of primary, secondary and tertiary amides. Primary and secondary amides are often associated. As a result, in the solid state, the first amide band can be shifted by 30-40 cm $^{-1}$ to the low-frequency side.

Deformation vibrations of the N - H bond ("Amide II " band) of primary amides appear in the region of 1620 - 1590 cm $^{-1}$ for. All primary amines in dilute solutions give a sharp Amide II absorption band , the intensity of which is between one-half and one-third the intensity of the C =O absorption band. In petroleum jelly or KBr tablets , the band appears in the range 1655 − 1620 cm $^{-1}$ and usually overlaps with the Amide I band .

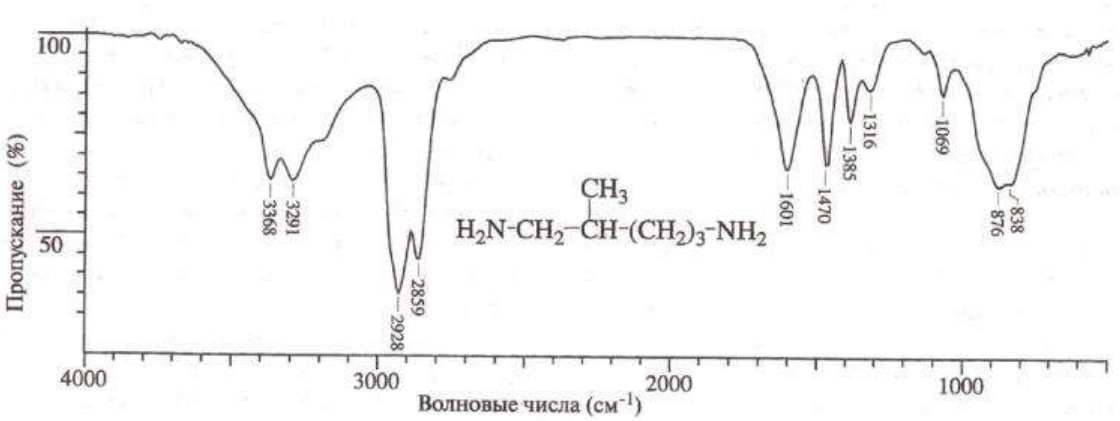
Deformation vibrations of the N - H bond ("Amide II " band) of secondary amines in the solid state are observed in the range 1570 - 1515 cm $^{-1}$ (in solution - 1550 - 1510 cm $^{-1}$).

Out-of-plane fan vibrations of N - H of primary and secondary amides appear in the form of a broad band of average intensity in the range 800 − 666 cm $^{-1}$.

Stretching vibrations (symmetric and antisymmetric) of the N - H bond of primary amides cause the appearance, respectively, of two absorption bands of average intensity around 3520 - 3400 cm $^{-1}$ (solution). In the spectra of solid samples, these bands are observed at 3350 − 3180 cm $^{-1}$. In the IR spectrum of secondary amines, these bands are observed at 3500 - 3400 cm $^{-1}$ (dilute solutions) and 3330 - 3060 cm $^{-1}$ (concentrated solutions or solid state).

Amino group 

The amino group is characterized by specific absorption bands caused by stretching and bending vibrations of the N -H bond and stretching vibrations of C- N (Table 2.4) (Fig. 2.30).



Rice. 2.30. IR spectrum of 2-methylpentanediamine-1.5.

Two bands of interacting stretching vibrations of N - H groups involved in hydrogen bonds in the primary amine: antisymmetric 3368 cm $^{-1}$, symmetric 3291 cm $^{-1}$ ("shoulder" about 3200 cm $^{-1}$);

Stretching vibrations C-H: 2928, 2859 cm $^{-1}$;

Deformation vibration N - H (scissor): 1601 cm $^{-1}$; δs _ CH_2 (scissor): 1470 cm $^{-1}$;

Stretching vibrations of C - N bonds : 1069 cm $^{-1}$;

Fan vibration N - H : 900-700 cm $^{-1}$.

Primary amino group

Stretching vibrations of the N - H bond appear in the form of two absorption bands at 3500 cm $^{-1}$ (antisymmetric vibrations) and
3400 cm $^{-1}$ (symmetrical vibrations).

Deformation vibrations of the N - H bond are observed in the region of 1650 - 1580 cm $^{-1}$. The intensity of the band varies from medium to high.

Secondary amino group

Stretching vibrations of the N - H bond are observed in the form of a single weak absorption band in the range 3350 - 3310 cm $^{-1}$.

Deformation vibrations of the N - H bond in aliphatic amines are difficult to detect. Aromatic amines absorb at 1515 cm $^{-1}$.

In the IR spectra of primary and secondary amines in the region 909 − 666 cm $^{-1}$, a wide absorption band of medium or high intensity is observed, caused by fan vibrations of the N - H bond .

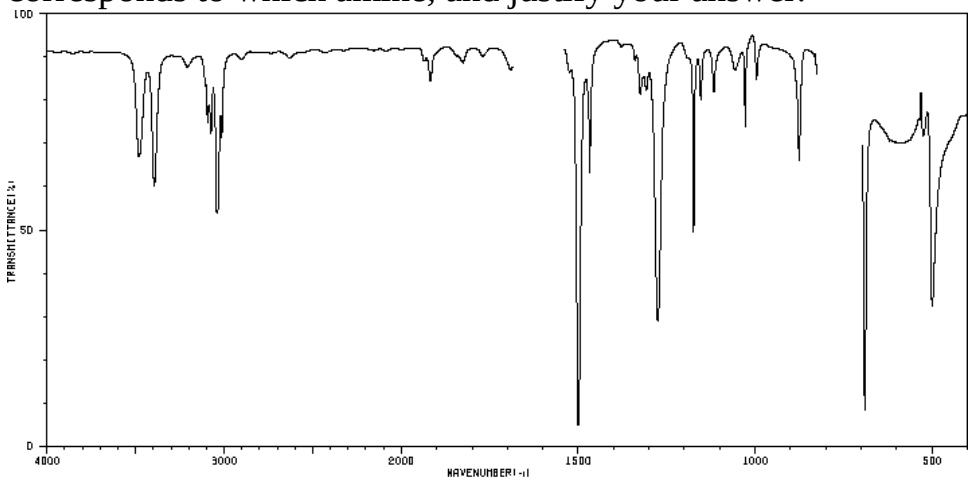
Table 2.4.

Stretching vibrations of the C - N bond in amines

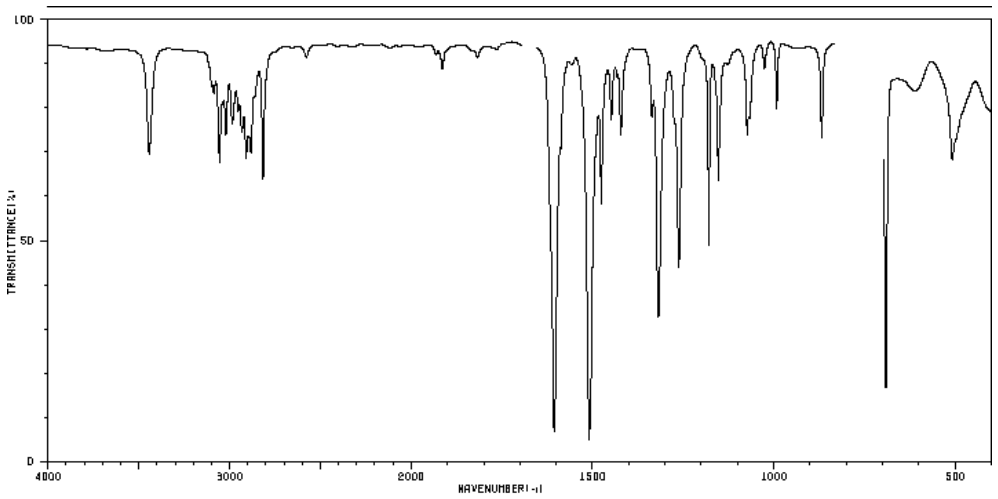
Amine	Region absorption, cm $^{-1}$	Absorption band intensity
Aliphatic (primary, secondary, tertiary)	1250 − 1020	s ., sl.
Aromatic: primary secondary tertiary	 1340 − 1250 1350 − 1280 1360 − 1310	 With. With. With.

Exercise

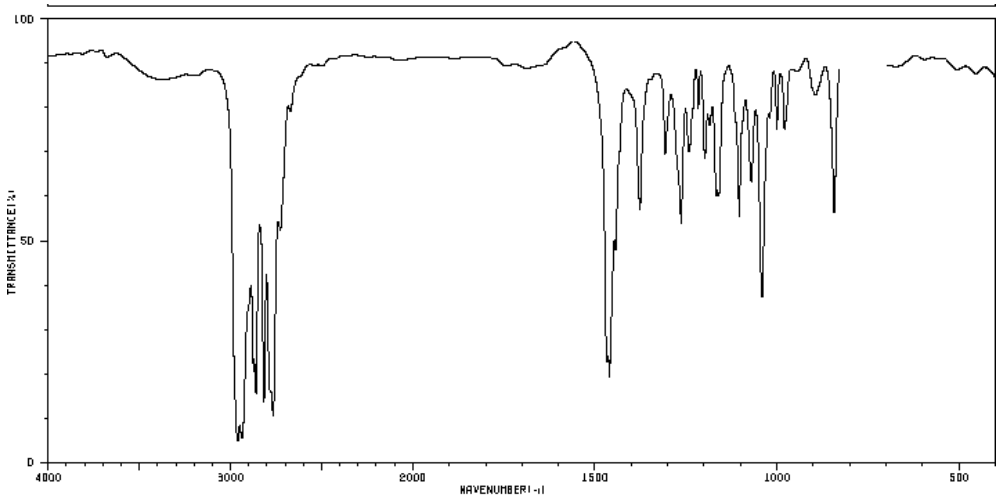
Below are the IR spectra of a primary, secondary and tertiary amine. In this case, two amines are aromatic, the third is aliphatic. Indicate which spectrum corresponds to which amine, and justify your answer.



Rice. 3.33. IR spectrum of compound 1, taken in CCl_4 solution.



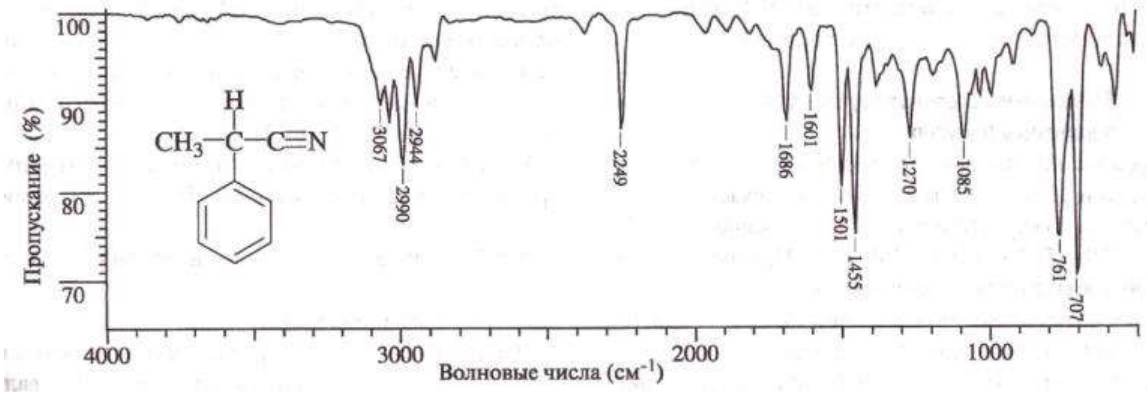
Rice. 2.31. IR spectrum of compound 2, taken in CCl_4 solution.



Rice. 2.32. IR spectrum of compound 3, taken in $CCl_{4\ solution}$.

Nitrile group 

The nitrile group is characterized by bands of low and medium intensity of stretching vibrations of the C≡N bond. Absorption is observed in the region 2260 - 2240 cm^{-1}, electron-withdrawing substituents lower the frequency of the absorption band to 2240 - 2222 cm^{-1} (Fig. 2.33).



Rice. 2.33. IR spectrum of α- methylbenzyl cyanide.

Stretching vibrations of aromatic CH: 3067, 3030 cm^{-1};

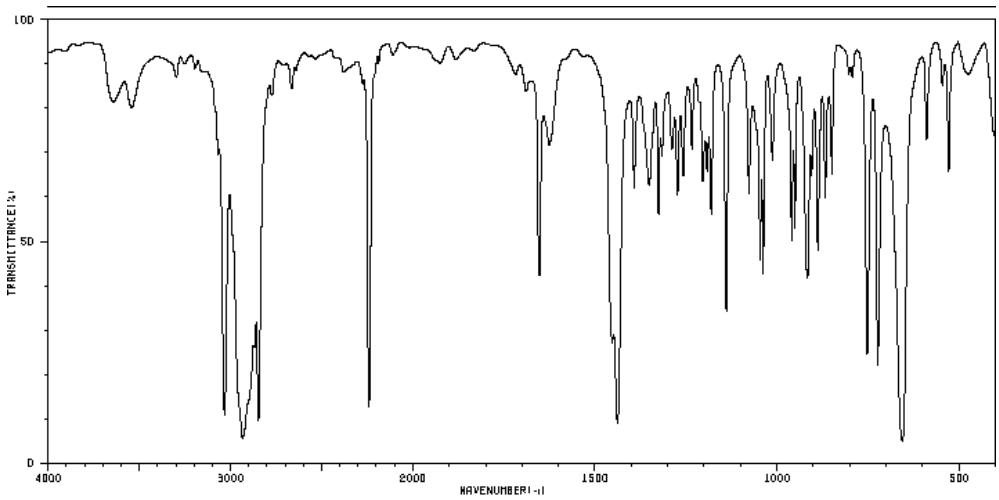
Stretching vibrations of aliphatic CH: 2990, 2944 cm^{-1};

Stretching vibration C ≡ N : 2249 cm^{-1};

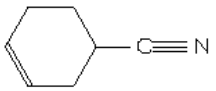
Out-of-plane deformation vibrations of aromatic CH:
761 cm^{-1}.

Exercise

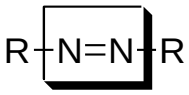
Describe the spectrum of 3-cyclohexene-1-carbonitrile below.



3068	66	1438	8	1258	62	1045	44	888	46
3033	10	1393	58	1234	68	1038	41	868	57
2934	5	1351	60	1204	80	1013	66	850	62
2846	9	1326	69	1192	64	980	47	762	23
2241	12	1316	66	1181	53	951	50	723	21
1652	41	1289	68	1140	33	916	39	656	4
1463	26	1274	58	1077	68	906	62	629	62

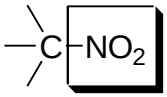


Rice. 2.34. IR spectrum of 3-cyclohexene-1-carbonitrile, taken in a film of the substance.

Azo group 

IR spectroscopy is of little information for identifying the -N=N- group: the stretching vibration of the N=N group in symmetrical azo compounds is prohibited and can only be observed in Raman spectra.

Unsymmetrical para-substituted azo compounds with electron-withdrawing substituents have weak absorption bands in the region of 1429 cm^{-1}.

Nitro group 

The nitro group is characterized by two absorption bands: antisymmetric stretching vibrations N = O in the region 1661 − 1499 cm^{-1}; symmetrical N = O stretching vibrations appear in the range 1389 − 1259 cm^{-1}.

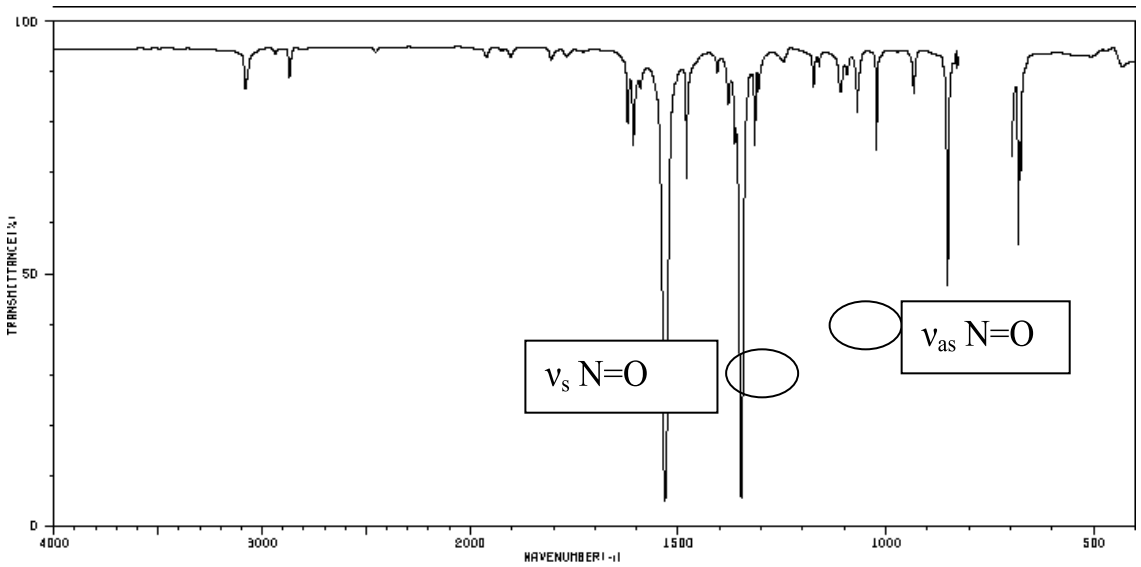
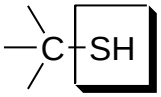
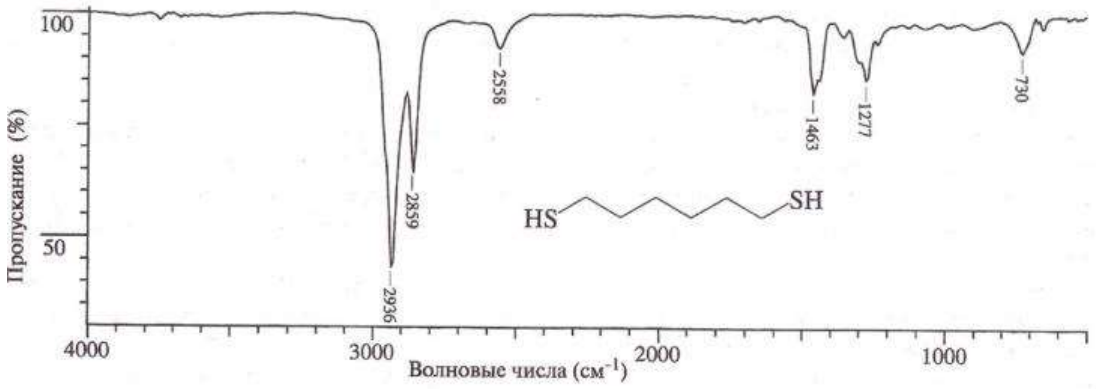


Figure 2 .35. IR spectrum of nitrobenzene, in CCl_4 solution .

Sulfanyl group 

the S - H bond in the region 2600 - 2550 cm^{-1} (liquid sample or solution) (Fig. 2.36). Despite the low intensity, the S - H band is quite easily identified, since the absorption bands of other groups almost do not fall into this region.

Absorption bands of stretching vibrations related to the C - S bond are observed in the region of 700 - 600 cm^{-1} . Due to their low intensity and changing position, these bands are of little use for structural analysis.

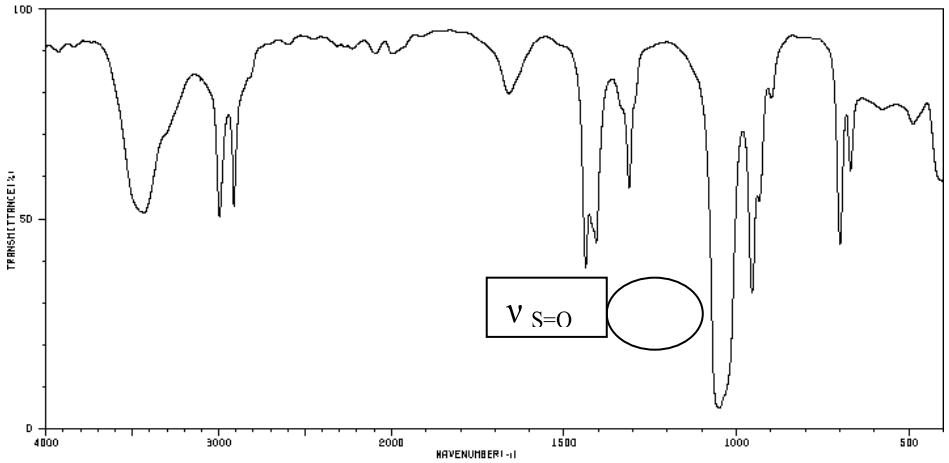


Rice. 2.36. IR spectrum of 1,6-hexanedithiol.
Stretching vibrations of aliphatic CH: 2936 cm^{-1} ;
Moderately weak stretching vibration band S - H : 2558 cm^{-1} ;
Stretching vibration C - S : 730 cm^{-1} .

Functional groups containing the S = O bond

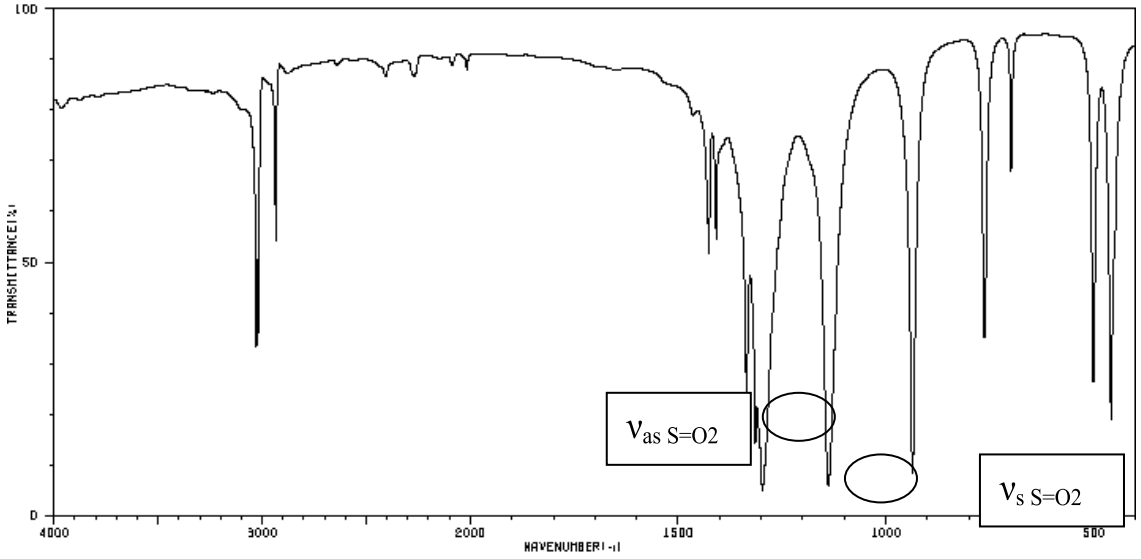
In sulfoxides, the absorption band of stretching vibrations of the S = O bond is intense and is observed in the region 1070 - 1030 cm-1 (Fig. 2.37). The formation of hydrogen bonds leads to a shift of the absorption band towards low frequencies. The S

= O vibration frequency increases with the introduction of an electron-withdrawing substituent into the sulfoxide molecule.



Rice. 2.37. IR spectrum of dimethyl sulfoxide, taken in a film of the substance.

In the IR spectra of sulfones, two intense absorption bands are observed in the region 1350 - 1300 and 1160 - 1120 cm $^{-1}$, caused by antisymmetric and symmetric stretching vibrations of the $SO_{2\ group}$, respectively (Fig. 2.38).



Rice. 2.38. IR spectrum of dimethyl sulfone in KBr .

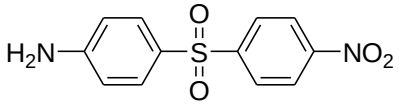
Sulfonyl chlorides absorb in the region 1410 − 1380 cm $^{-1}$ ($\nu_{as\ S=O}$) and 1204 − 1177 cm $^{-1}$ ($\nu_{s\ S=O}$).

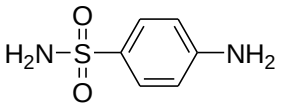
Sulfonamides absorb in the range 1370 − 1335 cm $^{-1}$ ($\nu_{as\ S=O}$) and 1170 − 155 cm $^{-1}$ ($\nu_{s\ S=O}$). In the spectra of primary sulfonamides in the solid state there are strong bands of N - H stretching vibrations at 33990 - 3330 and 3300 - 3247 cm $^{-1}$. Secondary sulfonamides absorb about 3265 cm $^{-1}$.

Sulfonic acids absorb at 1350 − 1342 cm-1 ($\nu_{as\ S=O}$) and 1165 − 1150 cm $^{-1}$ ($\nu_{s\ S=O}$).

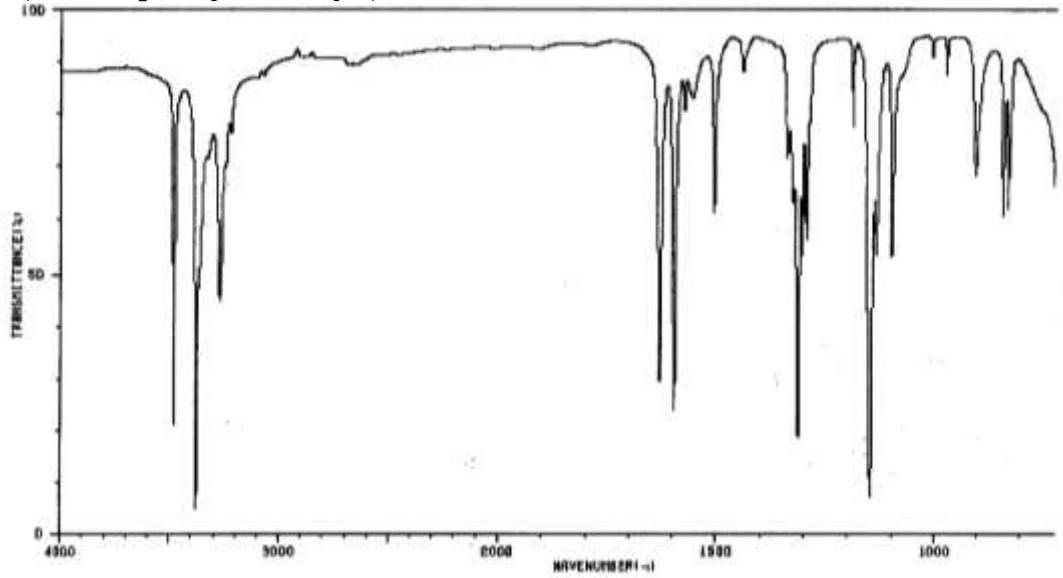
Exercise

Which of the following compounds does the IR spectrum in Fig. 2.39:





4-(4'-nitrophenylsulfonyl)b enzamine 4-aminobenzenesulfonamide



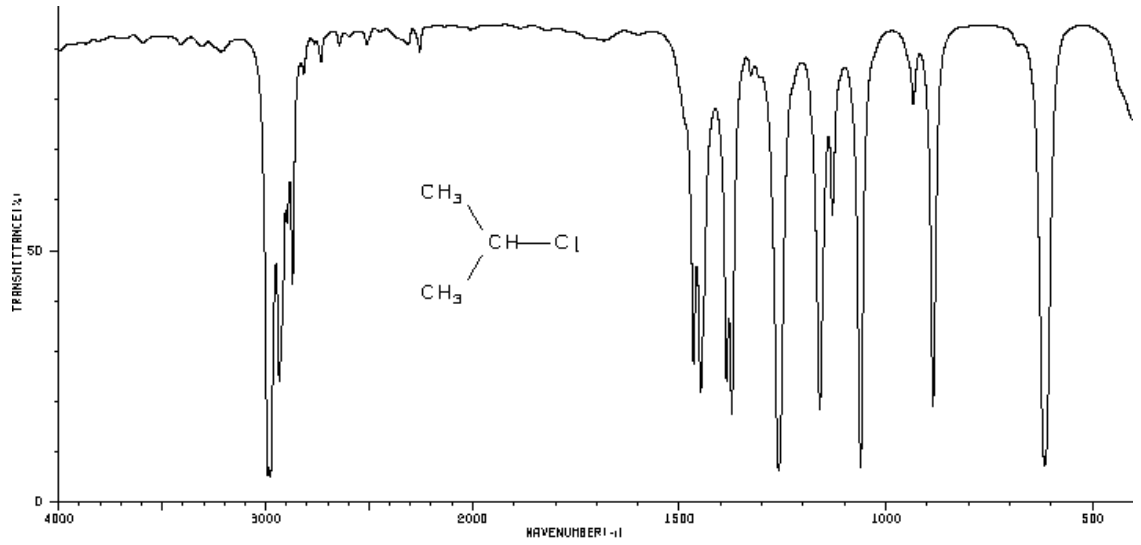
Rice. 2.39. Spectrum of an unknown compound.

