

Instrumental methods of analysis

Electrochemical methods of analysis

Electrochemical methods of analysis

- ▶ Electroanalytical chemistry includes electrochemical methods of analysis based on electrode reactions and on the transfer of electricity through solutions.
- ▶ Electrochemical processes are processes that are accompanied by simultaneous chemical reactions and changes in the electrical properties of the system, which in such cases can be called an electrochemical system.
- ▶ The electrochemical system contains an electrochemical cell including a vessel with an electrically conductive analyte solution in which the electrodes are immersed.

Classification of electrochemical analysis methods

1. Classification based on taking into account the nature of the source of electrical energy in the system. There are two groups of methods.

a) Methods without imposing an external (extraneous) potential. The source of electrical energy is the electrochemical system itself, which is a galvanic element (galvanic circuit). Such methods include potentiometric methods. The electromotive force — EMF — and electrode potentials in such a system depend on the content of the substance being determined in the solution.

Classification of electrochemical analysis methods

b) Methods with the imposition of an external (extraneous) potential:

- ▶ Conductometric analysis is based on measuring the electrical conductivity of solutions as a function of their concentration;
- ▶ Voltammetric analysis is based on the measurement of current as a function of the applied known potential difference and the concentration of the solution;
- ▶ Coulometric analysis is based on measuring the amount of electricity passed through a solution as a function of its concentration;
- ▶ Electrogravimetric analysis is based on measuring the mass of the product of an electrochemical reaction.

Classification of electrochemical analysis methods

2. Classification according to the method of application of electrochemical methods:

- ▶ a) Direct methods. The electrochemical parameter is measured as a known function of the concentration of the solution and, according to the indication of the corresponding measuring device, the content of the substance to be determined in the solution is found. .
- ▶ b) Indirect methods are titration methods in which the end of titration is fixed based on the measurement of the electrical parameters of the system.

Potentiometric analysis

- ▶ Potentiometric analysis (potentiometry) is based on the measurement of EMF and electrode potentials as a function of the concentration of the analyzed solution.
- ▶ In potentiometric measurements, two electrodes are used in an electrochemical cell: an indicator electrode, the potential of which depends on the concentration of the detectable (potential-determining) substance in the analyzed solution, and a reference electrode, the potential of which remains constant under the conditions of analysis.
- ▶ The EMF value can be calculated as the difference between the real potentials of these two electrodes

Potentiometric titration

- ▶ Potentiometric titration is a method for determining the volume of titrant spent on titration of the substance being determined in the analyzed solution by measuring the EMF (during titration) using a galvanic circuit composed of an indicator electrode and a reference electrode. During potentiometric titration, the analyzed solution located in the electrochemical cell is titrated with a suitable titrant. fixing the end of titration by a sharp change in the EMF of the measured circuit — the potential of the indicator electrode, which depends on the concentration of the corresponding ions and changes dramatically at the equivalence point.

Application of potentiometric titration

- ▶ Application of potentiometric titration. The method is universal, it can be used to indicate the end of titration in all types of titration: acid-base, redox, compleximetric, precipitation, titration in non-aqueous media. Glass, mercury, ion-selective, platinum, silver electrodes are used as indicator electrodes, and calomel, silver chloride, and glass electrodes are used as reference electrodes.
- ▶ Many medicinal substances are analyzed by potentiometric titration methods, for example, ascorbic acid, sulfamide preparations, barbiturates, alkaloids.

Advantages of the method

- ▶ The method has high accuracy and high sensitivity: it allows titration in cloudy, colored, non-aqueous media, separately determine the components of the mixture in one analyzed solution, for example, separately determine chloride and iodide ions during argentometric titration.

Conductometric analysis

- ▶ It is based on the use of the relationship between the electrical conductivity (electrical conductivity) of electrolyte solutions and their concentration.
- ▶ The electrical conductivity of electrolyte solutions is judged on the basis of measuring their electrical resistance in an electrochemical cell, which is a glass vessel with two electrodes soldered into it, between which the tested electrolyte solution is located. An alternating electric current is passed through the cell. The electrodes are most often made of metallic platinum, which is coated with a layer of spongy platinum to increase the surface of the electrodes.

Direct conductometry

In direct conductometry, the concentration of a substance in the analyzed solution is determined by the results of measurements of the specific electrical conductivity of this solution.

- ▶ When processing measurement data, two methods are used:
- ▶ the calculation method, the calibration graph method.

Application of direct conductometry

- ▶ It is used to determine the solubility of poorly soluble electrolytes, to control the quality of distilled water and liquid food products (milk, beverages, etc.), to determine the total salt content in mineral, sea, river water and in some other cases.

Direct conductometry

Advantages of the method:

- ▶ simplicity,
- ▶ high sensitivity (up to $\sim 10^4$ mol/l),
- ▶ relatively small error of determination — up to $\pm 2\%$.

Disadvantages of the method:

- ▶ the method is not very selective.