Functional group containing a C - Hal bond (Cl , Br , I , F)

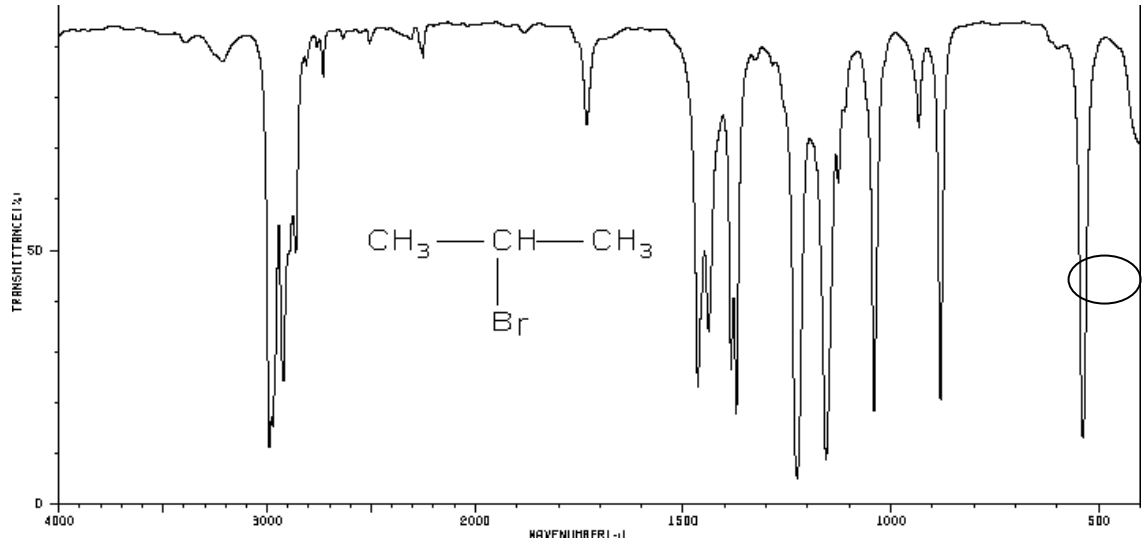
The strong absorption of halogenated hydrocarbons is due to stretching vibrations of the carbon-halogen bond (Table 2.5, Fig. 2.4 0 - 2.45).

Table 2.5
Absorption regions of stretching vibrations of C - Hal bonds

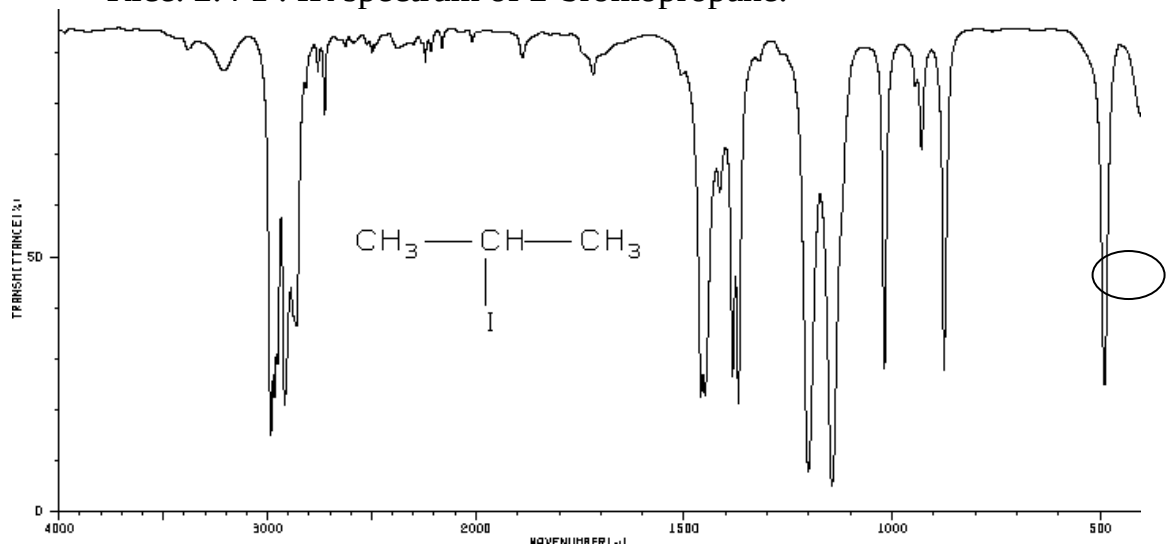
Halide	Halogen	Frequencies of stretching vibrations of the C - Hal bond , cm^{-1}
Aliphatic		
	I	600 − 500
	Br	690 − 515
	Cl	850 − 550
	F	1400 − 1000
Aromatic		
	Br	1080 − 1000
	Cl	1096 − 1089
	F	1250 − 1100



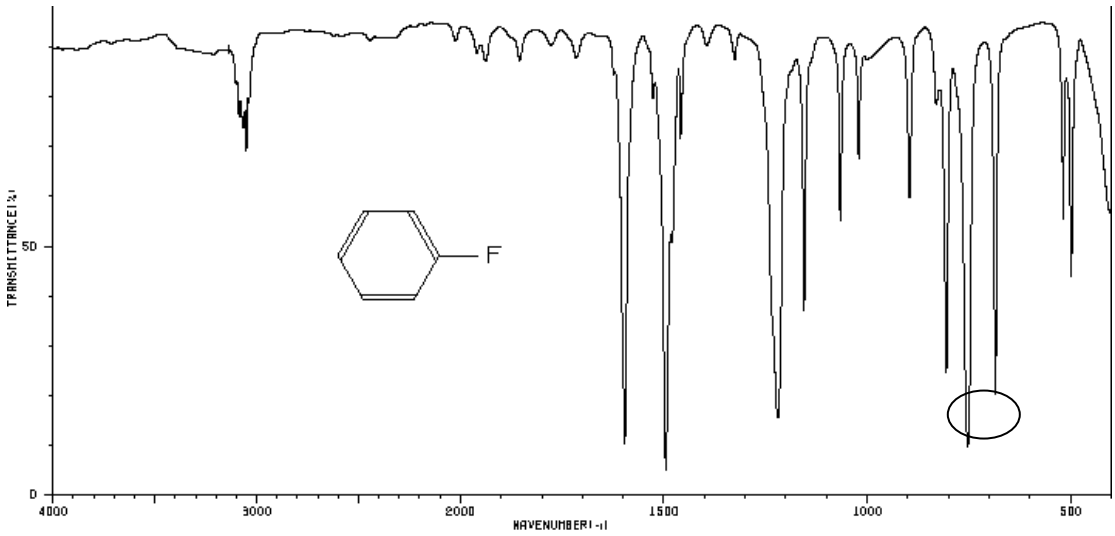
Rice. 2.4 0 . IR spectrum of 2-chloropropane.



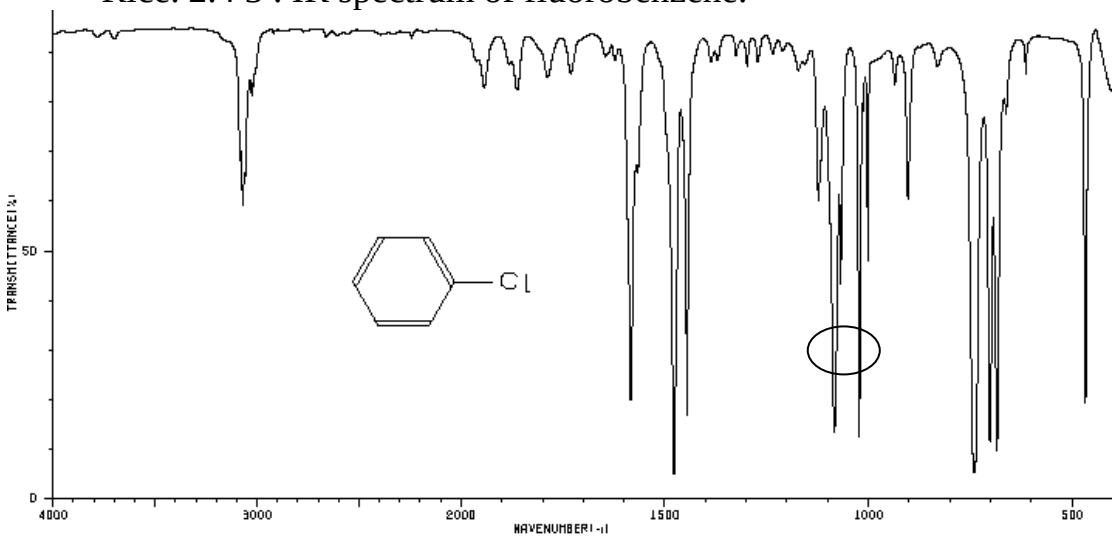
Rice. 2.4 1 . IR spectrum of 2-bromopropane.



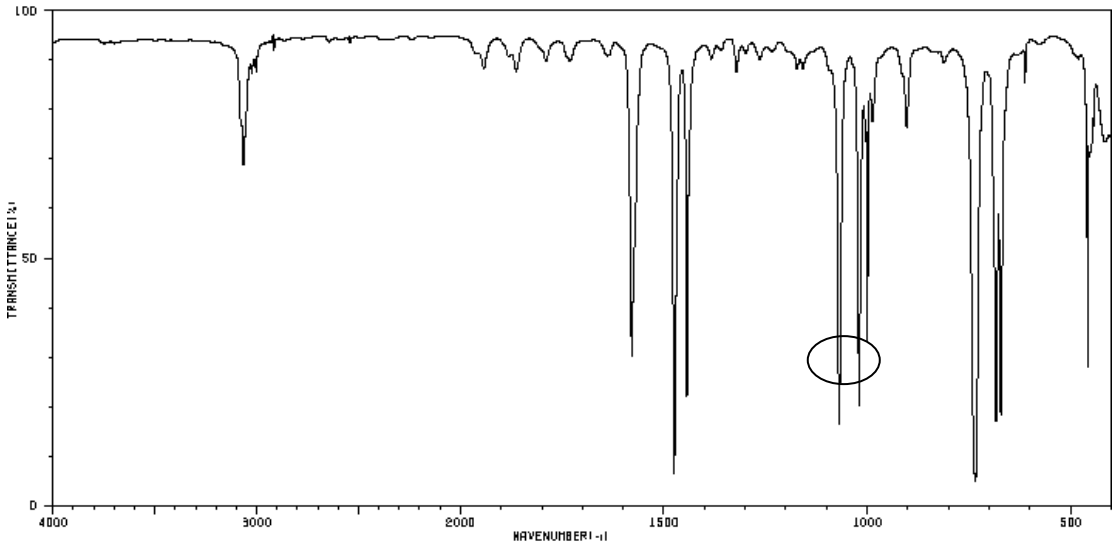
Rice. 2.4 2 . IR spectrum of 2-iodopropane.



Rice. 2.4 3 . IR spectrum of fluorobenzene.



Rice. 2.4 4 . IR spectrum of chlorobenzene.



Rice. 2.45. IR spectrum of bromobenzene.

Below is table 2.6, which provides information about the most important fluctuations in an easy-to-remember form.

Table 2.6
Infrared fluctuations of analytical value

Group	Frequency, cm^{-1}
HE	3650 − 3200 (p.)
N -H	3500 − 2900 (average)
S-N	3500 − 2700 (s. - av .)
S -H	~2550 (middle - middle)
C≡C _	~2200 (words)
Continuation of Table 2.6	
N ≡C	2200 (middle - next)
C=O	1850−1650 (s.)
C= C	~1650 (middle - middle)
C- N O_2	~1550 (s.) and ~1350 (s.); ~900 − 850 (average)
S-O -	1300 − 1000 (s. − av .)
C- F	1400 − 1000 (s.)
S-S l	800 − 600 (s.)
N-E r	650 − 500 (s.)
C- I	600 − 500 (s.)
S=O(IV)	1070 − 1030 (s.)
SO2 (VI)	~1150 (s.) and ~1330 (s.)

Questions and tasks for self-control

1. Which region of the spectrum is called the infrared region?
2. What changes in a molecule occur under the influence of infrared radiation ?
3. Which vibrations in a molecule are called stretching and which are called bending?
4. Which region of the spectrum is called the “fingerprint region”? For what analytical tasks is this spectrum region used?
5. What is the main analytical task of the IR spectroscopy method ?
6. Please remember the data in Table 2.3.

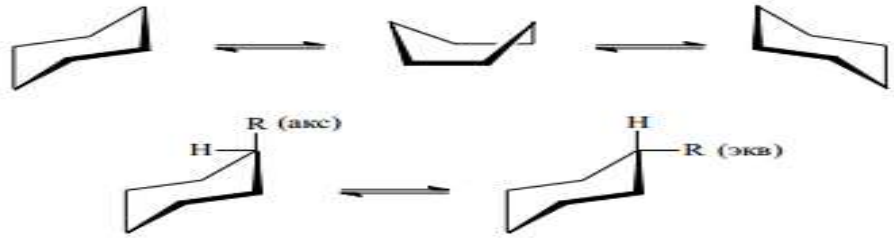
Lecture 8
Subject: Spectroscopy ^{13}C

Plan:
1. study of conformers in a solution of a cyclohexane molecule using the method of IR spectra of folk hydrocarbons.
2. Oxygen fluctuations.
3. Methodology for determining the presence of conformers in oxidized folk alcohol.
4. Spectra of carbonyl compounds, factors influencing the cost of frequency.

Study of the conformers of the cyclohexane molecule in solution using the method of IQ spectra of folk hydrocarbons. Infrared spectroscopy is especially widely used in the study of conformers in solution of the six-ethylene cyclohexane molecule. The cyclohexane molecule in solution is in a state of various conformers as a result of the conversion process that occurs in the people at home, and if the people have substituents, then as a result of their axial or equatorial state in relation to the people will increase further.

a) The infrared spectrum of cyclohexane and its derivatives is quite complex at home and at high temperatures, i.e. the spectrum consists of a set of conformer spectra.

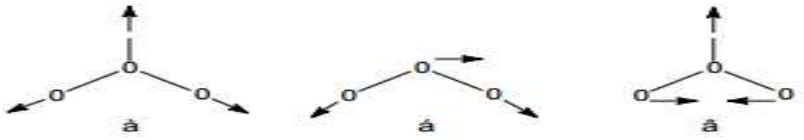
b) if spectra of compounds are obtained under frozen conditions (-90 C0, -100 C0), the spectrum is simplified with a significantly reduced number of frequencies in the spectrum. The main reason for this is that under these conditions the transition of cyclohexane and its derivatives from one conformer to another stops; as a result, the resulting spectrum will consist of the spectrum of one or two stable conformers.



Oxygen fluctuations. If in molecular spectroscopy, as a result of the normal vibration of the molecule, the length of the chemical tanks changes, and the angle between these parks changes little, then these types of vibrations are called stretching vibrations and are designated by the letter υ (nu).

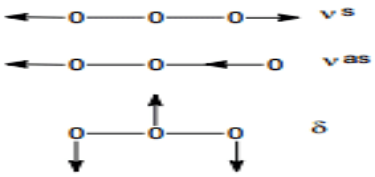
If, as a result of normal vibration, the angle between the valence parks changes, but the length of these parks does not change, such types of vibrations are deformation vibrations, denoted by the letter δ (delta). Stretching vibrations are divided into symmetrical (υ s) and asymmetrical (υ as); as a result of the first vibration, the length of the chemical parks lengthens, and in the second, a shortening is observed.

For example, if you see a water molecule, then the number of vibration frequencies is 3H-6 = 3. 3-6 = 9-6 = 3.



а - O-H гурухининг симметрик валент тебраниши (ν^s=3652 см$^{-1}$); б - O-H гурухининг асимметрик валент тебраниши (ν^{as}=3756см$^{-1}$); в - H-O-H молекуланинг деформацияли тебраниши (δ=1596 см$^{-1}$)

The above types can also be specified for the $SO_{2\ molecule}$.



Thus, the position of the infrared spectrum of polyatomic molecules can be interpreted as follows: determine the number of vibrations formed as a result of absorption, that is, the values of the spectrum frequencies and their meaning, as well as the stretching and deformation frequencies obtained during the performance of these works, with certain spectra of such substances. It is necessary compare.

The “fingerprint” area of the substance being tested in the infrared spectrum is 650-1300 cm-1. When some minor changes are made to a molecule, the number and values of frequencies change dramatically. 1500-1800 cm-1 is included in the absorption range of functional mechanisms and is the absorption range of diatomic units 3000-3600 cm-1 -OH, -NH, -NH2. In practice, mainly two types of spectrometers are used to obtain the infrared spectrum. One of them is made only in a NaCl prism, has a simple structure and takes up less space, but recently it has been clearly drawing its spectra - in a wide range from dual-beam spectrometers, pictures 1- and 2 show spectrometers with copies of UR-20 and Spekord .

12-расм. UR-20 (Германия, Карл-Цейсс Йена) спектрометрининг кўриниши.

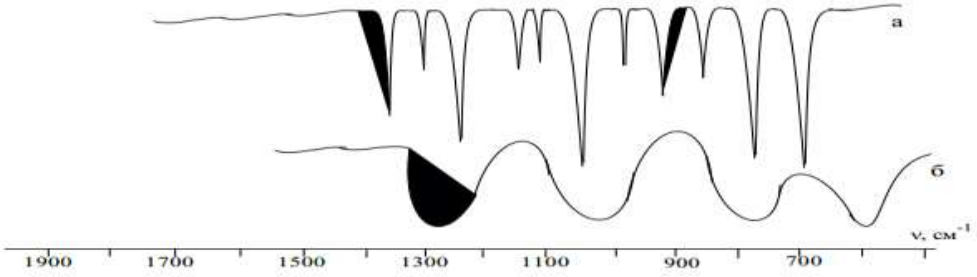
Method for determining the presence of conformers in oxidized folk alcohol. If there is a hydroxyl charge in the composition of oxidized population compounds, it can be located in the population in an axial or equatorial state. Experimental data also indicate different values of the deformation vibration of the axial and equatorial hydroxyl structure . Based on the studied data on the spectrum of alcohols in the solution state, it is also possible to determine the number of conformers. Since carbohydrates are part of polyhydric alcohols, when interpreting them it is necessary not only to evacuate the stretching and bending frequencies of vibrations of hydroxyl cells, but also to study frequencies between 700-1000 cm-1.

Glucopyranose

I-тури	2-тури	3-тури
Халқанинг тебра-ниши	Деформацияли тебраниш C_1-H (e-α аномер), (a-β аномер)	Пираноз ҳалқаси-нинг пулсацияли тебраниши.
α 917 ± 13 β 920 ± 5	844 ± 8 891 ± 7	766 ± 10 774 ± 9
крахмал 930 ± 4	844 ± 2	758 ± 2
декстрин 917 ± 5	844 ± 8	768 ± 7

Thus, in hydrocarbons, the nature (α or β) of glucoside gardens can be determined by the vibration frequencies of peoples and 1.3 vibrations.

The infrared spectrum of monosaccharides and polysaccharides is very different from each other, the spectra of monosaccharides, complex and all existing frequencies appear clearly, separately, but polysaccharide frequencies are simple in wide layers of spectra. The main reason is that in the polymer molecule There are a lot of structures that are similar to each other, so the frequency values are presented mainly in one area, as a result of which their shape appears in a broad manner.



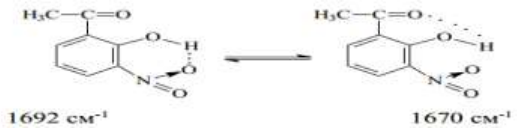
a-monosaccharide . b-polysaccharide

Spectra of carbonyl compounds, factors influencing the cost of frequency.

Sometimes the spectrum shows two similar “twin” frequencies instead of one absorption frequency in the absorption region of the carbonyl structure. This occurs in the following armors:

a) If the molecule contains two types of carbonyl charge,

b) When there is a balance of conformers in a solution, there are two types of stable hydrogen bonds inside the molecules,



d) If in the balance of conformers a solvent molecule participates in the rupture of the hydrogen tank inside the molecules.

Acid anhydrides, α- dicarboxylic acids and acid peroxides also form two frequencies similar to each other in polar solvents.

For the content of diamide gardens in the peptides and protein molecules, one can obtain information about the order of formation of hydrogen parks in peptides and the spatial structure of peptides (with 1600-1700 or α structure, β peptides and disordered structures).

Lecture 9

Topic : Fundamentals of mass spectroscopy.

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.

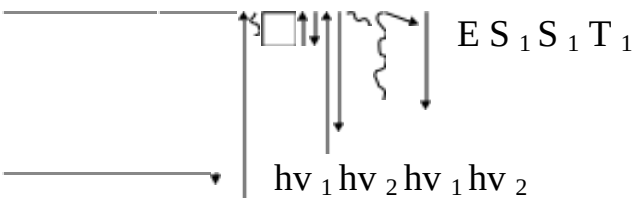
Based on the duration of the glow, two types of luminescence are distinguished: fluorescence and phosphorescence.

Fluorescence is luminescence with a duration of the order of 10^{-8} –10^{-10} s.

Phosphorescence is a glow that continues for a noticeable period of time after the cessation of excitation from 10^{-8} With up 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 S_0 to the excited state S_1. At room temperature, molecules are in the ground vibrational state. Upon transition to an excited state, the molecule enters one of the vibrational levels of the vibrational state.



a) b)

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 S_i to the unexcited state S_0 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.

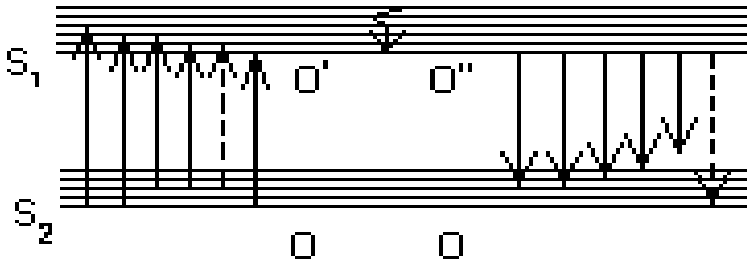
3 - The transition of a molecule from the excited state Si to the metastable state T1 , and then to the ground state S0 , either as a result of internal conversion with the release of heat (Fig. 6 - long wavy arrow), or with the release of a light quantum - phosphorescence. In the metastable state, the 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.

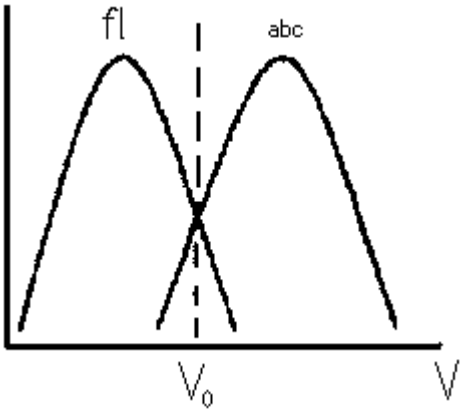
Luminescence output. The dependence of luminescence intensity on the wavelength or frequency of radiation is called the luminescence spectrum. The type of spectrum does not depend on the wavelength of the exciting electromagnetic radiation. The loss of part of the energy of absorbed light quanta to non-radiative 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 v_0, 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 .

$I_{lum} = k*C$, where k is the proportionality coefficient.

The higher the luminescence quantum yield, the smaller the amount of phosphor that can be detected by the luminescence method.

$In_{sq} = N_{lumen} / N_{light}$,

where V_{kv} is the quantum yield;

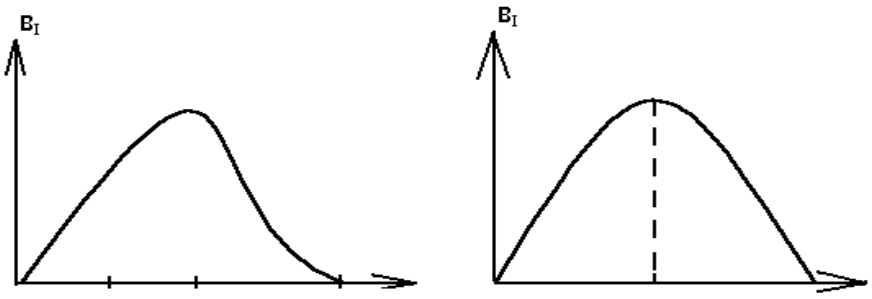
N_{lum} is the number of quanta emitted during luminescence;

N_{light} - 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} With ,%

Rice. 7. Dependence of luminescence output:

a - on the wavelength of the exciting light; b - on the phosphor concentration.

The luminescence yield for 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.

Questions for self-control

1. What is luminescence?
2. What types of luminescence do you know?
3. How is fluorescence different from phosphorescence?
4. What are phosphors?

5. What is the scheme of energy transitions of a molecule during fluorescence?
6. What factors does the luminescence output depend on?
7. What is concentration quenching?

Lecture 10

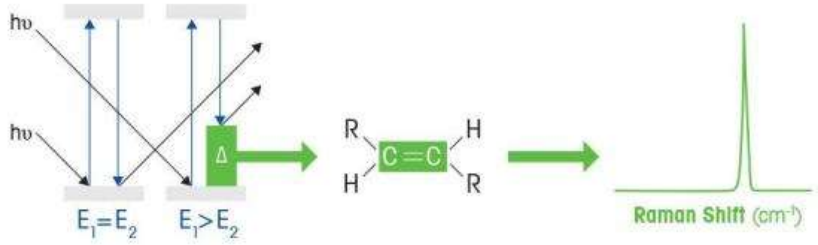
Subject : Patterns of decay of compounds with open and closed chains in mass spectrometry.

Raman spectroscopy (Raman spectroscopy) is a molecular spectroscopy technique based on the interaction of light with matter. It provides insight into the structure of a material or its characteristics, and in this respect is similar to Fourier Transform Infrared Spectroscopy (FTIR). Raman spectroscopy is based on the study of scattered light, whereas IR spectroscopy is based on the absorption of light. Raman spectroscopy provides information about intramolecular and intermolecular vibrations and helps to gain a more complete understanding of the reaction. Both Raman and FT-IR spectroscopy provide a spectral signature of molecular vibrations ("molecular fingerprint") and are used to identify substances. At the same time, Raman spectroscopy can provide additional information about low-frequency modes and vibrations that indicate features of the crystal lattice and molecular structure.

On-line Raman spectroscopy is used to monitor crystallization processes and identify reaction mechanisms and kinetics. Combined with analytical tools, this data enables deeper understanding and optimization of responses.

Principle of Raman spectroscopy

When light interacts with molecules in a gas, liquid or solid, the vast majority of photons are scattered, having the same energy as the incident photons. This process is called elastic or Rayleigh scattering. Some photons—about one in 10 million—after scattering acquire a frequency different from that of the incident photon. This process is called inelastic scattering or the Raman effect, named after Sir Chandrasekhar Venkat Raman, who discovered it and was awarded the Nobel Prize in Physics in 1930. Since then, the Raman effect has been widely used in various fields - from diagnostics in medicine to materials science and reaction analysis. The Raman effect allows you to find out the vibrational characteristics of a molecule, which gives an idea of how it is structured and how it interacts with other molecules.



Raman scattering process

From the point of view of quantum mechanics, the process of Raman (Raman) scattering is that when photons interact with a molecule, it can go into a virtual state with a higher energy. There are several possible scenarios for the molecule to exit this state. In one of them, a molecule can enter a state with a vibrational energy level that differs from the initial level, emitting a photon with a different energy. The difference between the energy of the incident photon and the energy of the scattered photon is called the Raman shift.

If the energy of the scattered light decreases, such scattering is called Stokes scattering. Some molecules are initially in an excited vibrational state, and then after transitioning to a virtual state with a higher energy, they can transition to a final state with an energy lower than that of the original excited state. This type of scattering is called anti-Stokes scattering.

Fundamentals of Raman Spectroscopy

How does Raman spectroscopy work?

Unlike _ FT-IR spectroscopy, which shows changes in dipole moments, Raman spectroscopy shows changes in the polarizability of molecular bonds. The interaction of light with a molecule can cause its electron cloud to deform. This deformation is called a change in polarizability. At certain energy transitions, accompanied by changes in the polarizability of molecular bonds, active Raman modes arise. For example, changes in polarizability upon interaction with photons occur in molecules that have homonuclear bonds: carbon - carbon, sulfur - sulfur or nitrogen - nitrogen. All these bonds give rise to active bands in the Raman spectrum, but in the IR spectra they will not appear or will appear weakly.

Since the Raman effect is weak, the optical components of the Raman spectrometer must be specially optimized and well adjusted. In addition, since organic molecules can be prone to fluorescence when exposed to short-wavelength radiation, long-wavelength monochromatic sources, such as solid-state diode lasers that emit light at 785 nm, are typically used.

Main Applications of Raman Spectroscopy

Raman spectroscopy is used in industry to solve a variety of problems, including:

- Study of crystallization processes
- Identification of polymorphic forms
- Study of polymerization reactions
- Study of hydrogenation reactions
- Chemical synthesis
- Biocatalysis and enzymatic catalysis
- Chemical processes in the flow
- Biological Process Monitoring
- Study of synthesis reactions

Raman and FT-IR spectroscopy

Comparison . Although FT-IR and Raman spectroscopy methods are in many cases interchangeable and complement each other well, there are differences that should be taken into account when choosing one or another method in practice. Most molecules with symmetry manifest themselves in both infrared and Raman spectra. A special case is represented by molecules with an inversion center. If the molecule has an inversion center, then the Raman and IR bands will be mutually exclusive, that is, the bond will be active in either the Raman or IR spectrum. There is a general rule: functional groups with strong dipole moment changes are clearly visible in the IR spectrum , while functional groups with weak changes or with a high degree of symmetry are better visible in Raman spectra.

Raman spectroscopy is recommended to be chosen in the following cases:

- if you want to study carbon bonds in aliphatic and aromatic rings;
- if it is necessary to identify bonds that are difficult to see in the IR spectra (for example, O–O, S–H, C=S, N=N, C=C, etc.);
- if particles in solution are being studied, for example when studying polymorphism;
- if low-frequency modes are studied (for example, in inorganic oxides);
- to study reactions in aqueous media;
- if it is easier and safer to monitor the progress of the reaction through a viewing window (for example, catalytic reactions at high pressure, polymerization);
- to study low-frequency vibrations of the crystal lattice;
- to determine the start and end points of the reaction, study the stability of the product in two-phase and colloidal reactions.

It is recommended to choose FTIR spectroscopy in the following cases:

- for studying liquid-phase reactions;
- if reactants, reagents, solvents and other components involved in the reaction fluoresce;
- if connections with a strong change in dipole moment are important (for example, C=O, O–H, N=O);
- if the reagents and reactants are of low concentration;
- if the solvent bands appear strongly in the Raman spectrum and can drown out the signal of the main components;
- if the reaction intermediates are active in the IR spectrum .

Benefits of On-Line Raman Spectroscopy

Raman spectroscopy has many advantages. Because Raman spectrometers use visible lasers, flexible silica fiber optic cables can be used to excite the sample and collect the scattered radiation. If necessary, these cables can be made quite long. Since visible light is used, samples can be placed in glass or quartz containers. Therefore, when studying chemical reactions, the Raman spectrometer probe can be inserted into the reaction medium or Raman spectra can be recorded through a window, such as an external sampling loop or flow cell. The latter method eliminates the possibility of sample contamination. Since quartz or high-quality sapphire can be used as the window material, Raman spectra of catalytic reactions can be observed in high-pressure cells. In catalyst research, on-line spectroscopy using the Raman effect is useful for studying reactions on catalytic surfaces in situ in real time. Another advantage of Raman spectroscopy is that hydroxyl bonds are not very active in the Raman spectrum, making the technique suitable for aqueous environments. Raman spectroscopy is considered non-destructive, although some samples may be affected by laser radiation. When choosing this method, it is necessary to consider how prone a particular sample may be to fluorescence. Raman scattering is a weak effect, and fluorescence can dampen the signal, making it difficult to obtain good data. This problem can often be solved by using an excitation source with a longer wavelength.

In terms of reaction analysis, Raman spectroscopy is sensitive to many functional groups, but is particularly effective in obtaining molecular structure information. The Raman spectrum characterizes molecules in a unique way. Because Raman spectrometry relies on bond polarizability and is capable of measuring low frequencies, it is sensitive to lattice vibrations that provide information about polymorphism. IR-Fourier spectroscopy in this regard is less informative. This makes it possible to use Raman spectroscopy with great efficiency in the study of crystallization and other complex processes.

Equipment for Raman spectroscopy. A modern compact Raman spectrometer consists of several main components, including a laser that serves as a source of molecular excitation to induce Raman scattering. Typically, modern Raman spectrometers use solid-state lasers with wavelengths of 532, 785, 830 and 1064 nm. Lasers with shorter wavelengths have a larger scattering area, so the resulting signal is more powerful, but

fluorescence is more likely to occur at these wavelengths. To avoid this, many Raman spectrometers are equipped with a laser with a wavelength of 785 nm. Fiber optic cables are used to transmit laser energy. Band-pass or edge-band filters are used to eliminate Rayleigh and anti-Stokes scattering, and the remaining Stokes-scattered light is transferred to a dispersive element, usually a holographic grating. The light hits the CCD detector and a Raman spectrum is generated. Because Raman scattering produces a weak signal, it is very important that the Raman spectrometer uses high-quality and well-aligned components.

Raman Spectra Analysis Software

If the spectrum is recorded continuously during the experiment, a kind of “molecular video” can be obtained, which will provide important information about the kinetics, reaction mechanisms and changes in the forms of the substance. Typically, such analysis is performed by experienced specialists who are able to isolate the most important areas of the spectrum and monitor changes in wave numbers. However, new software processing technologies (for example, the trend detection function in iC Raman 7 software) have made it possible to automate this procedure. Now researchers of all skill levels can easily extract the insights they need from data to make decisions quickly and confidently.

Lecture 11

Topic X-ray structural analysis (XRD)

Hydrolysis of functional derivatives of carboxylic acids Any functional derivatives of carboxylic acids under certain conditions are capable of hydrolysis. The cleavage reactions of functional derivatives of carboxylic acids can either be catalyzed by acids (acid hydrolysis), which produces carboxylic acids, or occur under the action of alkalis (alkaline hydrolysis or saponification). 55 a) acid hydrolysis Hydrolysis of esters: C O R OR' + H2O C O R OH + R' OH H+ + H+ C OH R OR' + + HOH C OH ROOHH R' + C OH R OH O R' H + C OH R OH + - R'OH - H+ δ1st stage - protonation of the oxygen of the carbonyl group and strengthening of the electrophilic center due to the formation of a carbocation; 2nd stage - nucleophilic attack of the katon center by a water molecule due to a lone electron pair with the formation of an oxonium ion; 3rd stage - reversible proton transfer from one oxygen atom to another with the formation of another oxonium ion; 4th stage - cleavage of an alcohol molecule to form a new carbocation; 5th stage - release of a proton (catalyst) with the formation of a carboxylic acid molecule. All stages of this process are reversible. The reverse reaction is an esterification reaction (formation of an ester from an acid and an

alcohol). Both forward and reverse reactions proceed through the same mechanism (SN). Hydrolysis of amides: ORC NHR' + H2O H+ ORC OH + R'NH3 + The reaction is irreversible, since the alkylammonium ion is nucleophilic 56 b) Alkaline hydrolysis Saponification of amides: C O R NH2 + NaOH C O R ONa + NH3 + OHC OR O NH2 H - NH3 C O R O C O RO - 1/2 - 1/2 δ+ 1st stage - attack on the carbonyl group by a strong nucleophile (hydroxide ion), leading to a tetrahedral intermediate. As a result of such an attack, the character of the oxygen atom completely changes - acquiring a whole negative charge, it turns from an electron acceptor (in the original compound) into an electron donor (+I-effect), and the carbon-nitrogen bond is more polarized. The former carbonyl carbon atom acquires sp3 hybridization, the phenomenon of conjugation of the amino group with the carbonyl disappears, the electron pair at the nitrogen atom is released, and its basic properties are enhanced. Stage 2 - elimination of an ammonia or amine molecule to form a carboxylic acid anion (carboxylate ion). Alkaline hydrolysis of carboxylic acid derivatives is practically irreversible, since it results in the formation of a stable carboxylate anion in which the negative charge is equally distributed between two oxygen atoms, and the carbonyl carbon loses its electrophilic properties (lack of positive charge). Acylation reactions (SN) Acylation is the introduction of a carboxylic acid residue (acyl CO R) into the substrate molecule . General scheme of acylation reactions: RCOX + HNuc RCO Nuc + HX acylation substrate product leaving reagent (nucleophile) of acylation group 57 Acylation of alcohols: δ+ δ− C O RX + H OR' C O R OR' + HX ester Acylation of thiols: Acylation amines: C O RX δ− δ+ C + HX O RN R' R" + HN R' R" acid amide Comparative activity of functional derivatives of carboxylic acids as acylating reagents Increased activity: RCO O- Na+ 30 kJ/mol). RCO SR' + R" NH2 RCO NHR" + R'SH RCO SR' + R" OH RCO OR" + R'SH CH3C O ~SCoA - Acetyl coenzyme A is the main acetylating reagent of a living organism. CH3C O ~SCoA + HO NH2 HO NHCCH3 + HSCoA O para-aminophenol paracetamol - acyl phosphates . The most active biological acylating reagents. Capable of acylating amines, alcohols , phenols and thiols. C O RPOX OH ~ O + R'SH RCO SR' + POX OH HO 8.3. Reactions of carbonyl compounds with the participation of a mobile α-hydrogen atom (CH-acid center) Under the action of bases (: B–), carbonyl compounds containing a hydrogen atom in the α-position are able to lose a proton, turning into a carbonanion (enolate ion), which is a strong nucleophile HCCOX α δ− + B- - BH CCOXCCOX − − resonance structures of the enolate ion This enolate ion is capable of reacting with various carbonyl compounds to form a new carbon–carbon bond. 59 Aldol addition reaction (AN type reaction) 2 R CH H R CH2 C OH HR CH COH aldol base R CH2 COHR CH COH - R CH COHR CH2 C OH + O H- ; - H2O + H2O; - OHcarbonyl component methylene component δ+ COH α The molecule that forms the carbonanion is called the methylene component of the reaction, the molecule that provides the carbonyl group is called the carbonyl component of the reaction. Examples of aldol addition reactions: 2 CH3 CH2 COH OHCH3 CH2 CH OH CH CH3 COH In this reaction, both the carbonyl and methylene components are the same compound. Cross-aldol addition reactions are possible between different carbonyl compounds, especially if one of them does not have an α- hydrogen atom: COHHCOHC CH3 CH3 H + C CH3 CH3 HOCH2 CH KOH O C O H C OH H CH2 C CH3 O δ+ α + CH2 C CH3 O

H KOH carbonyl methylene component component The aldol addition reaction is reversible. The reverse reaction is called aldol cleavage. These reactions play an important role in the biosynthesis and breakdown of important metabolites (for example, the biosynthesis of fructose from three-carbon fragments and its breakdown during glycolysis). 60 Ester condensation reaction (SN type reaction) Under body conditions, this reaction mainly involves thioesters: CHC + HSR' O R" SR' RCH2C O R" CH2C O SR' RCH + 2C O SR' α β β-ketoester thiol Scheme mechanism of ester condensation using the example of acetyl coenzyme A: acetyl-CoA acetoacetyl-CoA carbonyl methylene intermediate component component hemithioacetal Similar to the aldol addition reaction, ester condensation is reversible. The reverse reaction is called β- ketoester decomposition . Ester condensation occurs in a living organism, for example, during the biosynthesis of higher fatty acids, and the breakdown of β-ketoesters when using fats as a reserve source of energy. Carboxylation reactions (introduction of a carboxyl group) CO SR' RCH2 + RCHC O C SR' HO O O C O δ+ α δ+ thioester thioester of a dibasic acid Example: carboxylation of propionyl-CoA O CH3CH2C SCoA + CO2 O CH3CHNS SCoA COOH The reaction is reversible , the reverse reaction is called decarboxylation.

Lecture 10

Topic: X-ray method

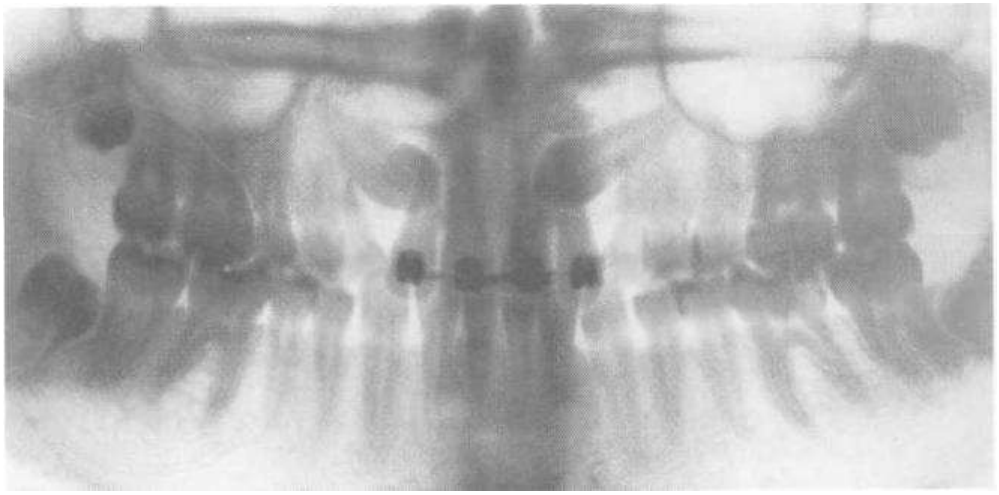
Plan

X-ray research methods

X-ray examination is necessary to clarify the diagnosis , determine the plan and prognosis of treatment, study the changes that occur during the growth of the child, as well as under the influence of therapeutic measures. Depending on the purpose, it is important to correctly select the most effective methods of x-ray examination. These methods are divided into intraoral and extraoral.

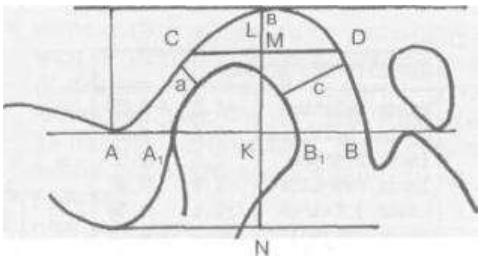
Intraoral Radiography is performed using dental devices of various designs. It allows you to study the condition of the hard tissues of teeth, their periodontium, alveolar processes and jaw bones in order to identify destructive changes, cysts, neoplasms, congenital and acquired defects, as well as clarify anomalies in the positions of the rudiments of teeth, the degree of formation of their crowns and roots, tooth retention, anomalies their shape, the relationship between the roots of primary teeth and the crowns of permanent teeth.

An intraoral radiograph of the median palatine suture is necessary to study its structure, the degree of ossification, changes that occur with slow or rapid opening of the suture during expansion of the upper jaw, and to clarify the indications for surgical plastic surgery of the frenulum of the upper lip if its fibers are woven into the median palatine suture and contribute to the occurrence of diastema.



Rice. 13.26. Orthopantomogram.

Extraoral X-ray methods . Extraoral radiography methods include panoramic radiography, orthopantomography, TMJ tomography and teleradiography.



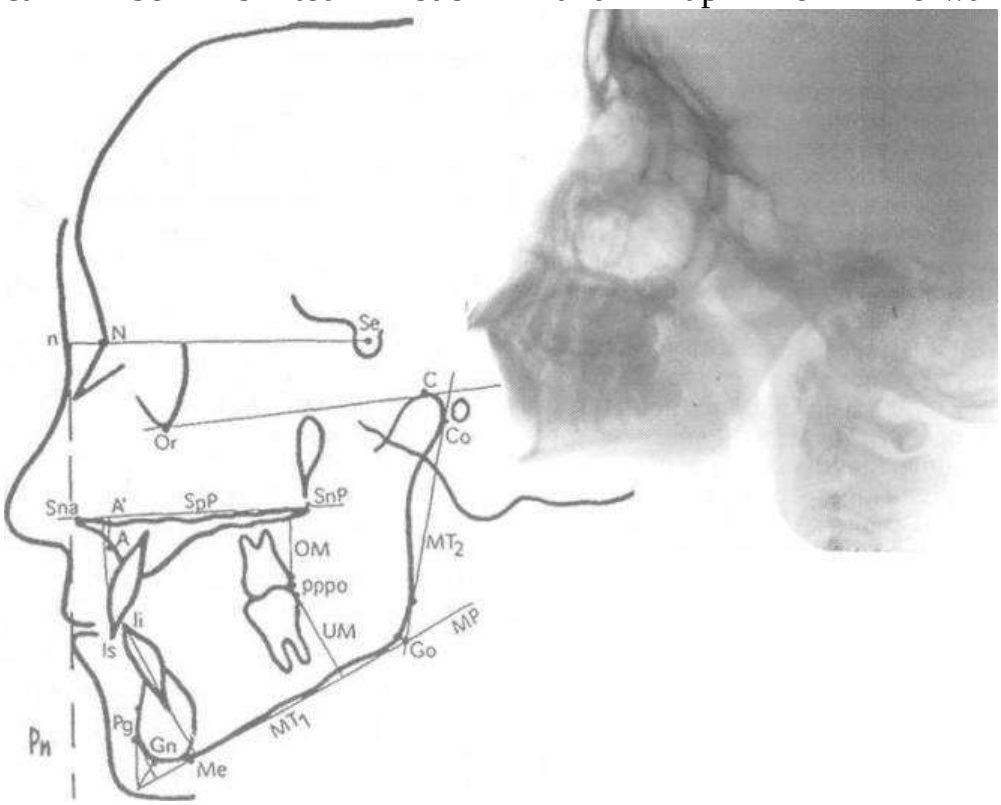
Panoramic radiography of the jaws. A panoramic radiograph of the upper jaw shows an image of its dental, alveolar and basal arches, vomer, nasal cavities, maxillary sinuses, zygomatic bones, and a radiograph of the lower jaw shows its dental, alveolar and basal arches, the edge of the lower jaw, its angles and branches . Compared to intraoral radiographs, panoramic radiographic images increase the object-film distance. Thanks to this, due to the large overview and magnification of the image by 1.8-2 times, you can obtain valuable diagnostic information.

Rice. 13.27. Interpretation of tomograms of the TMJ.

Orthopantomography, or panoramic tomography, provides a flat image of the curved surfaces of volumetric areas. Using orthopantomograms (Fig. 13.26), one can study the degree of mineralization of the roots and crowns of teeth, the degree of resorption of the roots of primary teeth and their relationship with the rudiments of permanent teeth, the inclinations of erupted and impacted teeth in relation to adjacent teeth and the median plane, dentoalveolar height in the anterior and lateral areas of the jaws, incisal overlap, asymmetry of the right and left halves of the face, the middle and lower parts of the facial skeleton.

Tomography of the TMJ. In radiology, there are at least 30 methods for studying the functions of the TMJ. In our country, tomography of the TMJ is widely used - layer-by-layer radiography, which improves the sharpness and clarity of the image of the anatomical formations of the selected layer. A tomogram (Fig. 13.27) makes it possible to obtain the most important indicators: the shape of the articular cavity, its width, depth and severity of the articular tubercle, the shape of the articular head and

the size of the joint space between the head and the cavity in its anterior, middle and posterior sections. In physiological occlusion, the articular heads are usually located in the middle of the articular cavity. With anomalies of occlusion, three main positions of the articular heads are observed: they can be in the middle of the articular fossa, they can be shifted back and up or forward and down.



Rice. 13.28. Teleroentgenogram of the head, performed in a lateral projection .

Teleradiography. This method of x-ray examination is used to study the structure of the facial skeleton, its growth, clarify the diagnosis and prognosis of orthodontic treatment, as well as to identify changes occurring during treatment. Telerent - genography is carried out in lateral and direct projections from a distance of 1.5 m. The subject's head is fixed using a cephalostat of various designs, the use of which ensures obtaining identical images (Fig. 13.28).

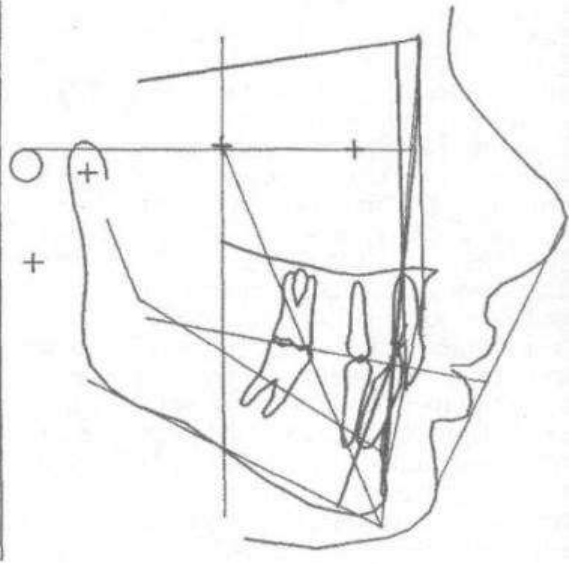
TRG in a direct projection makes it possible to diagnose anomalies of the dentoalveolar system in the transversal direction, in a lateral projection - in the sagittal and transversal directions. TRG shows the bones of the facial and cerebral skull and the contours of soft tissues, which makes it possible to study their relationships (Fig. 13.29).

To decipher the TRG, the image is placed on the screen of a negatoscope, tracing paper is attached to it, onto which the image is transferred.

TRG using the Schwartz method allows you to most fully study the size and position of the jaw bones. Using this method, it is possible to carry out craniometric, gnathometric and profilometric measurements. Using craniometry, the following is

determined: 1) the location of the jaws in the sagittal and vertical directions in relation to the plane of the anterior part of the base of the skull; 2) the location of the TMJ in relation to the plane of the anterior part of the base of the skull; 3) the length of the anterior part of the base of the cranial fossa.

RICKETTS 32 FACTOREN		
Molar Relation	-1.2	(-3.0)
Canine Relation	-0.5	(-2.0)
Incis Overjet	2.3	(2.5)
Incis Overbite	7.2	(2.5)
Lower 1 Extrus	-3.1	(1.3)
Inter-Incisal	156.2	(130.0)
A Pt Convexity	5.4	(0.8)
LFH Angle	37.8	(47.0)
Upper 6 to PTV	11.4	(18.0)
Lower 1 to A-PO	-2.4	(1.0)
Upper 1 to A-PO	1.3	(3.5)
Lower 1 to A-Po	9.2	(22.0)
Upper 1 to A-Po	14.6	(28.0)
OP to Xi Point	-3.8	(-3.0)
OP Inclination	21.6	(25.5)
Unterlippe/Aes.	-0.5	(-2.0)
Upper Lip Lngth	21.1	(24.0)
Lip Embras - OP	2.3	(-2.9)
Facial Depth	85.1	(89.0)
Facial Axis	82.4	(90.0)



Rice. 13.29. Copied teleroentgenogram of the head.

To analyze the TEG, the following points of the plane are used:

A - subspinal Downs point, the deepest on the anterior contour of the apical base of the upper jaw;

B - supramental Downs point, most distally located on the anterior contour of the apical base of the lower jaw;

Se - in the middle of the entrance to the Turkish saddle;

N - on the anterosuperior edge of the nasofrontal suture in the sagittal plane;

O r —the lowest located point of the lower edge of the orbit;

Go —the point of the angle of the lower jaw at the place where it intersects with the bisector of the angle formed by the tangents along the lower edge of the body and the posterior edge of the ramus of the lower jaw;

C - the highest point on the contour of the head of the lower jaw ;

Me —the most prominent point of the lower contour of the chin;

N is a point on the skin formed at the intersection with the continuation of the N-Se line;

Sna - anterior nasal spine;

Snp - posterior nasal spine;

Pg - the most anterior point under the protuberance;

NSe —plane of the anterior part of the skull base (it is drawn through points N and Se);

SpP —plane of the base of the upper jaw (passes through points Sna and Snp);

Pn - nasal vertical, which is drawn perpendicular to the NSe plane through the skin - point n ;

MR —plane of the base of the lower jaw.

The TRG separates the cranial part of the skull from the gnathic plane of the maxilla (SpP).

Options for the location of the jaws are determined by the facial, inclination angle and horizontal angle:

1) the front angle F is formed at the intersection of the N-Se and N-A lines (inner lower corner). Its size characterizes the location of the upper jaw in relation to the base of the skull in the sagittal direction. An angle less than the norm is characteristic of retrognathia, more than the norm - for prognathia; if he is in within the limits of our norms , they talk about normognathia;

2) the horizontal angle H is formed at the intersection of the line H (horizontal line) and P n (internal upper angle) and determines the position of the articular head of the lower jaw in relation to the base of the skull, which affects the shape of the facial profile;

3) the inclination angle J is formed at the intersection of lines P n and SpP (internal upper angle). If the angle J is greater than the average value, then the jaws are tilted forward, which Schwartz called anteinclination. If the angle is less than the average value, then the jaws are tilted back. This position of the jaws is called retroinclination.

The gnatometric method (according to Schwartz) allows:

• determine an anomaly that has developed as a result of a discrepancy in the size of the jaws (length of the body of the jaw, height of the branches of the lower jaw), anomaly in the position of the teeth and the shape of the alveolar process;

• identify the influence of the size and position of the jaw, as well as dental anomalies on the shape of the facial profile;

• determine the individual shape of the body length of the jaws and deviations in size.

The most important parameters of gnatometry:

1) basal angle B - the angle of inclination of the base of the jaws to each other (SpP - MR), characterizing the vertical position of the jaws;

2) the length of the body of the lower jaw MT is measured along the MR plane from the projection of point Pg on the MR to the point of its intersection with the tangent to the branch of the lower jaw;

3) the height of the MT branches is measured tangent to the posterior edge of the branch from the point of intersection with the MR plane to the projection of point C on the tangent;

4) the mandibular angle G is measured between lines MT_1 and MT_2, i.e. between the tangents to the lower edge of the lower jaw and the posterior surface of its branches;

5) the length of the upper jaw is measured from the intersection point of the perpendicular dropped from point A to SpP (point A') to point Sn.

Average individual norms according to Schwartz:

1) the length of the body of the lower jaw, with its normal development, is equal to the length of the base of the anterior cranial fossa (distance N - Se) plus 3 mm;

2) the length of the upper jaw in relation to the length of the anterior part of the skull base is 7:10;

3) the length of the body of the lower jaw is related to the length of its branches as 7:5.

Lecture 12

Topic: Solving chemical problems using spectroscopic and chromatographic analysis methods.

Bombardment of a substance by photons or other energy-carrying particles can cause several phenomena: first, electrons are knocked out from target atoms with the formation of vacancies, followed by relaxation, i.e. a return to the normal configuration, which can follow one of two paths - the emission of characteristic X-rays and the emission of secondary Auger electrons. Another analysis method is based on bombarding the target substance with positive H e + or $Ar^{+ ions}$. In this case, the energy of the ions reflected by the target (elastic collision) can be used to judge the nature of the atoms of the analyzed substance.

X-ray photoelectron spectroscopy. The relationship between the energies of the knocked-out X-ray quantum and the knocked-out photoelectron is given by an equation of the form:

$E_{St} = hv-(E_K + C)$,

where Eb_{is} the binding energy, i.e. energy of attraction of an electron to an atomic nucleus. This energy must be expended to knock an electron out of an atom. It is

related to the energy of the X-ray photon hv and the kinetic energy of the knocked-out electron E_k - it is measured.

C is a correction term that takes into account the design features of a particular spectrometer.

Binding energy is a specific characteristic of an electron of a given level in an atom of a given kind, so it can be used to identify elements.

Rice. 11. Schematic of a photoelectron spectrometer

When sample 1 is irradiated with high-energy radiation from source 2, electrons are knocked out from the atomic and molecular orbitals of the outer electron layer. The detached electrons pass through the input electron slit 3 into an electron spectrometer, which, using a magnetic or electrostatic field 4, sorts the electron beam by speed, forming an energy spectrum. The spectrum is focused on the output slit 5, recorded by a radiation detector 6 (photomultipliers or Geiger counters) and recorded by a recorder 7.

X-ray photoelectron spectroscopy (XPS), like other types of electron spectroscopy, is essentially a surface analysis method since electrons are unlikely to be knocked out from atoms more than 5 nm from the sample surface. This allows the XPS method to be used in a number of areas related to the study of surface properties. XPS can be used for the qualitative and quantitative determination of most elements of the periodic table, establishing the structure of chemical compounds, determining the energy and type of chemical bonds, and other purposes. For an XPS spectrum, it is enough to have a sample weighing 10 g. The method allows you to determine up to 10g and is one of the most promising optical methods of analysis.

Ultraviolet photoelectron spectroscopy (UV-PS). The main difference between spectroscopy of electrons knocked out by far -UV radiation and XPS is that the former can detect only valence electrons. This makes it possible to obtain direct information about chemical bonds, oxidation states and ionization potentials of molecules. However, due to the delocalization of electrons in molecular orbitals, assignment of spectral peaks may not be possible. UV-PS can be a specific method for identifying simple molecules.

Electron impact spectroscopy (EIS). Low-energy electrons usually lead to the transition of the target's valence electrons from ground to excited states, whereas in UV-PVS ions are immediately formed. Electron impact spectroscopy is based on this phenomenon.

The SEM method is based on measuring the decrease in the kinetic energy of bombarding electrons after scattering by target molecules, i.e. determining the energy required to excite valence electrons. Current equipment can only study gaseous samples and detect only forward scattered electrons. The data obtained provide

information about the energy difference between the ground and excited states, especially for vibrational and rotational energy levels. Therefore, SEM complements IR and Raman spectroscopy.

Auger electron spectroscopy (AES). If, under the influence of X-rays or energy-carrying electrons, an atom loses an electron from its inner shells, an electron from a higher energy level can take its place to fill the vacancies. The energy released during the transition is sufficient to remove another electron from the same shell of the atom. This is the Auger effect. OES is used mainly in the study of light elements, since X-ray fluorescence decreases in this region.

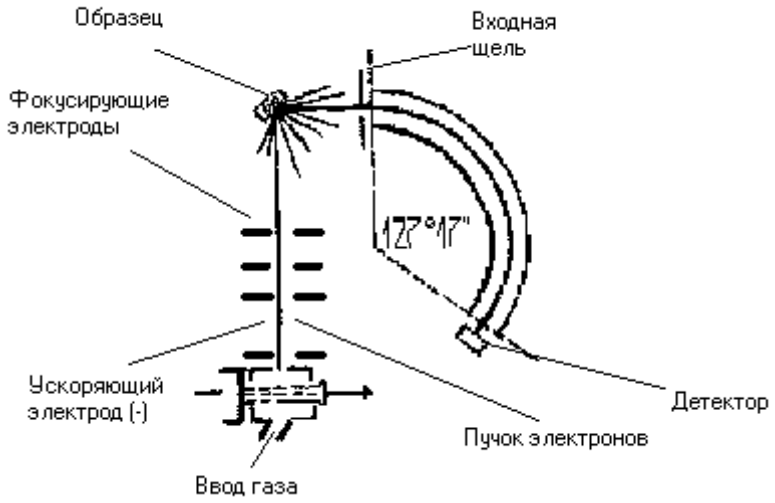
Rice. 12. Diagram of the probability of emission of Auger electrons and X-ray fluorescence depending on the atomic number

Auger electron spectroscopy is also used to study gases.

Ion scattering spectroscopy (ISR). When a solid sample is bombarded with a beam of positive ions, elastic collisions occur with target atoms, as a result of which the ions are scattered in random directions, and the recoil energy is absorbed by the mass of the sample. The energy E of a scattered ion is related to the energy E it had before the collision and is described by the equation:

$$\frac{M_n - M_0}{M_n + M_0} E = E_0,$$

where $M_n - M_0$ are the masses of the surface atom and the scattered ion, respectively. This equation is valid only for $M_n < M_0$. Energy E is most sensitive to small changes in Mn , provided that $M0_{is}$ only slightly less than $_{Mn}$. Most often, preference is given to noble gas ions, Ar and He , which do not enter into side reactions.



Rice. 13. Schematic of the ion scattering spectrometer

When gas atoms are bombarded with electrons, positive ions are formed, which are accelerated and focused on the sample at an angle of 45˚. The ions are scattered in all directions, but the electrostatic analyzer with a 127˚ circular sector selects those flying within a given small angle.

Questions for self-control

1. What does the schematic diagram of an X-ray photoelectron spectrometer look like?
2. What are the applications of X-ray photoelectron spectroscopy?
3. What is the difference between ultraviolet electron spectroscopy and photoelectron spectroscopy?
4. What is the electron impact spectroscopy method based on?
5. What is the Auger effect?
6. What is the circuit diagram of an ion scattering spectrometer?

Test on the topic

What happens first when a target substance is bombarded with photons or other energy-carrying particles:

1. relaxation, i.e. return to the normal configuration of atoms of matter?
2. knocking out electrons from atoms of a target substance to form vacancies?
3. some other process?

The basis of mass spectrometry is the separation of ions by m/z values (mass-to-charge ratio) and measurement of the number (intensities) of each type of ion. The method allows you to determine the molecular weight and molecular formula of almost any substance, consuming an insignificant (micro- or nanogram) amount of

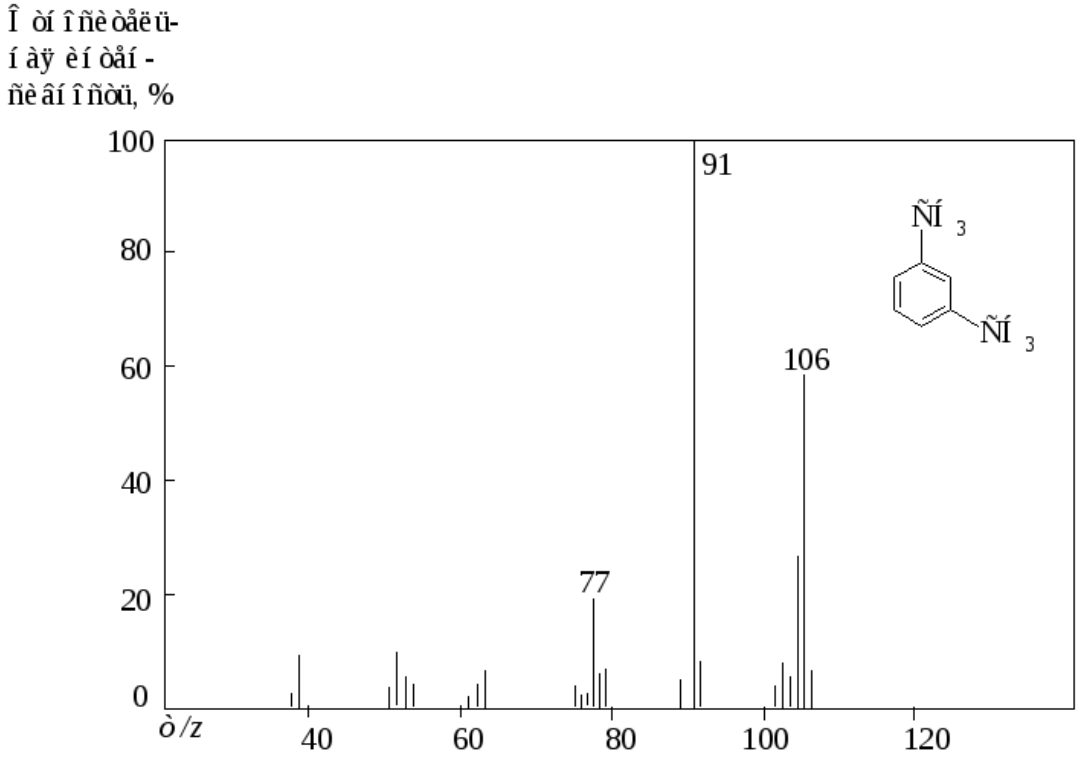
sample (destructive testing method). In addition, fragment ions carry useful information about the structure of the substance being studied.

When a molecule is ionized, a molecular ion $M^{+\bullet}$ is formed, the internal energy of which can be sufficient for decay with the release of a neutral particle m^0 and the formation of a fragment ion (fragment) A^+:

$$M \rightarrow M^{+\bullet} \rightarrow A^+ + m^0.$$

If the A^+ fragment ion has sufficient internal energy, then its further decay can occur with the formation of new fragments.

The mass spectrum is usually presented either in normalized form (as a percentage of the maximum, main peak) or as a percentage of the total ion current in tabular and graphical form (Figure 8.1).



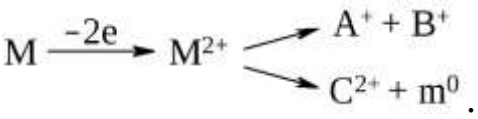
Rice. 8.1. Mass spectrum of m- xylene in normalized form (peak intensity with t/z 91 is 100%)

To obtain a spectrum as a percentage of the total ion current, the sum of the peak intensities of all ions is taken as a measure of the total ion current, and the relative contribution of each ion is calculated as a percentage.

It should be noted that the peak of a molecular ion is not always the main one in the spectrum if the fragment ions are more stable than the original molecule. Sometimes the decay of fragment ions can occur much faster than their formation. Such ions will

have low intensity, but are important in establishing fragmentation pathways (the order in which a molecular ion breaks down into fragments).

Typically, singly charged positive ions are observed in mass spectrometry, but sometimes ions with two or three charges are formed. Most often, such ions are found in the mass spectra of aromatic compounds:



The mass of a doubly charged ion in the spectrum is m/2.

In addition to the usual narrow peaks of ions, broadened low intensity peaks corresponding to metastable ions are often observed in the mass spectrum . Their maxima in the spectrum correspond, as a rule, to non-integer m/z values. Such ions are widely used to establish fragmentation pathways. If an ion with mass m_1 decays to form an ion with mass m_2, then a metastable ion $m^* = m_2^2 / m_1$ will be observed in the spectrum .

On the atomic scale, the mass of ^{12}C is taken to be 12.0000, but other elements have non-integer masses, for example, the mass of ^{1}H is 1.0078. Therefore, the masses of most ions have non-integer values, although they are close to them.

The resolving power of a mass spectrometer is a measure of its ability to separate two ions with any particular mass difference. At low resolution, the mass spectrum consists of a number of peaks with integer m/z values. At relatively high resolution, peaks can be split due to the presence of ions of different elemental compositions. The ion with m/z 28 can correspond to CO, N_2 or C_2H_4. If all of these types of ions are present, a low-resolution spectrum will show only one peak at m/z 28, while medium-to-high-resolution instruments will show three peaks at m/z 27.9949, 28.0061, and 28.0313, respectively. .

Many elements have some natural abundance of multiple isotopes, and because the mass to charge ratio is measured on a mass spectrometer, these isotopes show up in the mass spectrum. The most common isotope of carbon is ^{12}C, but natural carbon also contains isotopes ^{13}C and ^{14}C. The natural content of ^{14}C is so low that this isotope is practically invisible in the mass spectrum; the natural content of the ^{13}C isotope is 1.08%. Therefore, for example, in the mass spectrum, along with the peak of the molecular ion with m/z 16, corresponding to $^{12}CH_4$, there is an isotopic peak of the ion with m/z 17, corresponding to $^{13}CH_4$, the ratio of the peak intensities of these ions is 99:1. As the number of carbon atoms in a molecule increases, the probability of including at least one ^{13}C atom increases . A compound with twenty carbon atoms will produce a molecular ion M^+ and an isotopic peak of an ion with a mass greater by one unit $[M + 1]^+$, and the intensity of the latter relative to M^+ should be about $20 \cdot 1.08 = 21.6\%$. With a further increase in the number of carbon atoms, the probability of

including two ^{13}C atoms in one molecule increases, and then the $[M+2]^+$ ions become more noticeable.

For some elements commonly encountered in mass spectrometry of organic substances, Table. Table 8.1 gives the approximate natural abundance of the most common isotopes.

Table 8.1

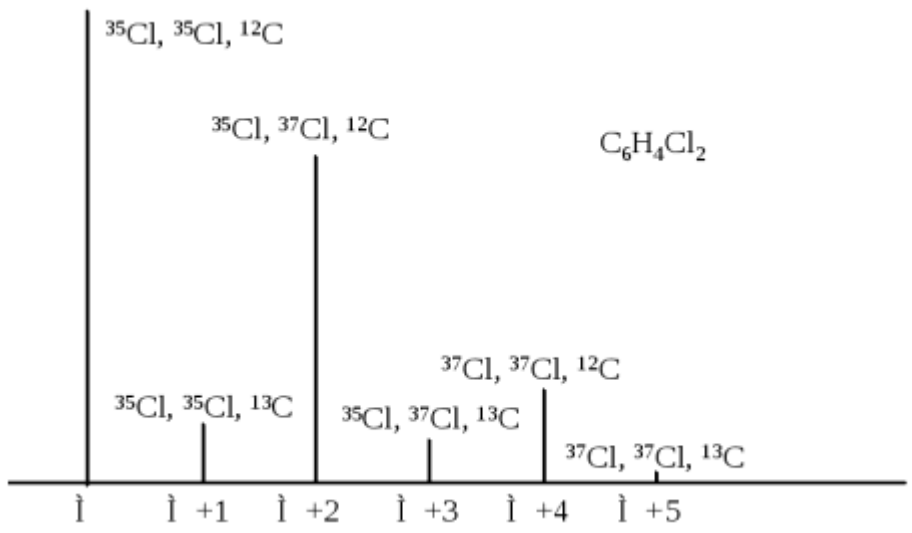
Natural abundance of the most common isotopes

elements commonly found in organic mass spectrometry

Element	Isotope (% natural content)
Hydrogen	^{1}N (99.99)
Carbon	^{12}C (98.9) ^{13}C (1.1)
Nitrogen	^{14}N (99.6) ^{15}N (0.4)
Oxygen	^{16}O (99.8) ^{18}O (0.2)
Fluorine	^{19}F (100.0)
Silicon	^{28}Si (92.2) ^{29}Si (4.7) ^{30}Si (3.1)
Phosphorus	^{31P} (100.0)
Sulfur	^{32}S (95.0) ^{33}S (0.7) ^{34}S (4.2)
Chlorine	^{35}Cl (75.5) ^{37}Cl (24.5)
Bromine	^{79}Br (50.5) ^{81}Br (49.5)
Iodine	^{127}I (100.0)

It should be noted that sulfur, chlorine and bromine have the most common isotopes, differing by two mass units. For this reason, chloro- and bromine-containing compounds are especially easy to recognize by mass spectrum. In this case, from the analysis of isotopic peaks in the region of the molecular ion, the number of chlorine and bromine atoms in the molecule can be determined.

In Fig. Figure 8.2 shows the molecular ion region in the mass spectrum of dichlorobenzene. The main peaks, spaced two mass units apart, correspond to the ^{35}Cl and ^{37}Cl isotopes, and the smaller peaks are due to the contribution of the ^{13}C isotope. The peak with the lowest isotope mass is usually taken as the molecular ion. Here, all six peaks correspond to a molecular ion.



Rice. 8.2. Isotopic contributions of carbon and chlorine in the region of the molecular ion of dichlorobenzene

A simple calculation of the probabilities of ion formation shows that the peak intensity of the M, M+2 and M+4 ions should be in the ratio 9:6:1. The number and relative intensity of isotopic peaks can be obtained by expanding the binomial $(a + b)^n$, where n –is the number of atoms under consideration, a and b are the relative natural abundance of isotopes.

If an ion contains two or more different isotope-containing elements, the relative intensity is calculated as follows: for an ion containing two chlorine atoms and two bromine atoms, the relative abundance will be:

for $Cl_2 (a + b)^n = (3 + 1)^2 = 9 : 6 : 1$

for $Br_2 (a + b)^n = (1 + 1)^2 = 1 : 2 : 1$.

These relative abundance values are combined as follows:

9. 6 1) ×(1 2 1) →(9 6 1) ×1 = 9 6 1

(9 6 1) ×2 = 18 12 2

(9 6 1) ×1 = 9 6 1

Amount 9 24 22 8 1.

Thus, the isotopic pattern for an ion containing $Cl_2 Br_2$ includes five ions M, M+2, M+4, M+6, M+8 with a peak intensity ratio of 9:24:22:8:1.)

To interpret (decipher) the mass spectrum , first of all, you should pay attention to the conditions of its registration, which affect the nature of the mass spectrum. Decoding

the mass spectrum can be greatly facilitated by data on physical constants, the method of preparation, the chemical properties of the substance, as well as other spectra of the substance being studied.

If the peak of a molecular ion has low intensity or its assignment (recognition) is difficult, then the correct assignment can be confirmed using soft ionization methods (chemical ionization, etc.), which make it possible to detect more intense quasi-molecular ions, most often $[M + H]^+$.

The molecular formula of the substance under study should be determined. This can be done using high-resolution mass spectrometry by accurately determining the mass of the molecular ion, studying the relative intensities in the molecular ion peak cluster and comparing them with reference data, and using the results of other analytical methods. A molecular ion with an even m/z value contains no or an even number of nitrogen atoms. In contrast, a molecular ion with an odd m/z value contains an odd number of nitrogen atoms. A molecule with an even number of nitrogen and phosphorus or halogen atoms contains an even number of hydrogen atoms. If the number of atoms of these elements is odd, the number of hydrogen atoms will also be odd.

The intensity of the molecular ion peak and the overall pattern of fragment ions in the mass spectrum sometimes help to assign the compound under study to a particular class. A spectrum containing many fragment ion peaks that increase in intensity as m/z values decrease generally indicates an aliphatic nature of the compound, whereas a spectrum with few peaks containing a strong molecular ion peak and doubly charged ion peaks is usually consistent with an aromatic structure .

At the next stage of deciphering the mass spectrum, one should identify the main fragment ions and try to establish the main directions of ion decay. The proposed fragmentation pathway is best tested by searching for the corresponding metastable ions.

The possibility of the presence of impurities must always be kept in mind. The most common contaminants are phthalate plasticizers (m/z 149, 167, 279) and silicone grease (m/z 133, 207, 281, 355, 429). Since the observed mass spectrum depends on the partial pressure of the components of the mixture in the ion source, even a minor (available in very small quantities) but more volatile component can dominate in it. When deciphering the composition of fragment ions, it should be taken into account that some fragment ions can arise from rearranged precursor ions.

There are many different types of mass spectrometers known. The schematic block diagram of the device is shown in Fig. 8.3. A vacuum is maintained in the instrument system from sample injection to ion registration inclusive.

Rice. 8.2. Schematic diagram of a mass spectrometer

Sample introduction is possible by direct injection into the ion source at the end of a metal rod (probe), or from the column of a gas or liquid chromatograph. In the case of combining a mass spectrometer with a chromatograph, it is necessary to remove the carrier gas from the ionization chamber using a vacuum pump (if the input is made from a gas chromatograph column) or the eluent, which is pre-sprayed when heated, to evaporate the solvent (if the input is made from a liquid chromatograph column) .

The most common ionization method is electron impact ionization , which involves exposing the substance under study (usually at a pressure of about 10^{-6} mm Hg) to a beam of electrons. The source of electrons is a heated cathode filament (most often tungsten). The electrons are accelerated in the electric field created in the ion source between the cathode and anode, the potential difference between which is usually about 70 eV. At this energy, numerous fragment ions are usually formed, which are useful from the point of view of elucidating the structure of the compound being studied. Electron impact in a vacuum produces both positively and negatively charged ions. Although both can in principle be studied, in most cases electron impact ionization mass spectra are recorded in the mode of positive ions, which are produced in larger quantities.

A modern ion source with electron impact ionization usually allows operation in the chemical ionization mode , in which the mass spectra contain fewer fragment ions than with electron impact ionization. Chemical ionization can detect molecular ions that are sometimes missing from electron impact ionization mass spectra. In chemical ionization, the substance under study (the partial pressure of which in the ion source is about 10^{-4} mm Hg) is mixed in the ion source with a reagent gas that is in large excess (the partial pressure is about 1 mm Hg). The most commonly used reagent gases are methane, isobutane or ammonia. A mixture of the test substance and reagent gas is subjected to electron shock. In this case , the molecules of the reagent gas that are in excess are first ionized , for example, $CH_4^{+\bullet}$ and CH_3^+ ions are formed from methane . Since the pressure of the reagent gas is quite high, ion-molecular reactions are usually carried out in the ion source, leading to the formation of secondary ions with a slight excess of internal energy:

$$CH_{4+}^{-\bullet} + CH_4 \rightarrow CH_5^+ + CH_3^\bullet$$

$$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2 .$$

Eventually, the secondary ions collide with the molecules of the substance being studied and ionize them. Ionization is usually accomplished by protonation:

$$M + CH_5^+ \rightarrow [M + H]^+ + CH_4 .$$

The resulting so-called quasi-molecular ions $[M + H]^+$ have an even number of electrons and, therefore, should be more stable than molecular radical ions generated by electron impact . The combination of greater stability with low excess internal energy leads to the fact that quasi-molecular ions have very high intensity in chemical ionization mass spectra.

Ions are separated according to their mass-to-charge ratio (m/z) in magnetic and/or electric fields. The combination of an electrical and magnetic analyzer produces a dual-focusing mass spectrometer , since the beam of ions from the ion chamber is first separated by kinetic energy by an electric field, and then the ions are struck by a magnetic field whose strength is varied so that each ion with a specific value m/z was focused on the ion collector one at a time.

In mass spectrometers with a quadrupole analyzer, ion separation is carried out using an electronic filter, which consists of four rod-shaped electrodes. With a suitable RF field, only an ion with a certain mass is allowed to pass between the electrodes and all other ions are prevented from passing through. Due to this filtering action, the quadrupole is often called a mass filter. By changing the frequency of the radio frequency field, the entire spectrum can be scanned extremely quickly.

Registration of the mass spectrum can be carried out using a diode matrix, the electrical signal from which is sent to a computer that records the spectrum.

Mass spectroscopy is used primarily in petroleum chemistry. Based on the mass of a molecular ion, the molecular mass of a hydrocarbon or heteroatomic compound isolated from oil can be determined with great accuracy. Based on the mass of a molecular ion, having a device with high resolution, it is possible to determine the elemental composition of a substance. Using low-resolution mass spectroscopy, it is possible to determine the qualitative composition of hydrocarbon mixtures based on the masses of the molecular ions of the components.

Quantitative analysis of complex mixtures is carried out mainly by gas chromatography-mass spectrometry. In this case, a block of a mass spectrometer with a gas or liquid chromatograph is used, which separates individual substances. Next, the substances one by one enter the mass spectrometer, which in this case can be considered as a chromatographic detector. The resulting mass spectrum can be processed on a computer, identifying the substance and determining its quantitative characteristics. The gas chromatography-mass spectrometry method has virtually no restrictions on the capabilities of analyzing the molecular composition of any mixture.

Practical lessons

Practical lesson No. 1

Absorption tables of the main chromophore groups. Solving problems related to the analysis of the UV spectrum of organic substances of a certain structure using tables.

The ultraviolet (UV) range extends from visible light to short-wave X-rays (50 nm). As a result of the absorption of UV and visible rays by organic substances, electrons (electrons involved in the formation of valence bonds) move from bonding orbits to free orbits. This state of the molecule is called an excited state. Because electrons are attracted to the nucleus, more energy is required to excite them. The wavelength of electromagnetic rays that form UV rays is 120-180 nm. Organic compounds have the ability to absorb rays in the UV range. The UV field is divided into two parts - the field with a wavelength less than 190 nm (called the far or vacuum UV field) and the near UV field - the field above 200 nm. Studying the absorption of substances in the far UV region requires sophisticated equipment. First, the oxygen and nitrogen in the air absorb UV rays in that area. Therefore, tools working in this area must have a vacuum device. Due to the complexity of this type of equipment, it is rarely used in laboratory teaching. The near-ultraviolet field is one of the most convenient measurement methods. In this area, since quartz has the property of transparency, prisms and measuring cups are made from it . The amount of substance required for testing is 0.1 mg. Due to these advantages, UV spectroscopy is the most common type of physical research method used in studying the structure of chemical substances.

Electrons in atoms and molecules occupy orbitals with very specific energies. The energies of atomic orbitals are represented by the sum of quanta. Molecular orbitals can be thought of as a linear set of atomic orbitals. This set consists of a bonding orbital normal state with antiparallel electron spins and an excited state from a relaxed orbital with parallel electron spins. Organic molecules σ and π heteroatoms containing bonding electrons and unpaired electrons are formed by p electrons. The electronic transitions that occur in the excited state of molecules are as follows:

high-energy quantum $\sigma \rightarrow \sigma^*$ transition, which means that the wavelength of the light quantum must be small to bring normal bonds into an excited state.

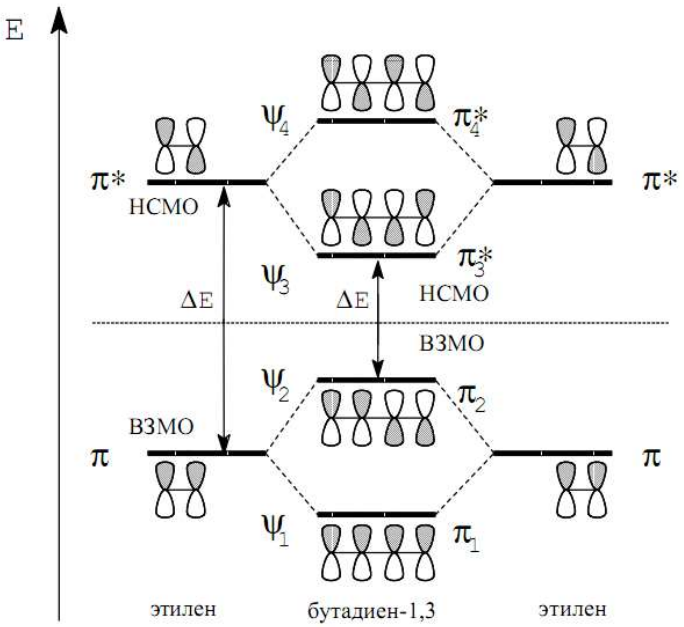
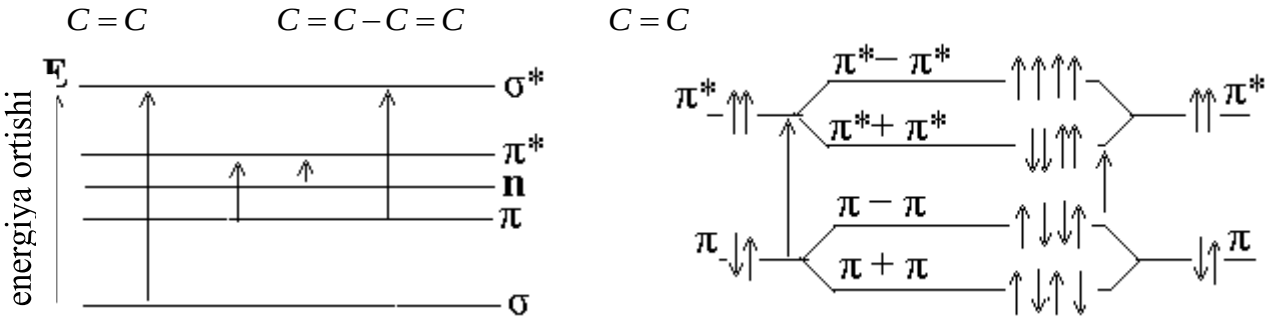


Figure 1. When electrons of organic molecules are excited, a transition occurs into energetic pg'ons according to the scheme (s- and p-electrons are in coinciding molecular orbitals, n-electrons are in unshared heteroatoms).



Painting. 2 Energy diagram of molecular orbitals forming two adjacent double bonds

Scheme of the energy transition during the excitation of electrons of organic molecules (molecular orbitals of s- and p-electrons of the corresponding molecules, lone pairs of electrons of heteroatoms).

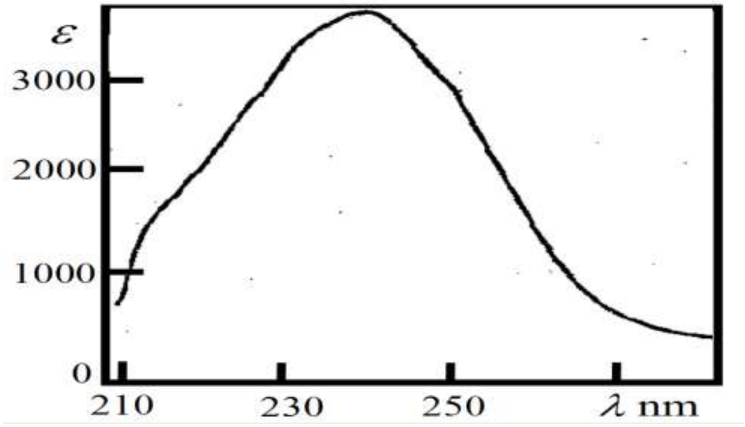
Molecular orbital formed by two adjacent double bonds $n \to \sigma^*, \pi \to \pi^*$ the necessary energy is required in small quantities to make the transitions. The energy of electrons in the n-state π is higher than in the -state, and the least amount of energy must be spent on their excitation. Transitions in this case are of great importance in practical work, since they occur in the near-VP field.

Chromophores are groups in a molecule that selectively absorb electromagnetic rays in the UV range. Examples of chromophores are substances containing a double bond or a heteroatom. Chromophore groups can be located in different positions in the structure of an organic substance, but the transition of the chromophore to the UV region absorbs electromagnetic rays at wavelengths almost close to each other, even in simple molecules or in molecules with a complex composition. Depending on the various chemical reactions of the chromophore groups,

the absorption maxima formed in the UV region may change. The shift of the absorption maximum wavelength to the far range is called a bathochromic shift, and the shift to the near range is called the hypsochromic shift.

The energy of n-level electrons π is greater than the energy of the -level. Therefore, a longer wavelength of quantum light is required for excitation. n $\rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions are of great practical importance, and only the operating range of the device corresponds to them. $\pi \rightarrow \pi^*$ transitions via isolated double bonds C=C and C=N are excluded. In addition, the trivalent compounds C $\equiv$C and $\equiv$CN (λ_{max} 160-180 nm). The measurement range used for isolated short bonds shows only the C=O transition (270 nm) of carbonyl groups. $\lambda \approx$ Groups in the UV range that selectively absorb electromagnetic waves are called chromophores. The main chromophores have absorption maxima in the range of 200-800 nm, and such systems are called coupled double bond systems. Orbitals with two adjacent double bonds are shown in Fig. 2-2. It is clear from the figure that π the interaction of 2-orbitals corresponds to an isolated double bond and forms 2 new orbitals: ($\pi+\pi$) bonding and ($\pi-\pi$) relaxing 2 orbitals, and an excited state will also occur. On the other hand, for bound systems of electrons, that is, $\pi+\pi$ for the transition from higher filled to lower vacant ($\pi \rightarrow \pi^{*)}$ orbitals, less energy is required compared to the excitation of electrons in an isolated double bond (*), and the junctions at the junction absorb a quantum of light with longer wavelength than the joints in the joint. With an increase in the number of neighboring pairs, energy is required to excite electrons, and in a long-wave field, a quantum of light is scattered and its energy decreases. In aromatic systems, electrons require less energy than isolated double bonds. Thus, the main chromophores in UV spectroscopy are bound C=C bonds, a carbonyl group, C=CC=O systems and an aromatic ring. The UV spectrum of organic compounds is characteristic, in which the absorption of specific chromophores and groups close to them is determined, that is, 1 chromophore shows the same absorption regardless of where the group is located. In both simple compounds and complex compounds, if 1 chromophore group is wrapped directly between similar chromophore groups, its absorption maximum can vary several times in different compounds in the UV spectrum. The shift of the maxima to the long-wavelength region is called bathochromic, and the shift to the short-wavelength region is called the hypsochromic shift. The absorption intensity in the spectrum is related to the probabilities of electronic transitions, but some part has a formal transition probability and actually manifests itself. There is a selection rule that corresponds to allowed and prohibited transitions. This rule reflects the fundamental symmetry of the molecule and also applies to the symmetry of electrons in the ground and excited states. The spin of the forbidden electrons changes. The intensity absorption of the corresponding allowed electronic transitions is usually high, and the absorption coefficient reaches 1000, which, like that of a forbidden transition, amounts to ε tens and sometimes hundreds of units. Spectrometers must have the following devices to generate the UV spectrum. The source of the UV irradiator is usually a hydrogen lamp (an electric arc in a hydrogen atmosphere at low pressure), which in practice produces continuous radiation in the range of 190-360 nm. To work on visible areas, a fluorescent lamp consisting of a tungsten spiral is used. From the source, the rays hit the mirror, and through the holes onto the quartz prism. The light returning from the mirror is

scattered in a prism, and then short sections of the spectrum are isolated using pinholes. As a result of the rotation of the prisms, the spectra are mixed with respect to the apertures. This produces a light beam with a fixed wavelength. The resolution ± will be 0.5 nm. Monochromatic rays are passed through a quartz cuvette, and the test solution in the cuvette is transparent to solvents in the UV range. The thickness of the cuvettes ranges from 1 to 10 cm, the most common cuvettes × have a cross section of 1.1 cm and require about 3 ml of solution to fill them. The intensity of light passing through the cell is measured using a photocell, the current strength in it is proportional to the intensity of the incident light. The current is amplified and recorded by a potentiometer. The intensity of the light beam is compared with the light passing through the test solution with the light passing through a clean probe in a similar cuvette. The resulting difference corresponds to the difference in the absorption of the test substance by the solution. This comparison can be made in two ways. If there is a light beam, cuvettes with the test solution and solvent are placed in its path. The spectrum is gradually tuned manually using the device to a specific wavelength. The light flux from modern recording devices is divided into 2 identical beams, one of which passes through the test solution, and the other through the solvent. In this case, the intensity of the light beam passing through the cuvette is compared, and a continuous change in wavelength is performed automatically. In one case or another, a UV spectrum of the substance is obtained and the optical density of the solutions is shown depending on the wavelength of the absorbed light.



D=log(I $_{o}$ |I)

The molar absorption coefficient at the maximum point is calculated using the following formula.

E = D |) (Cl)

Issue 1. After diluting a solution of cyclopentadiene containing 3.061 * 10 $^{-4}$ g in 9.3721 g of hexane (density 0.6603), the optical density of the solution per 1 cm λ of no more than 240 nm 1.1 will be equal to Calculate the absorption coefficient.

Solution. Determine the concentration of the solution in mol/l. Taking into account the density of the substance and solvent and knowing that the molecular weight of cyclopentadiene is equal to 66.10 of their difference, the following calculation is made.

V(volume of solution) =9.3721/0.6603=14.18 ml=1.418*10 $^{-2}$ l

C=3.061* $^{10-4}$ / 1.418*10-4 * 66.1=3.24*10-4 ^{mol} /l

ε=1.1/3.24*10 $^{-4}$ *1=3400 l/(mol*cm)

When processing a spectrum, the molar absorption coefficient is displayed as a function of wavelength (or frequency). Currently, the frequency scale (more precisely, the wave number) is expressed in cm $^{-1}$, in which case the energy changes linearly along the x-axis. Therefore, ε the value fluctuates over a very wide range (from 1000 to 10000), UB curves are sometimes expressed ε as lg to λ ga (or ν ga). In many cases, the spectrum appears in the form of single maxima (Fig. 2-3).

The width of the absorption maximum indicates that, in addition to electronic transitions at the main steps, there are also transitions associated with vibrations of molecules at additional steps. Many such additional transitions usually cause corresponding peaks to appear as 1 broad peak. In some cases, for example in aromatic compounds, the absorption maximum consists of a contour of several small lines caused by the vibration of additional points, with small maxima on 2 sides of the main one. Typically, characterizing the wavelength of UV spectra, their absorption maxima and molar absorption coefficients are observed at these maxima.

For example: in the spectrum of cyclopentadiene (Fig. 2-3), the entry can be given with sufficient accuracy. λ_{max} (in hexane) 240 nm (ε 3400) .

The UV spectrum of a substance has several absorption maxima, each of which corresponds to its own type of electronic transition. In this case, the spectrum is recorded numerically, indicating ε in parentheses the wavelength and the magnitude of the corresponding absorption maxima. If the spectrum has a relatively complex contour (for example, one of the maxima), then a direct picture of the spectrum in full will reveal its special character and draw certain conclusions. The molar absorption coefficient for each UV-absorbing substance must have a constant wavelength in the same solvent, and the absorbance of the analyte must be the same at a given concentration. The error in measuring optical density $\pm$ is always between 0.2 nm and 1 percent, depending on the design of the device. Based on this, ε it is possible to determine the concentration of a substance with high accuracy when the optical density of the measured solution is known. Measurements specific to wavelength absorption maxima are not required. Thus, the UV spectrum facilitates the quantitative analysis of solutions with high accuracy, in which changes in concentration are observed as a function of time, the latter concept being widely used in the study of the kinetics of chemical reactions.

Issue 2. The optical density of a solution of cyclopentadiene in heptane in the UV spectrum is λ 0.83 nl at a maximum of 240 nm with a cuvette light path length of 1 cm. If the molar absorption coefficient is 3400 l/(mol*cm)?

Solution. The concentration of the solution is determined as follows.

C=D/ ε l=0.83/3400*1=2.442*10 $^{-4}$ mol/l

Alkanes (hexane, heptane), ethanol, water, and sometimes dioxane are used as solvents in the UV spectrum. Concentration of the test solution (usually 10 $^{-4}$ -10 $^{-6}$ mol/l). They are selected so that their optical density is in the range of 0.3-07, which ensures maximum measurement accuracy. To obtain sufficiently small concentrations with high accuracy, the method of serial dilutions by weight of the solvent and solutions is determined with less error than the dilution method. Basically, if the

solvents are too pure and contain impurities, for example, the amount of aromatic compounds is 10 -5 ^{mol} / l, alkanes are inconvenient to work with. In a simpler version, the most convenient solvent is water purification. In some cases, when changing the solvent, the position of the absorption lines changes (by 2-10 nm) and their intensity changes (by 10-20%). As a rule, such a replacement affects the spectrum of polar substances and has virtually no effect on the UV spectrum of non-polar compounds: the interaction of chemical compounds with a solvent leads to a practically strong change in the spectra (often the formation of hydrogen bonds), as well as the degree of dissociation or change in the tautomeric forms of substances. In all such cases, it should be verified that the solutions satisfy the Bouguer-Lambert-Beer law. Thus, UV spectroscopy makes it possible to determine groups of studied compounds, chromophores and determine the presence of such substances in the composition. This method is widely used not only in laboratory practice, but also in the chemical and food industries, for example, in the determination of styrene in a mixture with divinylbenzene (GOST 10003-67), in the determination of carotenoids, in the determination of benzopyrines, etc. UV method spectroscopy is quite comparable with other methods of structural analytical chemistry, is predominantly empirical in nature and is not very informative. Moreover, the nature of absorption and the structure of the molecule do not prevent its widespread use in rigorous reasoning from the point of view of physics and mathematics.

Practical lesson No. 2

General table of the main absorption frequencies in IR spectroscopy . Methods of spectral analysis. Solving special problems of the 2nd type in IR spectroscopy (the problems indicate the gross formula of the substance)

Corresponds to the average infrared (IR) field of electromagnetic radiation, corresponding to the energy of a light quantum with a wavelength of 1-15 μm or a wave number of 400-4000 cm -1, incoming energy is required for vibrational excitation of atoms.

The vibrational steps of the molecules are quantized, the transfer of energy between them, in turn, the vibrational frequencies have only fixed exact values. When a quantum of light is absorbed, the molecule moves to a higher vibrational level, actually moving from a vibrational state to an excited state. After energy absorption occurs, the rotationally excited state or kinetic energy of the molecule is converted. The vibrational spectra of molecules appear in the form of two types of spectra: absorption in the infrared region (IR spectra) and combined light scattering spectra (CS spectra).

The vibrational spectra of polyatomic molecules are complex. Calculations are given only for simple diatomic molecules. Vibrational spectra are mainly vibrational in nature, that is, substances with a symmetrical structure are studied by comparing the spectra of most compounds according to their characteristic vibration frequencies. But this does not reduce the value of the method .

IR spectroscopy is stretching and bending vibrations . Vibrations in the direction of the bond of the atomic nucleus are called stretching vibrations and are denoted by the letter n ($n_{C=C}$ $n_{C=O}$, etc.).

Valence vibration

Valence-symmetric vibration (ν(s))

Stretching asymmetric vibration (ν(as))

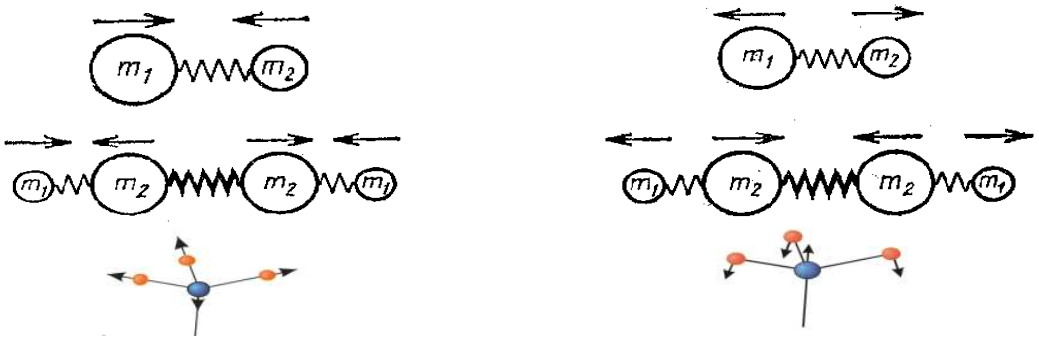


Figure 3. _ _ Types of vibration.

As an approximate mechanical model of stretching vibrations, we take a system of two spheres connected by rigid bonds (here the spheres represent atoms, and the bonds are chemical bonds). When the springs are compressed and stretched, the spheres oscillate around the equilibrium position, that is, harmonic vibrations are generated, and the equation is as follows.

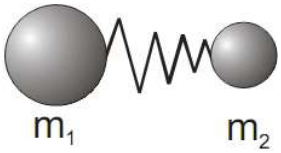


Figure 4 . Model of diatomic compound

$$E_v = hc[\omega_e(v+1/2) - \omega_e x_e(v+1/2)^2]$$

Here

ω_e is the corresponding t-band frequency,

$\omega_e x_e$ - anharmonic constant,

ν-quantum number of oscillations (0, 1, 2, …) Δν= 1

Normal vibrations number (N) is calculated as follows:

For linear molecules – N = (3 n -5)

For nonlinear molecules – N = (3 n -6)

The frequency of stretching vibrations is determined by the mass of the atom and the strength (energy) of the bond. The greater the mass q, the lower the oscillation frequency, for example:

$$\nu_{C-C} \approx 1000 sm^{-1} \qquad \nu_{C-} \approx 1000 sm^{-1}$$

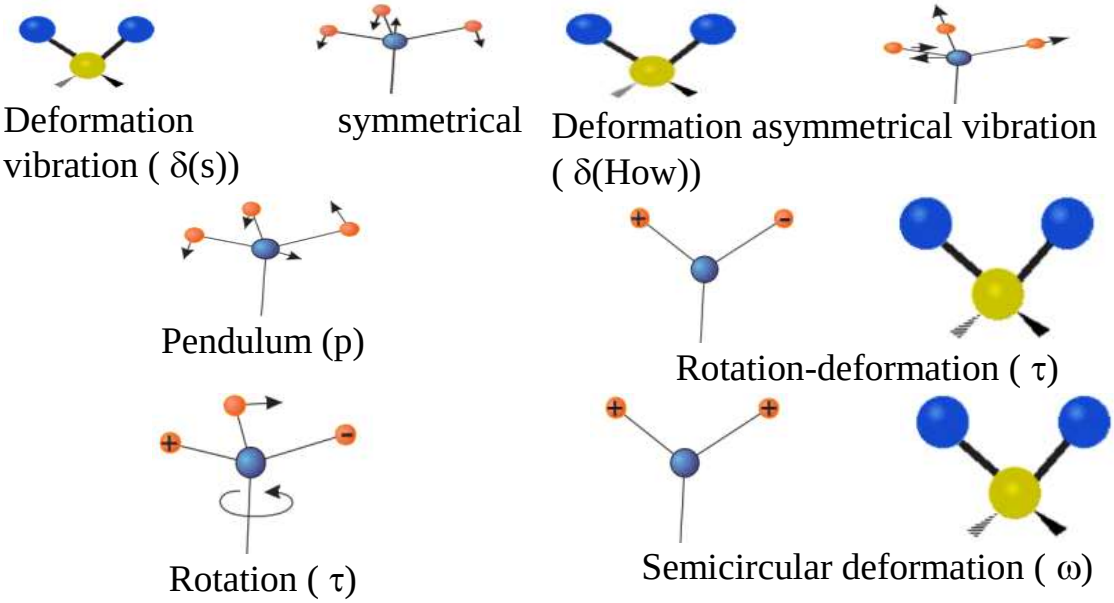
Dependence of the stability of a chemical bond on the vibration frequency.

$\nu_{C-C} \approx 1000 sm^{-1}$	$\nu_{C-o} \approx 1100 sm^{-1}$	$\nu_{C-N} \approx 1050 sm^{-1}$
$\nu_{C=C} \approx 1600 sm^{-1}$	$\nu_{C=C} \approx 1700 sm^{-1}$	$\nu_{C=C} \approx 1650 sm^{-1}$
$\nu_{C\equiv C} \approx 2200 sm^{-1}$		$\nu_{C\equiv C} \approx 2250 sm^{-1}$

It can be shown that the frequencies of the overtone vibrations change to a large integer relative to the ground state (by 2n , 3n, etc.). Typically, overtones are often of

low intensity: for the first overtone, the fundamental is 1-10% of the body; the third overtone is usually not produced.

two can be observed - in-phase (single-phase or symmetrical, ns) and antiphase (different-phase or antisymmetric, nas) valence oscillations (Fig. 3). Antiphase oscillations are always higher than in-phase oscillations.



5 pictures. The appearance of some deformation vibrations

Deformation vibrations are associated with a change in the bond angles of common atoms, which is determined by the value of d. The appearance of some deformation vibrations is shown in Fig. 4. Deformation vibrations always require less energy compared to oscillatory vibrations and have a lower frequency. molecular vibrations can increase rapidly as the number of atoms increases. In real molecules, the vibrations of atoms are connected and interact with each other. The spectrum of molecules consists of a complex set of different vibrations, and each of them appears in short frequency intervals .

Spectrum generation

The basis for obtaining the IR spectrum is the absorption of light when it passes directly through a substance. Of the wide range of IR rays, a medium field (400-4000 cm $^{-1}$) is usually used. It shows overtones in the near-IR (4000-14300 cm $^{-1}$) fields and is sometimes used in quantitative analysis. Far IR field on practice (100-400 cm $^{-1}$) correspond only to vibrations of the carbon-metal bond.

Like the UV spectrometer, the IR spectrometer is simple, but the design of the instrument is complex. IR rays are heat rays; usually its source is a ceramic crucible, which is ignited by a passing electric current. Using a mirror system, the light flux is divided into two identical beams, one of which passes through the cuvette with the test substance, and the other through the compared cuvette. The rays passing through the cuvettes pass through a system consisting of a rotating prism, a mirror and a light slit, which divides the rays into precisely defined beams, and this light enters a monochromator, which slowly changes frequencies. In the IR range, most substances are opaque, and prisms consist of single crystals of salts .

There are different ways to introduce samples of a substance into an IQ spectrometer .

1. It is convenient to obtain the spectrum of a substance in solutions in which the molecules do not interact. Therefore, any substance is absorbed in the IR region, and simple structural compounds are used as solvents, and its spectrum consists of a minimum number of lines; below 1300 cm $^{-1}$ it is almost transparent. If a substance is dissolved sequentially in one solvent or another, all CI spectra can be obtained. Cylindrical cuvette for solutions - thickness 0.1-1.0 mm, windows made of salt plastic. The cuvette is filled with a solution of 0.1-10 ml with a concentration of 0.05-10%.

2. The liquid substance is placed between the salt plates in the form of a short film (< 0.01 mm) due to capillary forces.

3. Solid samples are finely ground with vaseline oil to a paste and placed in a thin layer between salt plates. Vaseline oil itself consists of a mixture of hydrocarbons that are intensively absorbed in areas of ≈ 2900 cm $^{-1}$ and ≈ 1400 cm $^{-1}$. Hexachlorobutadiene is sometimes used to prepare the paste; it is transparent above 1600 cm $^{-1}$, and petroleum jelly is absorbed in the frequency range 1250-1500 cm -1
.

mix very well with ×potassium bromide (100 mg), then ~form a thin plate by pressing under a pressure of $4.5 \cdot 10^8$ Pa using a special device.

Regardless of the preparation method, the amount of substance to obtain the IR spectrum is 0.5-2 mg. Thus, the cuvette material is salt plates , and the sample should not contain water.

The most convenient in practice is the IR spectroscopy method. The device is simple, obtaining a spectrum takes only a few minutes.

CH bond in alkanes, stretching vibrations are observed at 2800-3000 cm $^{-1}$. In an alkane vibration $\nu_{WITH\ —\ H}$ manifests itself in the following areas according to the nature of the carbon and hydrogen bonds.

Part $_3$ $\nu^{with}{}_{CH}$ 2962 cm $^{-1}$ $\nu^{as}{}_{CH}$ 2972 cm $^{-}$
$_1$

channel $_2$ $\nu^{with}{}_{CH}$ 2 853 $\nu^{as}{}_{CH}$ 29 26 cm
cm $^{-1}$ $^{-1}$
CH ν_{CH} 2890 cm $^{-1}$

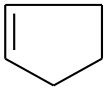
The lines are mostly, but less structured, and, in addition to interacting with each other, various oscillations usually occur in the CG. Individual vibration lines are formed in the region of 2800-3000 cm $^{-1}$ and overlap each other. These lines are useful for determining the shape of a substance only when there are few hydrogen bonds, as in polyhalogens. This is where they draw the line. The absence of lines in this area is reliable evidence that the substance does not contain a saturated carbon atom, the festive H atom.

ν_{KG} are located in the region of 1350-1470 cm $^{-1}$, characteristic parts of the spectrum are determined.

CH $_3$ d $^{with}{}_{CH}$ 1375 CH $_3$ d $^{with}{}_{CH}$ 1375 cm $^{-1}$
cm $^{-1}$
channel $_2$ $\nu^{with}{}_{CH}$ 2 $\nu^{as}{}_{CH}$ 29 26 cm $^{-1}$
853 cm $^{-1}$
channel $_2$ d $^{s}{}_{CH}$
1465 cm $^{-1}$

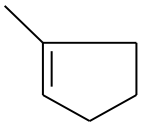
2 methyl groups on one carbon atom is considered sufficiently characteristic (hemylene exchange) for the formation of 2 close maxima (doublets) of approximately the same intensity. 1370 - 1385 cm $^{-1}$ shows in the field. $_{CD}$ lines 2100 - 2160 cm $^{-1}$ are considered characteristic when analyzing target detrital compounds and are located in a field where there are no other lines in the experiment.ν

C=C. 1600-1680 cm $^{-1}$ with isolated $_{C=C}$ double bond in compoundsν will be in the field. In cyclic systems, these values are mainly in cases where they are several times smaller. double garden the frequency of oscillations increases significantly with the speed of exchange. For example



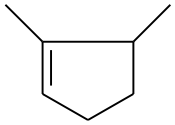
(I)

1612 cm $^{-1}$



(II)

1636 cm $^{-1}$



(iii)

1655 cm $^{-1}$

In the IR spectrum, alkenes (non-polar double bonds) are symmetrically substituted. Lines $\nu_{C=C}$ appear with much greater intensity. For example, as in spectra 1 and 3. For compounds that symmetrically alternate along double bonds (for example, in compound 2), these lines are quite intense. In the CS spectrum, C = C vibrations are in any case active and form any double bonds, strong lines (usually the most intense lines in the spectrum) than in the IR spectrum.

In addition to the presence of a double bond, the substance νhas characteristic lines $_{=CH\ (lines)}$, which are 3000 - 3100 will be located in the area of cm $^{-1}$.

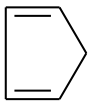
∂_{CH} at the double bond: for cis-isomers they are located in the region of 650-750 cm $^{-1}$, and for trans-isomers in the region of 960-970 cm-1 $^{\cdot\ 1}$. Thus, based on the given data of the vibrational spectrum (mainly KS), we can draw some conclusions about the presence of an isolated double bond in the substance and its exchange nature.

$\nu_{=CD}$ are constant in nature (2200-2300 cm $^{-1}$) and reliably distinguish deuterium atoms in a double bond from deuterium atoms in saturated hydrocarbons.

Adjacent diene systems show 2 lines in the region of 1500-1650 cm $^{-1,}$ which correspond to 2 types of stretching vibrations, symmetric and asymmetric. For example :

$CH_3CH = CH - CH = CH_2$ $\quad \nu^{s}_{C=C} = 1600 sm^{-1}$ $\quad \nu^{as}_{C=C} = 1650 sm^{-1}$

$\quad \nu^{s}_{C=C} = 1500 sm^{-1}$ $\quad \nu^{as}_{C=C} = 1620 sm^{-1}$



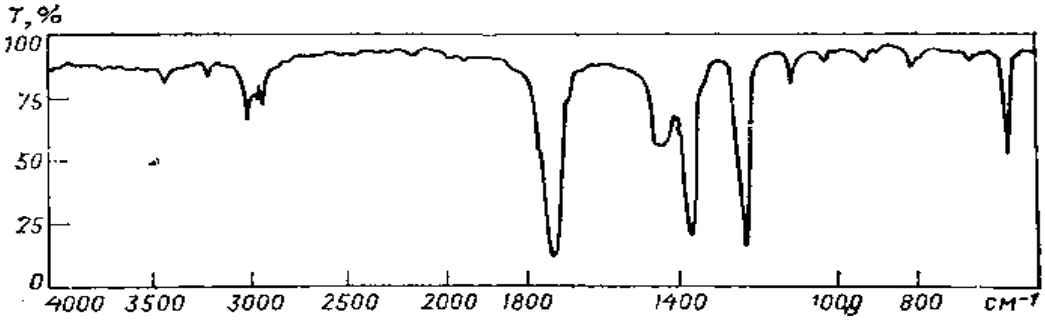
In general, it can be determined that a diene system has a trans configuration by comparing the relatively high-intensity vibrational lines of the diene system in the IR and CS spectra with isolated systems. Symmetric dienes (for example, butadiene 1,3) in the IK spectrum are more active in $\nu^{\text{the as}}{}_{C=C}$ vibration , similar to the $\nu^{C}{}_{=C}$ vibrations in the KS spectrum.

$\nu^{\sigma}{}_{C=C}$ intense lines are less likely to disappear.

3. Taking into account the structure of the compound, a set of tasks associated with determining the absorption frequencies of groups in it using a table solution methods

$C_{3H\_6}O$. Its spectrum I Q is shown in Fig. 13 .

Solution. From the given spectrum it follows that the compound does not contain a hydroxyl group, but contains a carbonyl group. Therefore, the compound may have the structure $CH_3 C O CH_3$ (acetone) or $CH_{3CH} \_ _{2H} \_ O$ (propionaldehyde). Among these two structures, the first is more probable and can be developed according to the following auxiliary features: the state with a frequency of $\nu_{C=O}$ 1715 cm^{-1} corresponds to an acyclic ketone; νVibrations of $C (O)N$ with a frequency of 2695-2830 cm^{-1} correspond to aldehydes; these lines are absent in the spectrum; There are two bands in the CH vibration field ν(only one type of CH_3 groups).



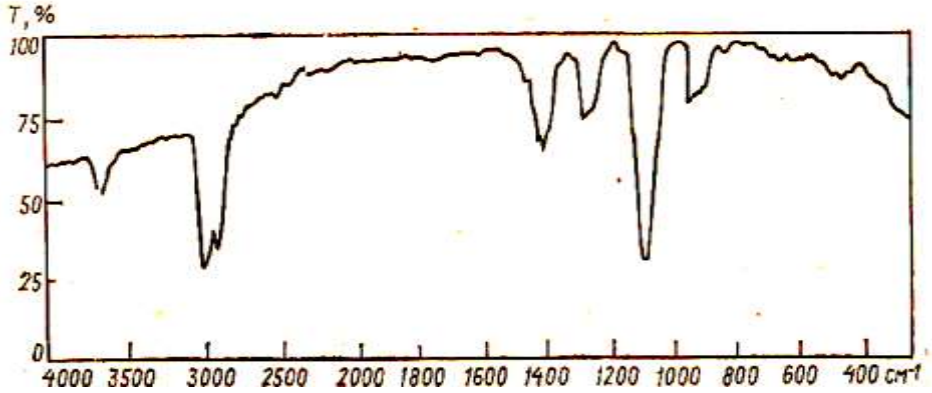
6 pictures. IR spectrum of acetone (1 example)

Example-2. Determine the structure of the compound $C_2 H_6 O$ from the IK spectrum in Figure 14.

Solution . According to this burto formula, 2 structures are suitable.

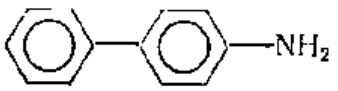
CH_3-O-CH_3 $C_2 H_5 OH$

According to the IR spectrum, since there are no hydroxyl groups (broad line 3200-3600 cm^{-1}), this substance is $C_2 H_5 OH$.

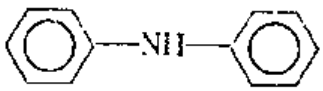


7 pictures. IR spectrum of ethanol (example 2)

Example-3. Calculate which of compounds A or B belongs to the spectral image shown in Fig. 3.11.



(A)



(b)

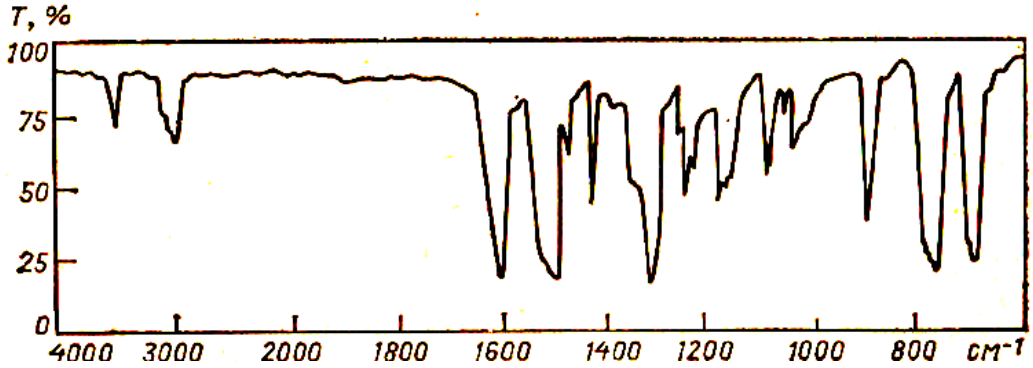
Solution The amino groups (position and intensity) should correspond to approximately 3400 cm^{-1} lines. This spectrum corresponds to diphenylamine (B), in which the line is single, which, in turn, corresponds to a secondary amine. Pay attention to the shapes of $n_{KG\ lines}$, the directions of the lines in the long-wave field basically coincide, the same is true in the short-wave field. If it corresponds to maximum lines in the region of 3000 – 3100 cm^{-1}, this really means that in this molecule the H atom in

aromatic or heterocyclic compounds is located around the double bond. The following conclusions are valid for areas of 1500-1700 cm $^{-1.}$ Corresponding to the lines in the low frequency part, showing that they have very low intensity, n $_{C(O)H}$ belongs to the aldehyde group (2695-2830 cm $^{-1}$), CH (2550-2600 cm $^{-1}$), C ≡N (2240-2260) groups and three gardens (ν $_{C}$ $_{≡}$corresponds to $_{C}$ 2100-2250 cm $^{-1}$).

The absence of IR spectrum lines in this region indicates that the compounds under study do not contain sulfhydryl and nitrile groups. Lines 2695-2830 cm $^{-1}$ exactly correspond to the lines of the carbonyl group. To make a final conclusion that a substance does not contain triple bonds, it must have a CS spectrum. (Precisely in symmetrical permutations).

Focus more strongly on the 1500-1700 cm $^{-1\ region.}$ If you have determined the absorption in the region of 3000-3100 cm $^{-1}$, then if you have determined the intensity (mainly the intensity ratio of the IR - KS spectra) and the position of the lines (or number of lines) in the region of 1500-1700 cm -1 you have determined the alkene, diene data or aromatic compounds. This can be judged by the presence of intensity of the curves in this region and the absence of a hydrogen atom around the double bond of the substance (νcorresponds to $_{=CH}$ in the spectrum).

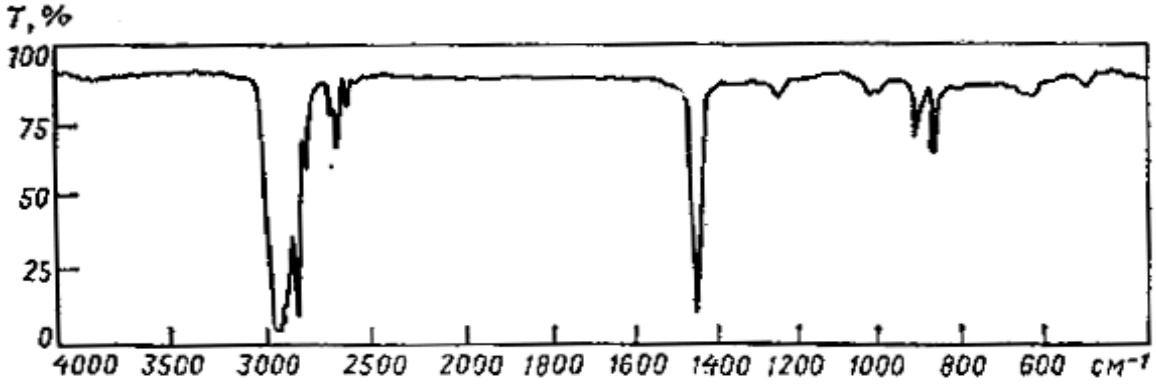
The spectrum of aromatic compounds should contain intense lines in the region of 650-900 cm $^{-1.}$ Absence of lines in the region of 1500-1700 cm $^{-1}$ (as well as 3000-3100 cm -1) The spectrum of the CS actually proves the absence of a double bond and an aromatic ring in the composition of the compound under study.



8 - picture. IR spectrum of diphenylamine (example 3)

Example-4. The IR spectrum corresponds to the compound C $_{6}$ H $_{12.}$ This is shown in Figure 15. Determine whether the compound contains a double bond.

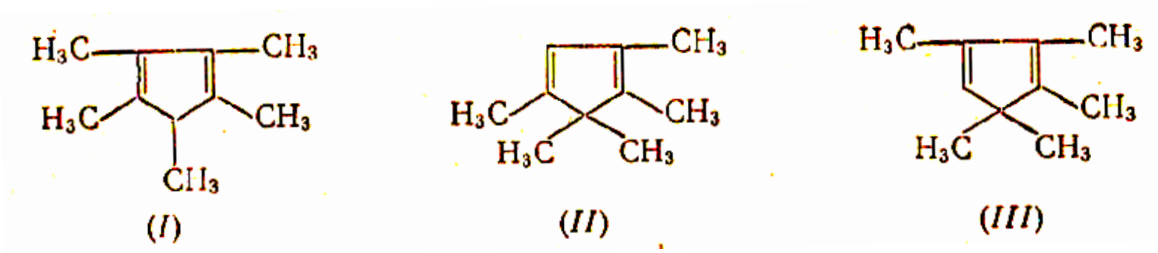
Solution. The absence of $_{C=C}$ and $ν_{=CH}$ lines in the spectrum ν, but it cannot be said that this is an answer from the IR spectrum. Thus, for the spectra of compounds (CH $ν_3$) $_2$ -C=C(CH $_3$) $_{2\ the\ C=C\ line}$ has very low intensity. The absence of these lines in the CS spectrum could determine the presence of a C=C bond in this mode in the lines of the CS spectrum.



9 - times m . Cyclohexane I Q spectrum (for 4 examples)

Example-5. pentamethylcyclopentadiene corresponds to the spectral lines shown in the figure. Determine the structure of a diene.

Solution. Pentamethylcyclopentadiene exists in the following 3 isomers.



in the spectrum of lines $\nu_{=CH}$ indicates that the diene has the structure of formula 1. νPay attention to the ratio of the intensities of the lines $^{\sigma}{}_{C=C}$ 1606 cm $^{-1}$ (small) and $\nu^{as}{}_{C=C}$ 1649 cm $^{-1}$ (medium). In the CS spectrum, this relationship is opposite and is most intense in the spectrum of the 1606 cm $^{-1}$ line.

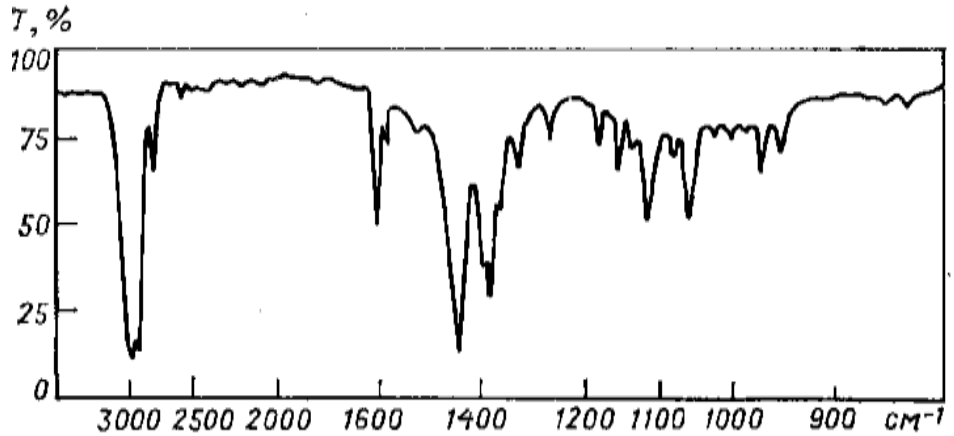


Figure 10. IR spectrum of 1,2,3,4,5-petamethylcyclopetadiene (5 examples).

Example-6 . Determine the structure of the hydrocarbon C_8H_{14} using the spectrum lines presented in the figure ·

Solution. According to Berto's formula, the substance can be a diene or an alkene. The presence of $_{C\equiv C}$ 2220 sm^{-1} lines νproves that it is an alkyne. In addition, the presence of lines in the spectrum $\nu_{\equiv of\ CH}$ 3313 cm $^{-1}$ indicates that the substance under study is octyne-1.

Example 7 . Determine the structure of the C_8H_{12} cyclohexadiene derivative from the IR spectrum shown in the figure. If $^{\sigma}{}_{C=C}$ 1581 cm $^{-1}$ and $\nu^{as}{}_{C=C}$ 1610 cm $^{-1}$ are known for cyclohexadiene.ν

Solution. 3010-3060 cm in the form of complex lines in the spectrum ˉ

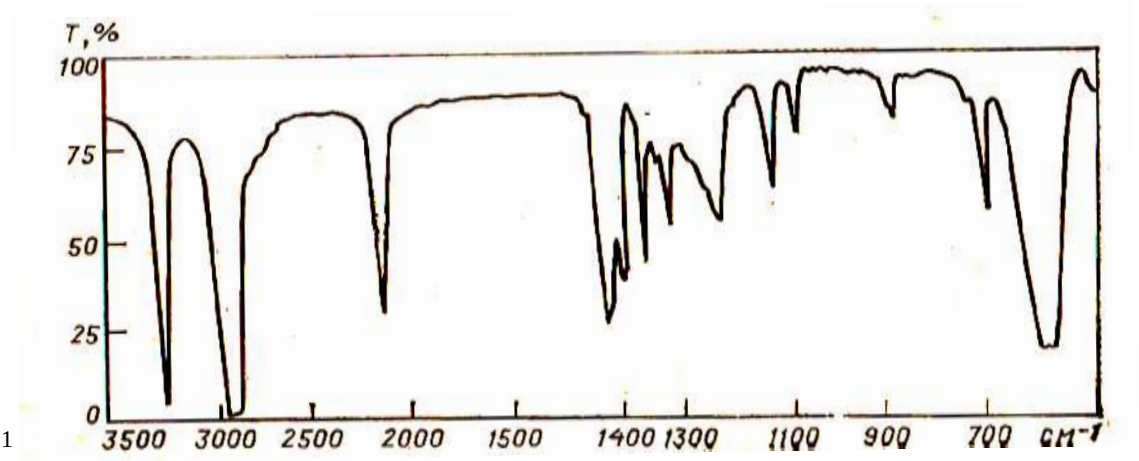


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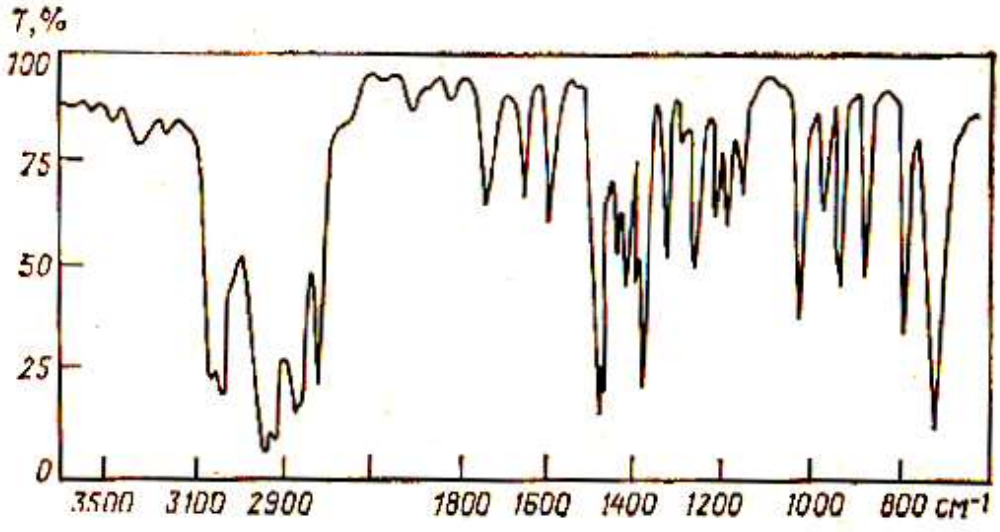
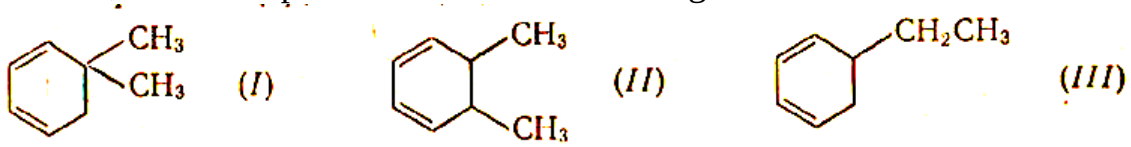
Figure 11. Octin-1 I Q spectrum (6 examples)



1 2 picture. The IQ spectrum of 5,5-dimethylcyclohexadiene (example 7) shows signals in c . At the same time, vibrations in the region of 1579 cm ν^{-1} and 1630 cm $^{-1}$ can be attributed to ^{s} -C=C- and ν^{C} =C- diene systems, which are sufficiently consistent with the frequencies of the spectra to indicate that it is a cyclohexadiene. In this case, there is no place for a double bond, and the diene, in turn, can correspond to one of the following 3 structures.



Rather corresponds to formula 1 (5,5-dimethylcyclohexadiene 1,3). Also in the spectrum, a doublet characteristic of geminal substituents (2 methyl groups on 1 carbon atom) appears in the region of CH bending vibrations.

Example-8 . Using the known IR spectrum (Fig. 3.16), determine the structure of the compound containing C_7H_{5N}.

Solution. The compressed spectrum shows the presence of a nitrile group ($\nu_{CH\equiv 2225}$ cm $^{-1}$), the signals of the aromatic ring complex ν_{CH} 3000-3080 cm $^{-1}$ are of medium intensity, the signals of the ν_{CC} ring δat 1600, 1500, 1480 cm $^{-1}$ and $_{CH}$ 760 and 790 cm $^{-1}$ reflect the presence of deformation signals and indicate the absence of

hydrogen atoms of the saturated hydrocarbon (absence of lines in the region of 2800-3000 cm $^{-1}$). In turn, this substance has the composition C_6H_5CN.≡

Practical lesson No. 3.

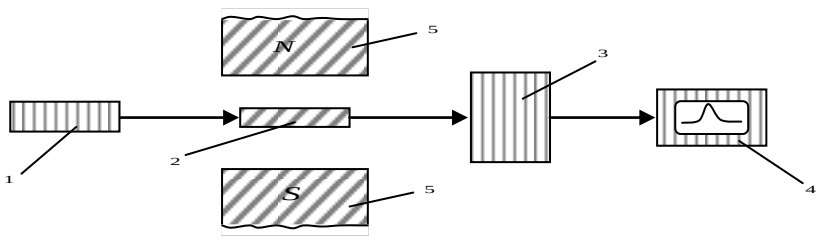
Solving special problems of the 2nd type in IR spectroscopy

(in the problems the gross formula of the substance is indicated)

Electromagnetic wave energy can only be absorbed by particles in a lower energy state, and the extent of absorption depends on the difference in the number of particles in the lower and higher states, but the difference is very small. With a magnetic field strength of 10,000 oersteds, $H = q\ 1+8\cdot10^{-6}$ is equal to protons, which means that a hundred thousandth of protons participate in the radiation. $\frac{n_1}{n_2}$

In 1936, Gorter tried to find paramagnetic resonance in lithium nuclei, but the attempt was unsuccessful. In 1944 E.K. discovered the absorption of high-frequency electromagnetic fields in $CuCl_2 \cdot 2H_2O$ Zavoisky salts. After this, work on NMR and EPR began to boil. In 1945, Purcell, Tory and Pound conducted the first successful NMR experiments in solid wax. Bloch, Hansen and Packard were the first to discover resonance in the protons of water. Since 1945, NMR technology has developed rapidly, and on this basis a large part of physical chemistry, radio spectroscopy, arose. Radio spectroscopy studies the interaction of radio waves with matter, while spectroscopy studies the interaction of light waves with matter. So, we can say that radio spectroscopy is part of a broader field - spectroscopy.

Instruments that measure paramagnetic absorption are called magnetic radio spectrometers. Of course, the principles of constructing instruments intended for observing NMR and ESR should be almost the same. They must have an electromagnet that creates a magnetic field with the required voltage, a source that generates an electromagnetic wave of the required frequency, and a cell in which the test substance is placed. An electromagnetic wave is directed at the cell and absorbed by it. So we need a device that measures this absorption. The diagram of the radiospectrometer is shown in Figure 6.6.



1 3 - picture. Block diagram of a magnetic resonance radio spectrometer.

1-source of electromagnetic waves; 2nd absorbing cell; 3rd receiver; 4-recording device; 5th magnet.

Since the proton is present in many compounds, ^1H NMR is the best studied. This is sometimes called proton magnetic resonance (PMR). For example, C_2H_5OH consider the PMR spectrum of ethanol (see Fig. 56). Based on the theoretical data given above, one can think that one absorption line will appear in the spectrum. In practice, three lines are observed. Their intensity is related to each other as 1:2:3, so they are $-OH_4$ associated with protons in groups . $-CH_2$ And . $-CH_3$

1 4 - picture. Low resolution NMR spectrum of α - ethanol.

b – high-resolution NMR spectrum.

v - NMR spectrum of pure ethanol.

The appearance of three separate lines in the spectrum means that the magnetic field acting on protons differs from the external magnetic field (from N $_{o)}$. This field can be written as:

$$H = H_0(1-\sigma)(1)$$

here the shielding σ constant is usually small. For example, for a proton it is approximately 10 $^{-2}$. This depends on the electronic structure around a given nucleus.

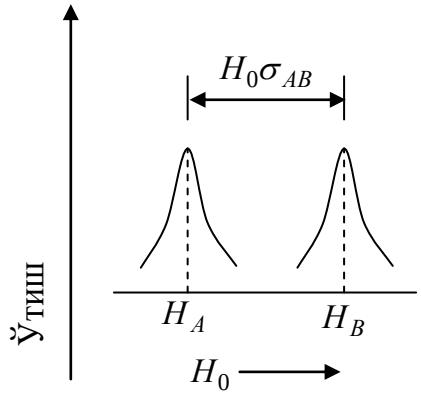
of two types, A and V. The magnetic field strengths acting on both protons are equal to :

$H_A = H_0(1-\sigma_A)$, $H_B = H_0(1-\sigma_B)$.

σ_A and σ_B are the shielding constants of the cores A and V. The distance between these two lines is:

$H_B - H_A = H_0(\sigma_A - \sigma_B) = H_0\sigma_{AB}(2)$

σ_{AB} - is called a chemical shift (chemical shift of A relative to V or V relative to a). Distance between lines A and V H_0 proportionally



1 5 - Image. Relative chemical shift between nuclei A and V.

5. Solving type I problems on PMR spectra, i.e. the spectrum of the substance, the structure or formula of the substance and the method of complete analysis of the spectra are given.

Protons with the same orbitals are called equivalent protons , and protons with different orbitals are called nonequivalent protons. Three signals are observed in the spectrum of ethyl alcohol, since there are three different groups of nonequivalent protons - CH_3 , CH_2 , OH, but three protons in CH_3 and two protons in CH_2 are equivalent protons in the groups. For protons to be stereochemically equivalent, they must be in the same position in space relative to the double bond or asymmetric carbon atom.

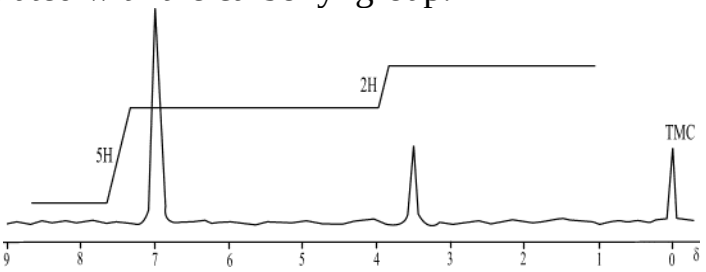
Thus, stereochemically equivalent protons can be thought of as chemically equivalent protons. The signal intensity is influenced by the following factors:

a) constant magnetic field (H_0), which determines the distance between the energy levels of nuclei;

b) temperature affecting the distribution of two energy levels;

c) radio frequency field, which determines the number of transitions per unit time.

NMR is a special electronic device that measures the signal surface in spectrometers and is called an integrator. The integrator draws a step curve based on spectrum signals. Each height of a "ladder" defines a signal surface corresponding to that "ladder". Therefore, the height of the ladder is proportional to the number of protons. On the integrator line, the height of the stairs is measured in millimeters or centimeters (photo). From the NMR spectrum of phenylacetic acid, based on the chemical shift values in the table below, it can be determined that the signal at 12 mu belongs to the proton of the carboxyl group, the signal at 7.2 mu belongs to the protons in the benzene ring, and finally the signal at 3.5 mu belongs to the protons of the methylene group associated with the carboxyl group.



1 6 - Image. PMP spectrum of phenylacetic acid ($SDSl_3$) .

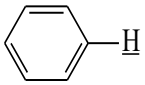
An integral line drawn across the spectrum is used to fully interpret the three signals. Knowing that the integral height of the signal of a carboxyl group containing one proton is 5 mm, the heights of the steps of the integral line are divided by the integral height of this one-proton signal.

$\frac{5}{5} : \frac{26}{5} : \frac{11}{5} = 1 : 5{,}2 : 2{,}2$	Thus, the number of protons corresponding to the signals in the spectrum is in the ratio 1:5:2. Quantitative measurements using an integrator on the surface of individual signals The integration process is considered complete

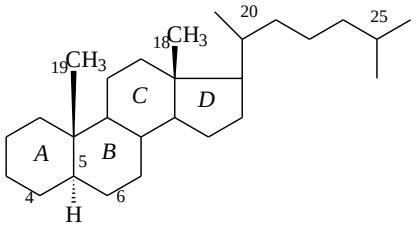
If we record the spectrum of a substance whose structure is unknown relative to the spectrum of a standard substance, we can determine the corresponding protons by calculating the intensity of each signal.

Proton chemical shift values

(solvent - chloroform, R - hydrocarbon radical) Table 1

Proton type	Chemical shift		Proton type	Chemical shift	
	mu	RS		mu	RS
1	2	3	4	5	6
$R-\underline{CH_3}$	0.9	54	$R-\underline{CH_2}-Cl$	3.7	220
$R-\underline{CH_2}-R$	1.3	78	$R-\underline{CH_2}-Br$	3.5	210
$R_3-\underline{CH}$	~2.0	120	$R-\underline{CH_2}-I$	3.2	190
$R_2C=\underline{CH_2}$	5.0	300	$R-\underline{CH}(Cl)_2$	5.8	350
$R_2-C=\underline{CH}$ (R)	~5.3	320	$R-O-\underline{CH_3}$	3.8	220
	7.3	440	$(R-O)_2-\underline{CH_2}$	5.3	320
$R-C\equiv\underline{CH}$	2.5	150	$R-C(=O)-\underline{H}$	9.7	580
$R_2C=CR-\underline{CH_3}$	~1.8	108	$R-O-\underline{H}$	~5.0	300
$C_6H_5-\underline{CH_3}$	2.3	140	$C_6H_5-\underline{OH}$	~7	420

Many general scientific works are devoted to the study of steroids using NMR spectroscopy, one of which is the article by Shuler and Rogers. By accurately measuring the chemical shift values of the methyl groups, important information about the structure of steroids was obtained (Figure 6.11).



Holestan

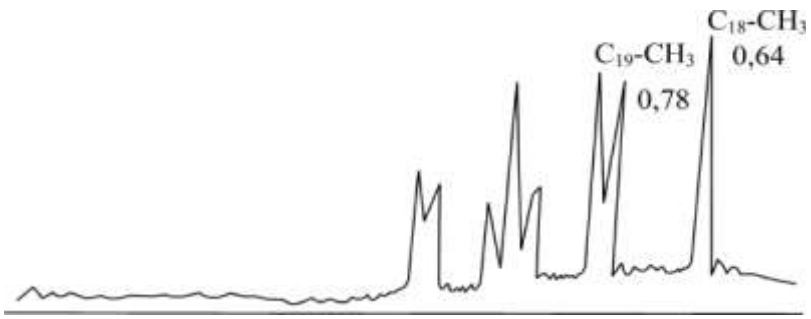


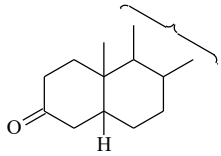
Figure 14. PMR spectrum of cholestane.

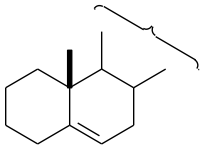
represent the signals of the protons of the methyl groups in S_{18} and S_{19}. Because the protons in the methyl group are equivalent, its width decreases, creating an intense

signal, and other narrow-shaped signals near these signals are the resonance frequencies of the secondary methyl groups at C_{20} and $C_{25.}$

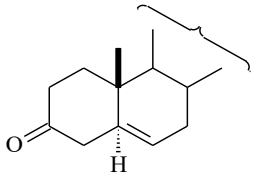
The signal that appears in the spectrum in the remaining ambiguous, undivided state is the signal of the protons of the cyclopentaphenanthrene skeleton.

Since the YAMR spectrum of stereoisomers has been carefully studied, the frequencies of the tertiary methyl group at C were calculated $_{18}$ and C_{19}, and Schuler and Rogers concluded that the resonant frequencies of such an angular methyl group depended on how the skeleton was oriented. When a carbonyl group is introduced into the third state, the frequency of the methyl group in ~S_{19} shifts towards a weak magnetic field (by 5-7 hertz). A similar situation was observed when a double bond was introduced into the 5th state of the ring (Δ^5) (~5 gs).





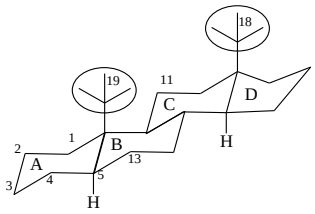
If CO =and CC are simultaneously present in the molecule =, then the displacement of the methyl group is the sum of the effects of both chromophore groups, and this value is 10-12 times greater, and this value is confirmed by experiment.



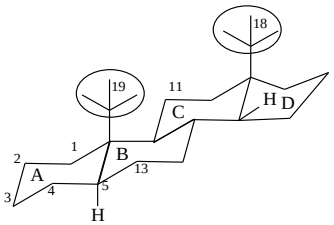
Practical lesson No. 4

Types of NMR spectrometers (N-60, Varian-100, Tesla-100). Introduce students to the operating principle of spectrometers and obtain a spectrum. Preparation of solutions. Familiarization with the process of integration and use in practice.

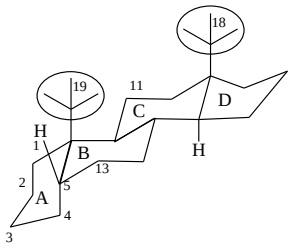
information was obtained on the influence of various functional groups in the molecule on the resonance frequencies of methyl groups at C_{18} and $C_{19.}$ When studying the PMR spectrum of steroids, the choice of the resulting compound as a standard is the resonance frequencies of the methyl groups at C18 $_{and}$ C19 . The unsubstituted androstane steroid can be used as this compound, but since its molecule has 6 asymmetric centers, theoretically there are 32 isomers. In each isomer, the corner methyl groups can interact differently with other parts of the molecule, resulting in resonant frequencies in different regions. In most steroids, the cleavage of the methyl group at C18 and C19 and the presence of a proton at C8- $_{olate}$ ($_{top}$ of β_{the} molecular plane) and C9- $\alpha_{cholate}$ (down the molecular plane) alleviate the above problem. Usually only the stereochemistry of C5 or $_{C14}$ ($_{or}$) αchanges β, so it has 4 standard compounds, namely 5 α, 14 α-androstane (I), 5 α, 14- βandrostane (II), 5 β, 14 α-androstane (III) and β5 , 14 β-androstane (IV):



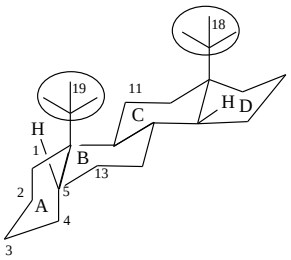
I



II



III



IV

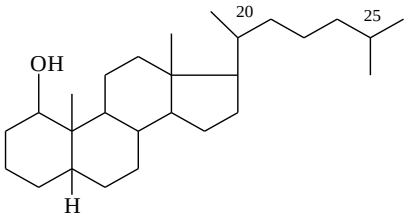
Signal values of methyl groups at C $_{18}$ and C $_{19}$ in androstane isomers

	C $_{19}$ -CH $_3$	C $_{18}$ -CH $_3$
I	0.79 mu	0.69 mu
II	0.767 mu	0.992 mu
III	0.925 mu	0.692 mu
IV	0.900 mu	0.992 m.e.

The amount of chemical shift is affected by the geometry of the molecule. When the angular methyl groups "observe" the rest of the molecular skeleton, they appear in the spectrum in a weak magnetic field. If ring A is rotated relative to the methyl groups in C19 $\rightarrow$(I III , II VI) $\rightarrow$, then the methyl group in ~C $_{19}$ moves into a weak magnetic field (8 G). If ring D , located far from C $_{19}$, "locked" (I $\rightarrow$II , III $\rightarrow$IV), the methyl group signal ~is observed in a strong magnetic field (1.5 g). Similarly, when the D ring is rotated downward from the plane of the molecule, the protons of the methyl group in C18 $\rightarrow$(I II , III $\rightarrow$IV) move into a weak magnetic field (~18 G).

C $_5$ does not affect the signal of the methyl group protons at C $_{18}$, since in this case ring A moves away from the methyl group at C18 .

Cholestan has 3 secondary methyl groups in the side chain. The PMR spectrum of cholestan-1-ol was taken for analysis ; clearly separated signals are shown in the region of resonance frequencies of the methyl group. αIn the absence of shielding of tertiary methyl groups in C $_{18}$ and C $_{19}$, doublet signals appear in a weak magnetic field of secondary methyl groups.



The four narrow signals in a weak magnetic field consist of two doublets, which represent signals corresponding to 6 protons in two secondary methyl groups, with

chemical shift values of 0.87 and 0.93 mu, respectively, C 25 and Groups of 20 are counted from (Fig. 6.12).

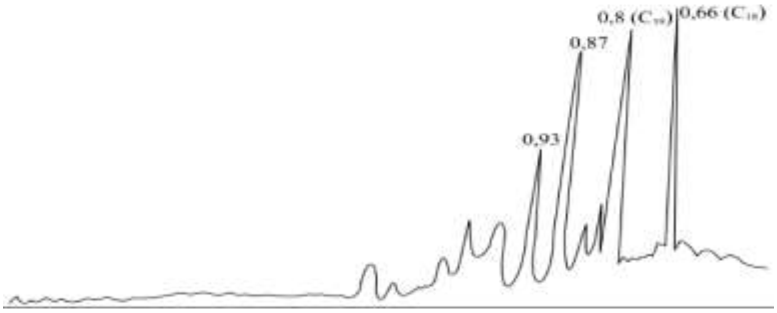
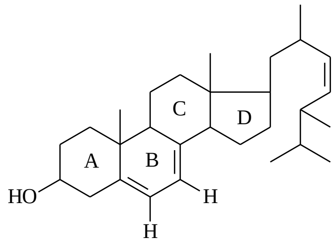
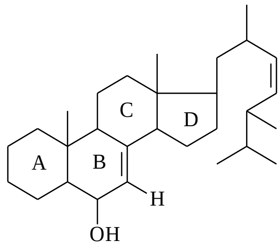


Figure 16. NMR spectrum of cholestane-1 α-ol.

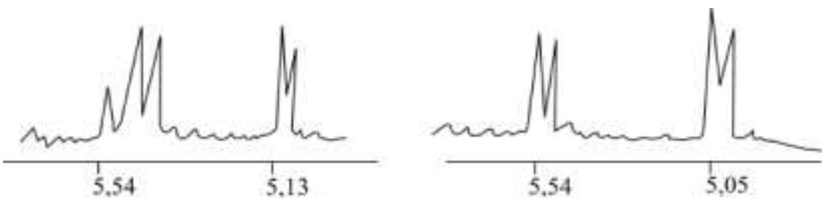
Thus, NMR spectroscopy provides important information for determining the nature of the groups surrounding the methyl group of steroids. The value of the resonance frequencies of methyl groups is mainly taken into account. YAMR can also be used to determine whether a steroid molecule has a double bond or not. Necessary information on the structures of ergostrine (V) and i -ergosterol (VI) was obtained by measuring the chemical shift values of the olefin protons. The difference between these isomers is determined by the abundance of one double bond in one, which is clearly visible in the spectrum.





ergosterol (V) i -ergosterol (VI)

ergosterol (V) has a diene structure in the V ring, then a quartet signal is formed in the region of olefin protons, that is, at 5.54, but the olefin proton in the i -ergosterol molecule forms a doublet, and its value is also 5.54. The 5.15-mu signals in the spectra of both compounds are signals from the protons of the double bond in the side chain (Figure 6.13).



IN VI

Figure 17. NMR spectra of ergosterol (V) and i -ergosterol (VI).

With the help of _ NMR analysis of the resonance frequencies of olefin protons in compounds with double bonds in the -C region was carried out 23.

Using mass spectroscopy, information was obtained on the molecular masses of steroids and closely related compounds, as well as on the structure of the side chain.

Reed studied the mass spectra of cholestane, ergostane, and stigmastadian and determined that the formation of fragment ions occurs when bonds held by substituents are broken. In general articles devoted to the mass spectrum of steroids, it has been established that the formation of ions occurs through the cleavage of methyl groups and side chains. Ions are formed when a water molecule leaves steroids with a hydroxyl group. The polycyclic nature of steroids increases the intensity of the molecular ion, and they form fragments with high mass, and in some cases, a rearrangement process is also observed.

Practical lesson No. 5

NMR solution of type problems based on the spectra of the ^{1}H isotope, that is, the spectrum of the substance, the structure or formula of the substance and the method of complete analysis of the spectra are given.

The stable isotope of the carbon atom ^{13}C has a magnetic moment (I = 12), but its amount in any organic substance does not exceed 1.1 percent. The fact that this isotope is so rare often makes direct measurement of resonant frequencies difficult.

^{13}C NMR spectroscopy also has the parameters “chemical shift” and “spin-spin influence constant”, similar to PMR spectroscopy, with the difference that the ranges of these parameters are much larger than those of protons.

The values of the chemical shift ( ) in the δ^{13} C spectrum are very easy to measure, since it lies in the formation range - 0-250 mu. Since this interval is very large, the signals in the spectrum are very clearly separated and formed without overlap, which is the reason that there is no need to carry out integration work, as in PMR, i.e. the molecule has the same chemical nature - the more carbon atoms differ from each other, the more signals will be displayed. The amount of chemical shift of the signal is influenced by the type of atoms to which the carbon is bonded and the nature of the lateral chemical bonds. When a carbon atom is bonded to oxygen, it creates a signal in a region of predominantly weak magnetic field. Signals from aliphatic hydrocarbons appear in a stronger magnetic field than signals from aromatic hydrocarbons.

The very small amount of the ^{13}C isotope in substances causes the absence of spin-spin interaction between carbon and carbon (^{13}C - ^{1Z}C) in the NMR spectra. This situation is explained by the simplicity of the ^{13}C spectrum signals, but in a deep analysis of the spectra it is necessary to take into account the influence of spin-spins between nuclei (H) associated with carbon (^{13}CH). For example, the CH group gives a doublet signal in the ^{13}C spectrum and its constant is J_{CH} = 125 G, if the carbon atom is connected by a double bond, then the constant of the similar C=CH group is about 170 G, ≡and in the -CH group it is equal to 250 G. Signals of this value are easy to find in the spectrum. Various substituents have a significant effect on the value of the spin-spin interaction constant. Similar to the proton spectrum, the proximity or distance of a proton from carbon also affects the chemical shift.

^{13}C gives a CH doublet, CH_2 triplet, CH_3 quartet in the spectrum. For example, signals of acetic acid in the carbon spectrum (Fig. 17) .

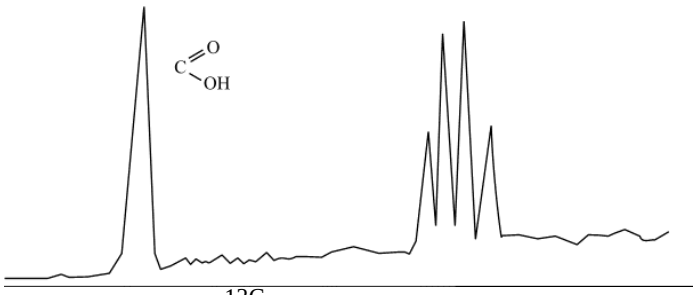


Figure 17. ^{13C} spectrum of acetic acid .

The influence of groups and bonds close to the carbon atom in the molecule on the value of the spin-spin constant can be seen using the example of simple methane derivatives :

J (^{13}C, ^{1}H) in methane derivatives.

table 2

Connections	(^{13}C , ^{1}N), Gs	Connections	(^{13}C , ^{1}N), Gs
Ch $_3$ -ON	141	(CH $_3$) $_3$ N	131
CH $_3$ -CH ≡_	136	CH3NH2 _ _ _	133
CH $_3$ -HO $_2$	147	-	-
CH $_3$ COOH	130	CH $_3$ -OS $_6$ H $_5$	143
CH $_3$ CH	127	CH $_3$ -C $_6$ H $_5$	126
CH $_3$ -F	149	CH $_3$ -CH $_3$	126
CH $_3$ Cl, CH $_3$ Br, CH $_3$ -I	150 +2	(CH $_3$) $_2$ CO	126
CH $_2$ Cl $_2$	178	(CH3) $_2$C = CH2	126
CH $_3$ -C ≡CH	132	CH $_3$ CCl $_3$	134
(CH $_3$) $_2$ C=O	138	(CH $_3$) $_2$ NH	132

The easiest way to avoid complex signals in the ^{13}C spectrum is to eliminate the interaction of all protons with carbon by specifying an auxiliary frequency, in which case the resulting spectra will be simple and consist of single signals. For a deeper study of the structure of matter, the spectra obtained taking into account the spin-spin effect between carbon and protons are called the “off” (outside) resonance mode of the ^{13}C spectrum. As an example, the spectra of the ethyl thiocyanate compound “from” without resonance (a) and in its used state (b) is presented in Fig. 6.2 : $H_3C—CH_2—S—C≡N$

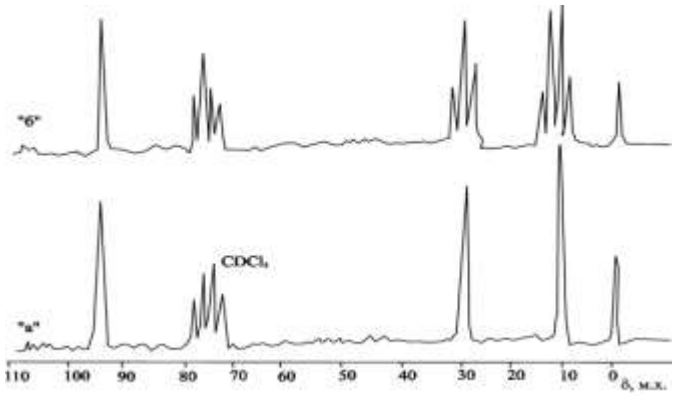
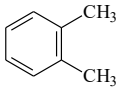
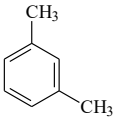
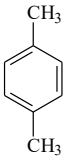


Figure 19. $^{13C\ spectrum}$ of ethyl thiocyanate (solvent - CDSL $_3$) .

^{13}C aromatic compounds , by which one can determine how the CH $_{3\ groups}$ in benzene homologues are located in relation to each other in the ring.



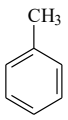


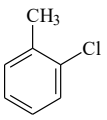


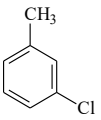
δ(CH $_3$) q 159.2 mu

δ(CH $_3$) q 157.2 mu

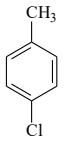
δ(CH $_3$) q 157.7 mu







δ(CH $_3$) q 156.9 mu δ(CH $_3$) q 158.2 mu δ(CH $_3$) q 157.6 mu



δ(CH $_3$) q 157.5 mu

Chemical shift values also depend on the state of hybridization of carbon atoms, sp ^{3} - 0-50 m.u., sp ^{2} -100-150 IU, and sp -hybridization shows a signal in the range of 70-100 IU.

C isotope with $^{\text{a magnetic}}$ moment in organic substances is very small, to obtain a spectrum the amount of sample compared to the PMR spectrum must be several times larger, but if its amount is insufficient, the spectrum signals appear with very low intensity," and in many cases their may be confused with noise from the spectrometer recording devices. In such cases, a YAMR shifter is used to obtain high intensity spectra Fure .

Practical lesson

Determination of the structure of organic matter of unknown composition. (according to the given data IK- , NMR- ^{1}H , NMR- ^{13}C).

Mass spectroscopy is fundamentally different from other spectroscopy methods based on the absorption of electromagnetic vibrations. Structural mass spectroscopy is based on the fragmentation of organic molecules under the influence of electron impacts and recording the mass of the resulting fragments.

If a flow of electrons passes through the vapors of a substance, their energy gradually increases. When this energy reaches a certain level, electrons collide with molecules, electrons break away from molecules and molecular ions are formed.

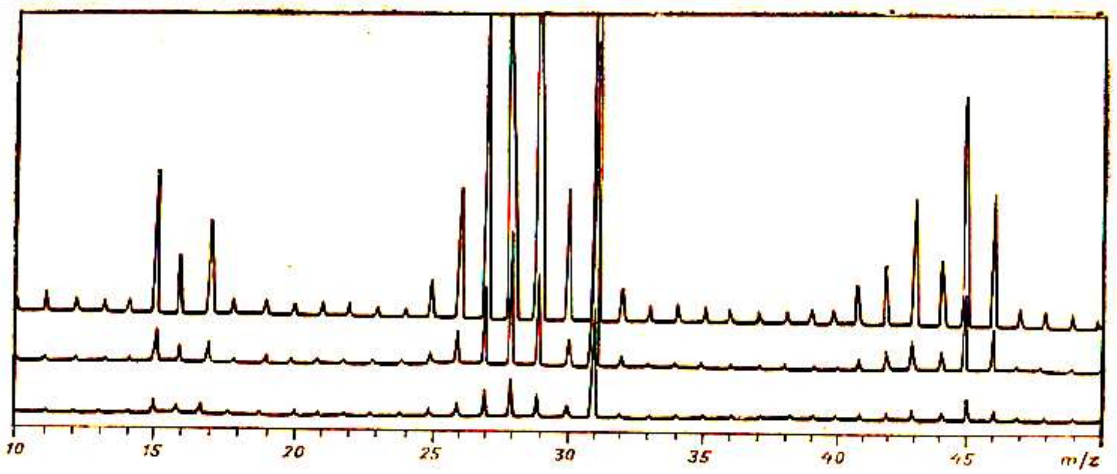
$$ABCD + e^- \rightarrow ABCD^{+*} + 2e^-$$

A molecule is a molecular ion

The lowest energy of bombarding electrons, i.e., the energy at which a molecular ion can be formed from a given molecule, is called ionization energy. (U_E) Ionization energy is a unit of measurement for the strength of a molecule; the stronger the bond between the electron and the molecule, the higher the ionization energy; the weaker the bond, the lower the ionization energy. Typically, the ionization energy of organic molecules is 9-12 eV. ($\approx$10 eV for cyclohexane, 9 eV for benzene $\approx$)

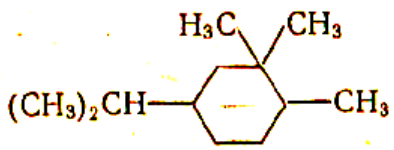
If the ionization energy of electrons exceeds the ionization energy of formation of a molecular ion, this will be enough to break the bond in the molecule. As a result of such interruption, decomposition into molecular ions occurs with the formation of low-mass ions (fragments). Electrons with an energy of 30-100 eV are used in experiments using mass spectroscopy methods. This ensures the formation of fragments of molecular ions exceeding the ionization energy. In many cases, the actual structure of the ions resulting from electron impact has not been determined. Standard organic chemistry structural symbols are commonly used to create a structural image of fragments. Despite the existence of such conventional images, measuring the resulting

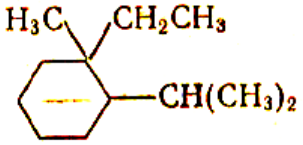
fragments according to the empirical nature of the fragmentation law and determining their relative quantity provides valuable information about the structure of an organic compound. To obtain mass spectra, small amounts of the substance are transferred to an ionization chamber using a system of special vapor transfer devices. The vacuum in the chamber is high (residual pressure $^{-6}$ is about 10 mm Hg). The molecules of the substance are bombarded in a stream of electrons, which is due to the appearance of radiation at the heated cathode. The potential difference between the cathode and anode accelerates the electron energy to a certain level (for example: up to 30 $\pm$ 2 eV). The resulting ions are ejected from the ionization chamber at a certain potential difference. The flow of electrons is accelerated and fixed under the influence of a strong electron field and magnetic field. Particles formed when molecules of a substance are bombarded with electrons can be positive, negative or neutral. When a stream of particles is passed through a magnetic field, neutral particles do not change their direction, but positive and negative particles are deflected in different directions. The magnitude of the deviation is directly proportional to the charge of the ions and inversely proportional to their mass (m/z). Typically, positively charged particles are detected in mass spectroscopy. It should be noted that the charge of a particle is equal to a unit of equivalent mass of the ion according to the m/z rule. If a recording device is installed in the path of ions emerging from a magnetic field, then particles with different m/z values give bifurcated signals. The intensity of the signals is proportional to the m/z values of the amount of substance. Analyzing ions based on their m/z values is usually done using a magnetic field. The ions are gradually fixed in the collector. The recording device records through a generated electrical pulse. Spectra can be recorded on photographic paper using a mirror galvanometer. Typically, registration is carried out on galvanometers with different sensitivities. A typical photogram of the obtained mass spectrum is shown in Fig. 20 .



The intensity of the signals is expressed in millimeters of their height. Peak height and maximum intensity are calculated as 100%, and the intensity of the remaining peaks is proportionally expressed as a percentage. Low-abundance peaks are identified relative to the conversion of their intensity to a high-speed scale for quantification. Peaks with intensity less than 3% are not taken into account by the rule. In mass spectroscopy, an image is taken in the form of the intersection of a set of straight lines, the intensity of which is proportional to the wavelength, and the representation, expressed as a percentage, is shown in Fig. 2.

1. propanol mass spectrum _ following m / z to the tops_ has : 168, 139, 125, 97. A or B 2_ _ from structure which to one higher range Right _ _ _ _ will it come ?

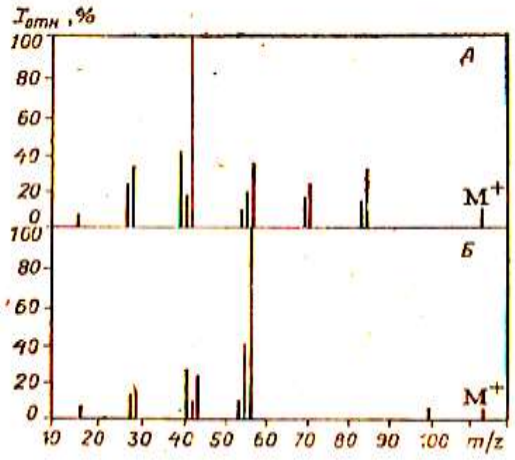


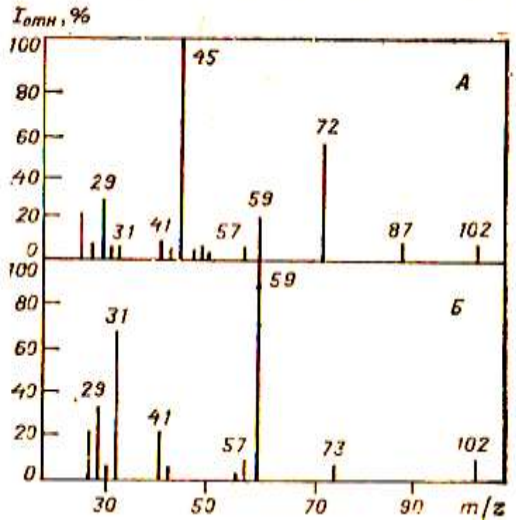


(A) (B)

2. The mass spectrum of propanol has the following form: m/z- 24 (14), 28 (11), 29 (17), 31 (100), 39 (6), 41 (10), 42 (13), 43. (4), 45 (5), 58 (5), 59 (15), 60 (10). Which isomer of the spectrum does it correspond to? Show how the ions form the main fragment.

3. The figure shows the mass spectrum of n-octane and 2,2,4-trimethylpentane. What is the structural formula of substances A and B?





Issue 3 Issue 4

4. The figure shows the mass spectra of isomeric ethers - ethyl isobutyl and ethyl isofluorobutyl. Create the structures of substances A and B. Explain the main direction of fragmentation of ions.

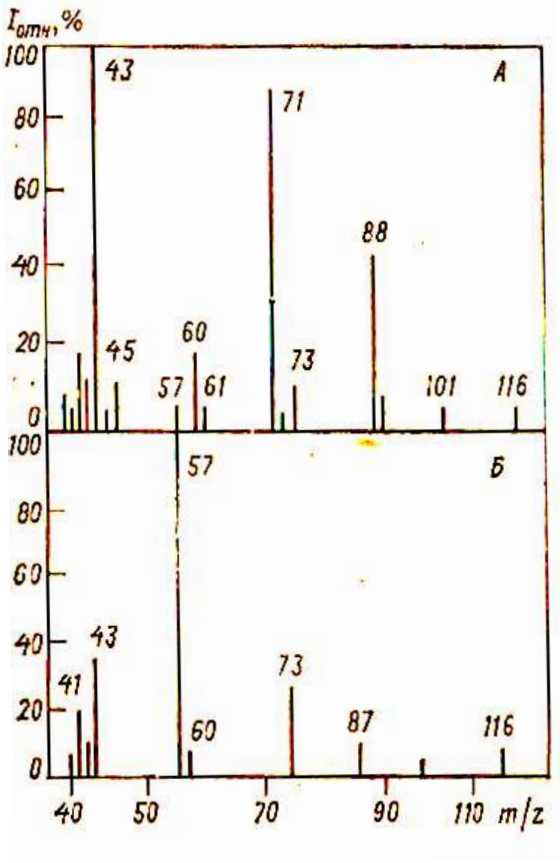
5. Propose the structure of 2 normal isomers of the ester $C_6H_{12}O_2$ based on mass spectrum data. Explain the main direction of ion fragmentation. Write down the mass spectra of substances A and B in numerical form.

6. Secondary heptanol has the following mass spectra (m/z): A-116(25), 98(12), 73(72), 55(100), 45(8), 44(10), 43(48), 41(12), 39(10), 31(25); B-116(18), 101(8), 98(10), 70(7), 59(4), 55(20), 45(100), 44(10), 43(20), 41(17)), 39(7), 31(8); V-116(18), 98(5), 87(30), 70(4), 69(40), 59(100), 58(12), 57(20), 45(14), 43(27)), 41(48), 39(11), 31(44).

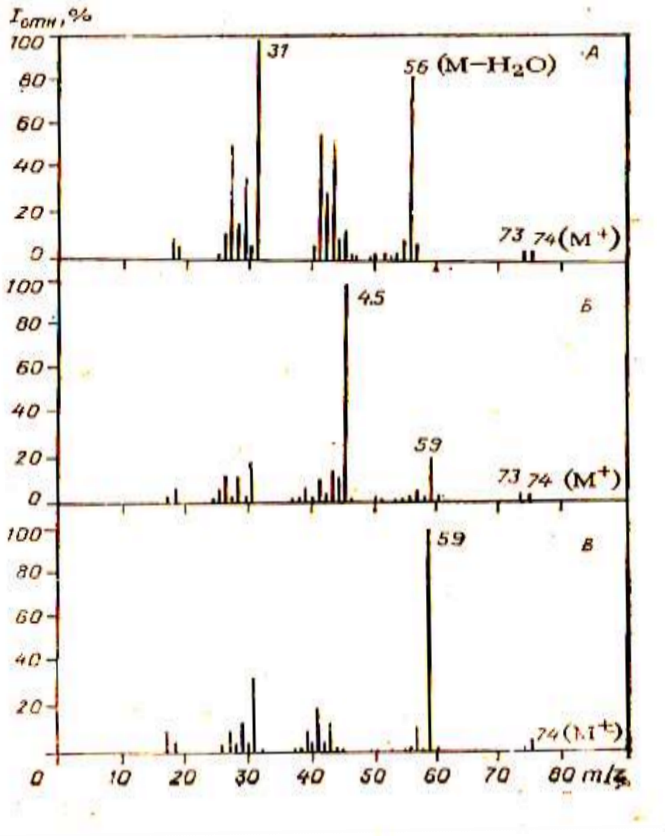
7. What isomer of butanol corresponds to the mass spectra of AB? Explain the main direction of ion fragmentation.

8. Which of the 1- and 2-chloroheptane substances corresponds to the mass spectrum of AB? Explain the reason for the formation of 2 molecular ion peaks in the mass spectrum of this compound. Express the main direction of fragmentation.

9. The mass spectrum of pentanol isomers is shown below. What is the structural formula of the substances before AB?



Task 5



Task 7

10. Which amino acid ethyl ester (A or B) does the mass spectrum shown in the figure correspond to?

CH_3CH_2-CH(NH_2)-$COOC_2H_5$ (A) CH_3-CH (NH_2)-CH_2-$COOC_2H_5$ (B)

REPUBLIC OF UZBEKISTAN
MINISTRY OF HIGHER EDUCATION, SCIENCE AND INNOVATION

NAMANGAN STATE UNIVERSITY

«APPROVED»
Vice-Rector for academic Affairs
O'QUV-USLUBIY B.D.Kholmatov
BOSHQARMASI
«____» _____ 2023

WORKING TRAINING PROGRAMM
BY SUBJECT
PHYSICAL RESEARCH METHODS

For 4th year full-time education

Field of knowledge:	**100000- Humanities**
Field of education:	**140000- Natural sciences**
Direction:	**5140500 - Chemistry**

Namangan-2023

Item/module code FTUB406		Academic year 2023/2024	Semester 7	ECTS credits 6
Item/module type required		Language of instruction Russian		Number of hours per week 4 hours
1	Item name	Classroom lessons (hours)	Self-study(hours)	Total load (hours)
	Physical research methods	6 0	120	18 0

1. SUBJECT CONTENT

The purpose of teaching the subject is to provide knowledge on the use of physical research methods in quality control of chemical, food, pharmaceutical and various industrial products and the rational choice of a method for solving a specific analytical problem, to form a scientific worldview.

The objectives of the subject are to prepare students to understand the physical meaning of each method, its parameters, the dependence of the values of spectroscopy parameters on the structure of matter, as well as to solve spectral problems associated with each method.

II. MAIN THEORETICAL PART (LECTURES)

II.1 . _ The subject content includes the following topics :

1-topic. Theoretical foundations of chromatography.

Classification of chromatography methods. Thin layer chromatography and its basics (TLC).

2-topic. Gas-liquid chromatography.

Sorbents and eluents. Detectors used in chromatography (UV, diode array, fluorescent, refractometric, electrochemical, mass spectrometric).

3-topic. Classification of molecular methods spectroscopic analysis.

Chromophore groups. Chromophores, bathochromic and hypsochromic shifts. UV spectra of ethylene and acetylene derivatives. Absorption of diene and polyene systems.

4-topic. Application of IR spectroscopy to identify functional groups and characteristic components.

Characteristic frequencies and intermolecular interactions, their influence on the frequency value. Stretching and bending vibrations, their types, fundamental and overtone frequencies.

5 - topic. Vibrations of oxygen-containing compounds .

Determination of the type of hydrogen bonds by the intensity and value of the hydroxyl group. Method for determining the presence of conformers in saturated cyclic alcohols. Spectra of compounds containing a carbonyl group, factors influencing the

frequency value.

6-topic. Nuclear magnetic resonance (NMR) spectroscopy.

Physical characteristics of the nuclear magnetic resonance spectroscopy method. Types of nuclear magnetic resonance spectroscopy methods .

7 - topic. Spin-spin effect constants.

Resonance states of the main functional groups, the value of the spin-spin effect constant. Geminal and vicinal protons, constant values. Using the spin-spin effect constant in studying the spatial structure of a molecule.

8-topic. Spectroscopy of the ^{13}C isotope.

Spectroscopy of the ^{13}C isotope, its characteristics, chemical shift values, "off" resonance spectra.

9 - topic. Fundamentals of mass spectroscopy.

Ionization . Decoding the results in the mass spectrum .

10- topic . Patterns of decay of compounds with open and closed chains in mass spectrometry.

Ionization methods . _ Fragment ions, metastable ions. Rearranged and multiply charged ions .

11-topic. X-ray diffraction analysis (XRD).

Basics of SAR. Steric factors. Crystals. Elements of symmetry. The effect of X-rays on the molecules of substances.

12-topic. Solving chemical problems using spectroscopic and chromatographic analysis methods.

Solving chemical problems using spectroscopic and chromatographic analysis methods.

II . 2. Hourly distribution of lectures

No.	Themes	watch
1	Theoretical foundations of the chromatographic method.	4
2	Gas-liquid chromatography.	4
3	Classification of molecular spectroscopic analysis methods.	4
4	Application of IR spectroscopy to identify functional groups and characteristic components.	2
5	Vibrations of oxygen-containing compounds.	2
6	NMR spectroscopy.	2
7	Spin-spin effect constants.	2
8	Spectroscopy of the ^{13}C isotope.	2
9	Fundamentals of mass spectroscopy.	2
10	Patterns of decay of compounds with open and closed chains in mass	2

	spectrometry.	
eleven	X-ray diffraction analysis (XRD).	2
12	Solving chemical problems using spectroscopic and chromatographic analysis methods.	2
	Total:	30 hours

III . 1. DISTRIBUTION OF PRACTICAL LESSONS

No.	THEMES	Watch
1	Absorption tables of the main chromophore groups. Solving problems related to the analysis of the UV spectrum of organic substances of a certain structure using tables.	2
2	General table of the main absorption frequencies in IR spectroscopy . Methods of spectral analysis. Solving special problems of the 2nd type in IR spectroscopy (the problems indicate the gross formula of the substance)	2
3	Solving special problems of the 2nd type in IR spectroscopy (the problems indicate the gross formula of the substance)	2
4	Types of NMR spectrometers (N-60, Varian-100, Tesla-100). Introduce students to the operating principle of spectrometers and obtain a spectrum. Preparation of solutions. Familiarization with the process of integration and use in practice.	2
5	NMR solution of type problems based on the spectra of the ^{1}H isotope, that is, the spectrum of the substance, the structure or formula of the substance and the method of complete analysis of the spectra are given.	2
6	The integration method analyzes the solution of type II problems on the NMR spectra of the ^{1}H isotope, i.e. in which only the gross formula and spectrum of the substance are given.	2
7	NMR spectra of the ^{13}C isotope are similar to the method of NMR spectra of the ^{1}H isotope for solving problems of types I and II .	2
8	Solving chemical problems in an online system based on Cambridge University database.	2
9	Analysis of IR , $^{1H\ NMR}$ and $^{13C\ NMR\ spectra}$ of given substances using computer modeling programs .	2
10	Determination of the structure of organic matter of unknown composition. (according to the given data IK- , NMR- ^{1}H , NMR- ^{13}C).	2
	Total:	20

IV . 1. HOUR DISTRIBUTION OF SEMINARS

No.	SEMINAR TOPICS	watch
1	The influence of various solvents on the shift of UV spectra .	2
2	Operating principles of modern IR spectrometers.	2
3	IR spectrum frequencies and vibration types.	2
4	Spin-spin effect constants.	2
5	Study of organic substances using mass spectrometry.	2
	Total:	10

I V.1. SUBJECTS OF INDEPENDENT WORK	
1	Preparation for practical training
2	Preparation for seminars
3	Types of modern mass spectrometers and principles of their operation.
4	Types of modern IR spectrometers and principles of their operation
5	Types of modern NMR spectrometers and principles of their operation
6	Combined use of UV, IR, NMR and mass spectrometry methods in determining the structure of substances.

V. EXPECTED RESULTS (FORMED COMPETENCIES)

A student who has mastered the program should know:

• types of physical research methods;
• laws of optical, radio spectroscopic and mass spectroscopic methods;
• types of electronic transitions, types of vibrations and their frequencies;
• magnetism of atomic nuclei, diamagnetic, shielding and paramagnetic processes;
• double resonance type;
• paramagnetism of free radicals;
• have an understanding of the processes of ionization and dissociation;
• parameters and units of measurement of ultraviolet, nuclear magnetic resonance and mass spectroscopic methods;
• determine the spatial position of the structure of a substance and tautomeric manifestations in solution using spectral parameters;
• similarities and differences between infrared and proton magnetic resonance (PMR);
• know and be able to use methods of simultaneous use of ultraviolet, infrared, nuclear magnetic resonance and mass spectroscopy in determining the structure of substances;
• knows how to analyze the results obtained by all spectroscopic methods;
• Determination of the presence of intramolecular and intermolecular hydrogen bonds in substances using IR spectroscopy;
• determination of keto-, enolamine-, imine-tautomeric forms based on the study of IR spectra of solutions of substances;
• must have skills in identifying cis and trans isomers using ultraviolet, infrared and nuclear magnetic resonance.

VI. EDUCATIONAL TECHNOLOGIES AND METHODS

- ✓ □ lectures;
- ✓ □ interactive case studies;
- ✓ □ seminars (logical thinking, quick questions and answers);
- ✓ □ work in groups;
- ✓ □ individual projects
- ✓ □ projects for teamwork and protection

VI I. _ REQUIREMENTS FOR OBTAINING LOANS.

Credits allocated for the subject are provided to students in case of positive results of various types of control for each semester.

Intermediate (IC) and final (IC) types of control are used to assess students' knowledge in the natural sciences. Rating by type of control: 5 – “excellent”, 4 – “good”, 3

– “satisfactory”, 2 – “unsatisfactory” according to the assessment criteria.

Intermediate control is carried out once a semester in the form of written work.

During the semester, students are regularly assessed and graded for each subject in practical (seminar) classes. This takes into account the student’s timely and complete completion of practical (seminar) training and independent educational assignments, as well as his activity in the classroom.

In addition, when assessing by type of intermediate control, grades received for practical (seminar) classes and independent study assignments are taken into account. In this case, the average of the scores obtained from each intermediate type of control is re-averaged with the score obtained from the intermediate type of control.

The assessment obtained at the intermediate control is recorded in the protocol as the result of the intermediate control.

Final control is carried out at the end of the semester in the form of a test or written work according to the approved schedule.

Evaluation criterion for intermediate (IC) and final (IC) types of control:

The student makes independent conclusions and decisions, can think creatively, independently observe, can apply the acquired knowledge in practice, understands the essence of the subject (topic), knows, knows how to express, tell and is considered to have an understanding of the subject (topic) - score “5” (Great);

When a student conducts independent observation, knows how to apply the acquired knowledge in practice, understands the essence of the subject (topic), knows, knows how to present, tell and has an idea about the subject (topic) - grade “4” (good);

When the student knows how to apply the acquired knowledge in practice, understands the essence of the topic (subject), knows, knows how to present, tell and has an idea about science (subject) - grade “3” (satisfactory);

When it is considered that the student has not mastered the science program, does not understand the essence of the subject and has no idea about the topic (subject), he is given a grade of “2” (unsatisfactory).

BASIC LITERATURE :

1.Introduction to Spectroscopy, Fifth Edition Donald L. P. Lampman, George S. Kriz, and James R. Vyvyan Department of Western Washington University, Bellingham, Washington. Cengage Learning. 786 p.

2. Physical research methods in chemistry. Pentin Yu.A. 2012

3. Becker Y. "Spectroscopy". Per. from German M. _ " Technosphere ", 2009, 528 p .

4. Elsa Lundanes, Leon Reubsaet, Tyge Greibrokk, Chromatography Basic Principles, Sample Preparations and Related Methods. Wiley-VCH Verlag GmbH & Co. KGaA, Boschstr. 12, 69469 Weinheim, Germany. 2014 Pp 223.

5. Khaitbaev A . Kh ., Maulyanov WITH . A . Toshov X . WITH . Organic Tuzilishini UB - va IR - spectrum usullari yordamida tagilil kilish . ЎзMU bosmahonasi. 2020 84 b.

ADDITIONAL LITERATURE:

6. Mirziyoyev Sh.M. Erkin na farovon, democrat Uzbekiston birgalikda barpo etamiz. UzR President lavozimiga tantanali marosimiga ba gishlangan Oliy Majlis palatalarining qushma mazhlisidagi nutk, Toshkent, 2016. 56-b.

7. Mirziyoyev Sh.M. Tanqidiy taҳlil, qatii tartib-intizom va shakhsiy zhavobgarlik - har bir raҳbar faoliyatining kundalik qoidasi bolishi kerak. Mamlakatimizni 2016 yilda izhtimoiy-iqtisodiy rivozhlantirishning asosy yakunlari va 2017 yilga muljallangan iqtisodiy

dasturning eng mukhim ustuvor yўnalishlariga bagishlangan Vazirlar Makhkamasining kengaitirilgan majlisidagi maruza , 2017 January 14 - Tashkent, Uzbekistan , 2017. 104-b.
8. Yunusov T.K., Zainutdinov U.N., Uteniyazov K., Salikhov Sh.I. Kimyoda fizikavy usullar. Tashkent. "University", 2007
9. Vasilyeva V. I. Spectral methods of analysis. Practical guide. Moscow Lan", 2014. 416c. http://e.lanbook.com/books /element.php?pl1 id=50168
10. Tarasevich B.N. IR spectra of the main classes of organic compounds. Reference materials. Moscow. MSU-2012. 54 p.
11. Prech E. Determination of the structure of organic compounds. Spectral data tables - trans. from English - Knowledge Laboratory, M.: Mir: BINOM. 2012. - 438 p.
12. Yashin Ya.I., Yashin E.Ya. Gas chromatography. M.: TransLit., 2009. - 512 p.
13. Sychev K.S. A practical guide to liquid chromatography. M.: Technosphere. 2010. - 272 p.
14. Khaitbaev A.Kh., Eshimbetov A.G., Toshov Kh.S. Ph- and IR-spectral methods for studying organic compounds. Services qўllanma. ЎзMU bosmahonasi. 2015 72 b.
INTERNET RESOURCES
15. Mass spectra database. - http: //www.massbank.jp/
16. Database of the National Institute of Modern Industrial Science and Technology, Japan. - http://riodb01.ibase.aist.go.jp/sdbs/cgi -bin/direct_frame_top.cg
17. Database of the US National Institute of Standards and Technology on properties of compounds. - http://webbook.nist.gov/chemistry/
18. Practical course on NMR spectroscopies http://www.chem.msu.su/rus/teaching/nifantev/2006 NMR.pdf
19. www.nuuz.uz. _
20. www.nallib.uz .
21. www.ziyo.net.uz. _
22. www.xumuk.ru .

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GLOSSARY

Absolute retention time

Absolute Retention Time . This term is sometimes used for the time elapsed between the injection of a sample and the occurrence of the maximum zone concentration of a substance. This time is more often and correctly called retention time. In some cases it is defined as the center of mass or the first moment of the distribution of concentrations. For unsymmetrical peaks, the two definitions are different. Symbol: T_R.

Absolute retention volume

Absolute Retention Volume. True retention volume. This is the volume of gas corresponding to the absolute retention time. For this reason, the use of these two terms should be avoided. Symbol: V_R.

Adsorbent

Adsorbents. Materials, usually having a large specific surface area, that adsorb organic vapors more strongly than the carrier gas . The value of the adsorption constant depends on the structure, molecular weight, polarizability and dipole moment of the vapor molecules, so it differs from substance to substance, making separation possible. The most useful adsorbents in GC are: graphitized carbon black, silica gel, zeolites (molecular sieves), aluminum oxide, porous polymers and activated carbons.

Adsorption chromatography

Adsorption Chromatography . A variant of chromatography in which an adsorbent is used as a stationary phase. Also called gas adsorption chromatography.

Adsorption

Adsorption. A physicochemical process in which there is a difference in concentration at equilibrium in a bulk phase (gas or liquid) and at the interface between that phase and another phase. Adsorption can occur at the gas-solid , liquid-solid, or gas-liquid interfaces . In all cases, such adsorption leads to some retention of the substance. This is the significant or only contribution in gas adsorption chromatography, but in gas-liquid chromatography, a significant contribution to retention can be made by adsorption at the gas-liquid or liquid-solid interface, or at both of these interfaces.

Adsorbent activation

Activation of Adsorbent. Many adsorbents used in gas chromatography readily adsorb water and possibly some contaminants found in the laboratory atmosphere during storage. In this case, the surface of the adsorbent becomes much less polar and the adsorption energy is significantly reduced, the product gives low retention volumes and exhibits a low degree of selectivity. Additionally, since the carrier gas is typically dry, sorbates are slowly desorbed and column retention properties are slowly altered, preventing reproducible results from being achieved. Before using an adsorbent in gas adsorption chromatography, it is necessary to remove these sorbates from its surface in a dry atmosphere or under vacuum. This is especially true for molecular sieves, silica gel and alumina.

Vapor phase analysis over liquid

Headspace Analysis. Headspace analysis is an analytical technique for volatile substances contained in a complex matrix, such as biological fluids, foods or beverages. It consists of analyzing an aliquot of the gas phase that is in equilibrium with the sample contained in a closed vessel. This eliminates the rapid contamination and destruction of the column by repeated injection of nonvolatile substances contained in these samples, and therefore requires less experimental work than solvent extraction and involves less risk of contamination. Calibration is a critical task because the solubility of analytes in the matrix is often very different from their solubility in pure water.

Apiezon

Apiezon. Originally manufactured as vacuum lubricants, these products, which are believed to be saturated hydrocarbons with high molecular weight, are obtained as residues from the molecular distillation of heavy petroleum fractions. As a stationary phase they are much more polar than sivalane and contain significant amounts of polar products (oxidation products) which can be removed by simple liquid chromatography on florisil. The most popular is apiezon L; areas M and N are also used. Their maximum temperature of use is about 250 °C.

Argon ionization detector

Argon Ionization Detector. This detector was described by Lovelock in 1958. It is more sensitive than the flame ionization detector and has a shorter time constant. However, it is more sensitive to contamination and has a lower linear dynamic range. The operating principle of this detector is based on the reaction of organic vapors with excited, metastable argon atoms, resulting in the ionization of these vapors to produce electrons, which are collected. The resulting current is a measure of the mass flow of substances through the detector. Metastable argon atoms are formed when argon collides with accelerated secondary electrons formed as a result of irradiation of the gas contained in the detector cell with p-rays emitted by radioactive foil (^{90}Sr, ^{63}Ni, ^{3}H) placed on the detector wall. The detector does not respond to He , Ne, Kg, H_2 , N_2 , O_2 , CO, CO_2 , CH_4 , halogens and fluorocarbons, which all have an ionization potential greater than the excitation potential of argon. The detector signal is extinguished by water.

Peak asymmetry

Peak asymmetry. The ratio of the front and back half-widths of the peak. Sometimes the ratio of the front and rear parts of the peak width at a certain fraction of the height , for example, 0.10. Symbol: As.

Airgel

Aerogels. Many of the adsorbents used in GC are prepared in the liquid phase, from a dispersed gel-like system. If the solvent contained in the gel can be removed without significant shrinkage of the gel matrix and the dry structure is not destroyed, the product is called an airgel. This is the case with silica gels and with glass gels obtained by alkaline etching of borosilicate glasses followed by heat treatment, which creates uniform pores with somewhat controlled sizes. Gels that shrink or break when the dispersing agent is removed are called "xerogels".

B

Bypass injector

Injector . A type of injector in which a gas chamber, which can be isolated from the main flow with sample and can then be introduced into the main flow of mobile phase using taps.

IN

Eddy diffusion

Eddy Diffusion. Contribution to zone erosion due to the uneven distribution of linear flow velocities around filler particles in a packed column. Molecules move along the column, following paths of varying lengths at varying speeds. This results in a contribution to the variance of residence time that depends not on the nature of the substance and its retention, but on the particle size and particle size distribution, and probably on the quality of the packing, although this latter factor has never been properly investigated .

External standard

External Standard. A pure substance or calibration mixture injected periodically into the column between sequences of: controlled product flow sample analysis.

Internal standard

Internal Standard. A substance added in a known quantity to an aliquot of a mixture to be analyzed. After proper calibration, the quantitative composition of the mixture is obtained from the ratio of the peak areas of the substances of interest and the internal standard. The substance(s) used as an internal standard must be chemically similar to the analytes, elute fairly closely, but be well separated from all other components.

Throttle delay time

Hold-up Time (Volume) Cm . GasHold-up Time (Volume)

Gas delay time (volume) (Gas Hold - up Time (Volume)). The retention time (retained volume) of an inert or unretained substance on a chromatography column. In a GC, the gas retention volume is essentially equal to the column volume available to the gas phase. Symbol: tm or t_0 .

Retention time

Retention Time. 1) Absolute or total: time elapsed between sample injection and elution of peak maximum. 2) normalized: absolute retention time minus dead time or "air" retention time. 3) corrected: absolute retention time corrected for gas compressibility. 4) effective : absolute retention time corrected for both mobile phase compressibility and gas retention time in the column; also called fully corrected retention time, 5) specific: effective retention time at standard temperature and pressure divided by the amount of liquid phase in the column or the total surface area of the adsorbent. 6) true: synonymous with given. 7) complete: see absolute.

Air retention time

Air Retention Time . An obsolete term for gas delay time.

Peak cutting and weighing

Cutting and weighing the peak (Gut and Weigh). Method for determining peak area in quantitative analysis. The peaks of each component of the mixture in the chromatogram are cut out with scissors and pieces of paper, together with a square of paper having a known side length , are weighed. Errors occur due to incorrect drawing of the zero line, incorrect cutting of peaks and insufficient uniformity of the paper. This method is very economical in terms of capital investment and very expensive in terms of labor.

Peak height

Peak Height. The maximum difference between the detector signal and the background during peak elution. The distance between the maximum of a peak and its base, measured along the axis of the signal. Symbol: p.

Plate height

Plate Height. Column length corresponding to one theoretical plate. Height equivalent to a theoretical plate . Symbol: N.

Height equivalent to theoretical plate

Height Equivalent to a Theoretical Plate. A measure of the efficiency of a column. The value obtained by dividing the column length by the number of theoretical plates. Symbol: VETT (NETR) or N.

Size exclusion chromatography

Displacement chromatography . A type of chromatography in which the mobile phase is displaced immediately after sample introduction by a fluid retained more strongly than the last component of the eluted sample. This method has found very little use in gas chromatography, probably under the influence of the erroneous belief that the displacer should be much more sorbed or dissolved than the most retained component of the mixture being analyzed. It just needs to be held a little more firmly. The value a=1.2 is, of course, quite large.

G

Carrier gas

Carrier Gas. Mobile phase in gas chromatography. Gas -Solid Chromatography . A type of chromatography in which gas is used as the mobile phase and an adsorbent as the stationary phase.

Gas adsorption chromatography on adsorption layers

- Adsorption Layer Chromatography . A type of chromatography in which an adsorbent is used as a stationary phase, modified by the application of a small amount of liquid with a low vapor pressure, usually constituting one monolayer or some fraction of a monolayer. Also called gas adsorption chromatography on modified adsorbents. See chap. 7. Gas volume of the column (Interstitial Volume). The portion of the column volume accessible to the gas phase. Also called dead volume or gas retention volume. It includes the volumes of space between particles and pores within particles.

Gas-liquid chromatography

Gas -Liquid Chromatography . A type of chromatography that uses a gas as the mobile phase and a non-volatile liquid as the stationary phase.

Helium detector

Helium Detector. Argon ionization detector (Lovelock detector) operating with helium as the carrier gas. Since metastable helium has a higher energy than the ionization potential of all molecules except He and Ne, this makes sensitive detection of all gases and vapors possible. Extremely sensitive to contamination.

Pressure gradient

Pressure Gradient. The difference between the inlet and outlet pressure of the column, divided by the length of the column. Pressure differential along the abscissa.

GC-MS

GC–MS (GC–MS). Analytical instrument and methods that use it. It is a combination of a gas chromatograph, which separates the components of a mixture, and a mass spectrometer, which analyzes the column eluate and produces mass spectra for the separated substances.

D

Deactivation

Deactivation. Treatment of the stationary phase carrier and possibly the column walls and gas lines to remove active adsorption sites that have high adsorption energies and possibly slow desorption kinetics and are responsible for peak tailing and even partial or complete loss of some sample components. Decontamination is accomplished primarily by
1) application of non-volatile, highly polar compounds (e.g., detergents) or suitable polymers,
2) chemical surface treatment (e.g., acid or even aqua regia washing), 3) silanization, or 4) use of polar vapor mixed with gas. -a carrier (for example, water vapor or ammonia).

chromatography

Chromatography is a physicochemical method for separating and analyzing mixtures of gases, vapors, liquids or dissolved substances using sorption methods under dynamic conditions.

Absorption - absorption.

Matter consists of many identical atoms that are capable of moving to different energy levels, emitting or absorbing quanta of different frequencies.

Wave number /ῦ/ - the number of waves per unit distance.

Radioactivity detectors - radioactive radiation counters. Depending on the principle of action, they are divided into ionization, scintillation, etc.

Wavelength / λ / - the distance between two adjacent wave maxima.

Diffraction is the scattering of X-rays as they pass through a substance.

Diffusion is the process of transfer of substances/ions, molecules, particles of dispersed systems from an area of higher to an area of lower concentration.

Intensity / I / - in practice, the intensity is taken to be the signal value in arbitrary units, for example, the number of divisions of the instrument scale.

Emission is a spontaneous process, because an atom always strives to move from an excited /unstable/ state to a more stable state with lower energy.

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.

Fire resistance is the ability of products to ignite or burn with greater or lesser intensity.

The plane of polarization is the plane in which the magnetic field oscillates.

Absorption is a forced process that increases the energy of an atom due to the absorbed photon.

Radioactive background is the level of radioactive radiation caused by the natural radioactivity of the environment and cosmic rays.

Radionuclides are chemical elements subject to radioactive decay. Each radionuclide has a constant, unique half-life, which can range from a few seconds to millions .

Light is electromagnetic radiation that has a dual (wave and corpuscular) nature.

The absorption spectrum is the totality of all absorption spectral lines.

A spectral line is a collection of photons of the same frequency. When absorbed, it is called absorption, when emitted, it is called emission.

The absorption spectrum of a substance is a graphical representation of the distribution of energy absorbed by it over wavelengths.

Spectrophotometry - absorption of monochromatic light.

The emission spectrum is the totality of all emission spectral lines.

Fluorescence is a glow with a duration of about 10^{-8}-10^{-10} s.

Phosphorescence is a glow with a duration of the order of 10^{-8} s to several. hour.

Photocolorimetry - absorption of polychromatic / white / light in the region of 380-760 nm.

A photon is a material particle with a certain mass and momentum, deviating from a straight path under the influence of gravity, but unlike other material bodies, moving only at the speed of light.

The photoelectric effect is the phenomenon of electron separation from atoms of substances under the influence of a light flux.

Chromophores are groups of atoms that cause selective absorption of light in a certain region of the spectrum, as a result of which a substance containing chromophoric groups can be colored in a certain color.

The electromagnetic spectrum is the totality of all frequencies / wavelengths /.

Electron paramagnetic resonance / EPR / - manifests itself in electrons whose energy levels are split in a magnetic field into two sublevels with the electron spins oriented either along the field or against the field.

Nuclear magnetic resonance / NMR / - manifests itself in the nuclei of atoms that have a magnetic moment.

General issues

1. What is the consumer value of consumer goods, consumer properties, their relationship and interrelation?
2. What characterizes product quality and quality levels?
3. What factors influence product quality?
4. What is a production batch, sample /sample/ - spot, combined, average, average sample?
5. What is the sampling technique for quality control of consumer products?
6. What properties of goods are considered physical and chemical when determining product quality?
7. What methods exist for measuring the properties of products ?
8. What is the classification of instrumental methods for studying product quality?
9. What are organoleptic methods for analyzing product quality?
10. What factors influence the optical properties of food products?
11. What methods are used to study the physicochemical properties of products ?
12. What methods exist for determining the optical characteristics of products?
13. In what units is wavelength measured in the SI system?
14. What is the electromagnetic spectrum?
15. What are the main areas of the electromagnetic spectrum that you know?

16. What are optical analysis methods based on?
17. What are nuclear analysis methods based on?
18. What are X-ray analysis methods based on?
19. What are radionuclides?
20. What is radioactivity and its types?
21. What methods exist for recording radioactive radiation?
22. What are the indicators /doses/ of radiation?
23. What is a radioactive background?
24. What thermophysical properties of products need to be measured?
25. How can functional groups of food ingredient molecules influence the formation of product properties ?
26. What methods of microscopic examination do you know?
27. What is mass spectrometry used for?
28. What types of chromatographic studies do you know?
29. What methods can be used to determine the color characteristics of non-luminous bodies?
30. How do you understand the concept of “thermal resistance”?

31. Theoretical basis of the nuclear magnetic resonance method.
32. Areas of application of mass spectrometry.
33. Ion scattering spectroscopy.
34. What methods can be used to determine the color characteristics of non-luminous bodies?
35. Flame emission photometry.
36. X-ray photoelectron spectroscopy.
37. Proton magnetic resonance.
38. What is light in colorimetry?
39. Chemical shift in the nuclear magnetic resonance method. Formula for calculating chemical shift.
40. What is the basis of color measurement using photoelectric colorimeters?
41. Describe the concepts of “color” and “light”.
42. Schematic diagram of a mass spectrometer.
43. Basic colorimetric and photometric quantities.
44. Areas of application of atomic absorption spectroscopy.
45. Theoretical foundations of the atomic absorption spectroscopy method.
46. Schematic diagram of nuclear magnetic resonance devices.
47. Electron paramagnetic resonance.
48. Chromatic and achromatic color.
49. Theoretical foundations of atomic emission spectroscopy.
50. What is the basis of color measurement using comparators?
51. Auger electron spectroscopy. Areas of use.
52. Electron impact spectroscopy.
53. What is the basis for measuring color in visual colorimeters?
54. Atomic emission spectroscopy.
55. Basics of color measurement.
56. What is organoleptic evaluation of food products?
57. What is the difference between photo and spectrometric methods of analysis?
58. What types of luminescence do you know?
59. The essence of the infrared spectroscopy method.
60. What photometric and spectrometric analysis methods do you know?
61. What thermometric characteristics do you know?
62. List the optical analysis methods used to control the quality of consumer products?
63. What are phosphors?
64. What are optical atomic spectroscopic methods of quality control based on?
65. Theoretical foundations of X-ray spectral analysis.
66. What quantities and units of measurement of radioactivity do you know?
67. What is the essence of the phenomenon of luminescence?
68. What are radioactivity detectors?
69. The essence and theoretical foundations of electromagnetic radiation /EMR/, its parameters.
70. What is concentration quenching?
71. The essence of gas chromatography.

72. Liquid and liquid solid-phase chromatography.
73. Give a classification of the most important chromatographic methods of analysis.
74. What methods of analyzing the thermal properties of products do you know?
75. What is radioactivity, radionuclides, radioactive background, types of radioactivity?
76. What are chromophores?
77. What is color?

MAIN LITERATURE:

1.Introduction to Spectroscopy, Fifth Edition Donald L. P. Lampman, George S. Kriz, and James R. Vyvyan Department of Western Washington University, Bellingham, Washington. Cengage Learning . 786 p .
2. Physical research methods in chemistry. Pentin Yu.A. 2012
3. Becker Y. "Spectroscopy". Per. from German M. _ " Technosphere ", 2009, 528 p .
4. Elsa Lundanes, Leon Reubsaet, Tyge Greibrokk, Chromatography Basic Principles, Sample Preparations and Related Methods. Wiley-VCH Verlag GmbH & Co. KGaA, Boschstr. 12, 69469 Weinheim, Germany. 2014 Pp 223.
5. Kha and Tbaev A . Kh ., Maulyanov WITH . A . Toshov X . WITH . Organic Tuzilishini UB - va IK - s pectr _ usullari yordamida ta holil qilish. ЎзMU bosmahonasi. 2020 84 b.

ADDITIONAL LITERATURE:

6. Mirziyoyev Sh.M. Erkin na farovon, democrat Uzbekiston birgalikda barpo etamiz. UzR President lavozimiga tantanali marosimiga bagishlangan Oliy Majlis palatalarining qushma mazhlisidagi nutk, Toshkent, 2016. 56-b.
7. Mirziyoyev Sh.M. Tanqidiy taҳlil, qatii tartib-intizom va shakhsiy zhavobgarlik - har bir raҳbar faoliyatining kundalik qoidasi bolishi kerak. Mamlakatimizni 2016 yilda izhtimoiy-iqtisodiy rivozhlantirishning asosy yakunlari va 2017 yilga muljallangan iqtisodiy dasturning eng mukhim ustuvor yўnalishlariga bagishlangan Vazirlar Makhkamasining kengaitirilgan majlisidagi maruza , 2017 January 14 - Toshkent, Uzbekistan, 2017. 104-b.
8. Yunusov T.K., Zainutdinov U.N., Uteniyazov K., Salikhov Sh.I. Kimyoda fizikavy usullar. Tashkent. "University", 2007
9. Vasilyeva V. I. Spectral methods of analysis. Practical guide. Moscow Lan", 2014. 416c. http://e.lanbook.com/books /element.php?pl1 id=50168
10. Tarasevich B.N. IR spectra of the main classes of organic compounds. Reference materials. Moscow. MSU-2012. 54 p.
11. Prech E. Determination of the structure of organic compounds. Spectral data tables - trans . from English - Knowledge Laboratory, M.: Mir: BINOM. 2012. - 438 p.
12. Yashin Ya.I., Yashin E.Ya. Gas chromatography. M.: TransLit., 2009. - 512 p.
13. Sychev K.S. A practical guide to liquid chromatography. M.: Technosphere. 2010. - 272 p.
14. Khai Tbaev A.Kh., Eshimbetov A.G., Toshov Kh.S. UV and IR spectral methods for studying organic compounds. Services q ўllanma. ЎзMU bosmahonasi. 2015 72 b.

INTERNET RESOURCES

15. Mass spectra database. - http : // www . massbank . jp /
16. Database of the National Institute of Modern Industrial Science and Technology, Japan. - http : //riodb01.ibase . _ _ aist . go . jp / sdbs / cgi - bin / direct_frame_top . _ _ _ _ cg
17. Database of the US National Institute of Standards and Technology on properties of compounds. - http :// webbook . nist . gov / chemistry /
18. Practical course on NMR spectroscopies http :// www . chem . msu . su / rus / teaching / nifantev /2006 NMR . pdf
19. www . nuuz . uz .
20. www . nallib . uz .
21. www . ziyo . net . uz .
22. www . xumuk . ru .