Conductometric titration

- ▶ During conductometric titration, the titration process is monitored by changing the electrical conductivity of the analyzed solution located in a conductometric cell between two inert electrodes (usually made of platinum). According to the data obtained, a conductometric titration curve is drawn, reflecting the dependence of the electrical conductivity of the titrated solution on the volume of the added titrant.

Conductometric titration

- ▶ The end point of titration is most often found by extrapolating sections of the titration curve in the area of its slope change. At the same time, the use of indicators that change color near the end point is not required.
- ▶ Various types of reactions are used in conductometric titration: acid-base, redox, precipitation, complexation processes

Conductometric titration

Advantages of the method:

- ▶ titration can be carried out in cloudy, colored, opaque media
- ▶ , the sensitivity of the method is quite high — up to $\sim 10^{-4}$ mol/l
- ▶ , the determination error is from 0.1 to 2%
- ▶ The analysis can be automated.

Disadvantages of the method:

- ▶ Low selectivity

Polarography

- ▶ Polarographic analysis (polarography) is based on the use of the following dependencies between the electrical parameters of an electrochemical (in this case, polarographic) cell to which an external potential is applied and the properties of the analyzed solution contained therein.

Qualitative polarographic analysis

- ▶ A connection is used between the magnitude of the external electric potential applied on the microelectrode, at which reduction (or oxidation) of the analyzed substance on the microelectrode is observed under these conditions, and the nature of the substance being reduced (or oxidized).

Quantitative polarographic analysis

- ▶ A connection is used between the magnitude of the diffusive electric current established in the polarographic cell after reaching a certain value of the electric potential applied on the microelectrode and the concentration of the substance being determined (reducing or oxidizing) in the analyzed solution.

Quantitative polarographic analysis

- ▶ The electrical parameters — the magnitude of the applied electric potential and the magnitude of the diffusion current — are determined by analyzing the resulting polarization. or volt-ampere curves that graphically reflect the dependence of the electric current in a polarographic cell on the magnitude of the applied potential of the microelectrode. Therefore, polarography is sometimes called direct voltammetry.

Classical polarographic analysis

- ▶ It is based on the use of a mercury dripping microelectrode. In the vessel into which the analyzed solution with the substance to be determined is introduced, there are two electrodes — a microcathode and a macroanode connected to an external source of direct electric current. A negative electric potential gradually increasing in absolute magnitude is applied to the microcathode.

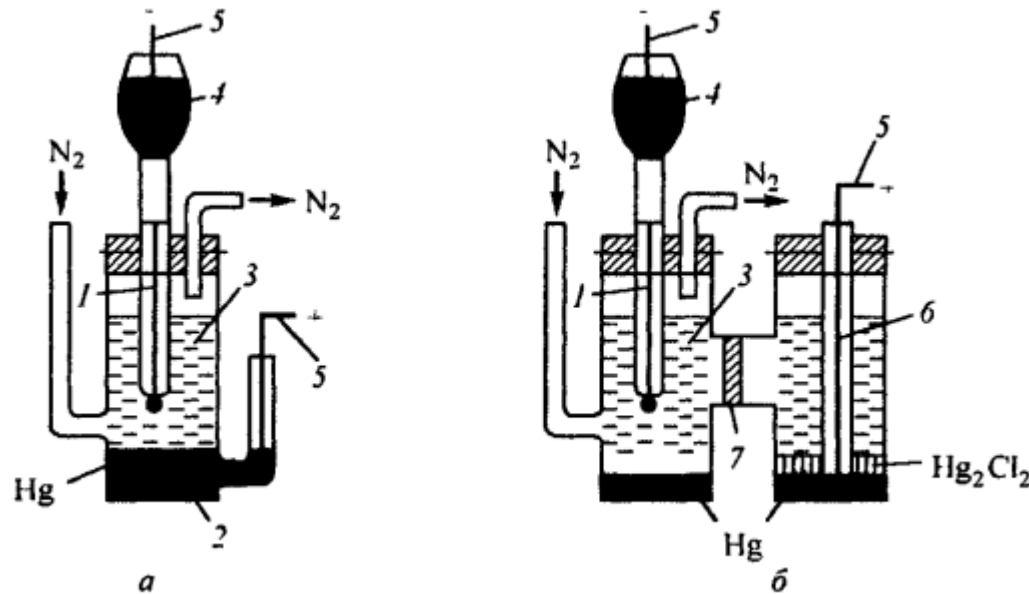
Classical polarographic analysis

- ▶ The microcathode placed in the cell is a glass capillary filled with liquid mercury connected by a hose to a reservoir containing liquid mercury. Mercury flows out of the capillary slowly, drop by drop (that's why such an electrode is called a dripping mercury electrode) coming from the reservoir. The macroelectrode — the anode — in this case is liquid mercury at the bottom of the vessel. In practice, a saturated calomel electrode, rather than a mercury electrode, is most often used as a macroelectrode anode, in relation to which the potential of a dripping mercury microcathode is usually measured.

Classical polarographic analysis

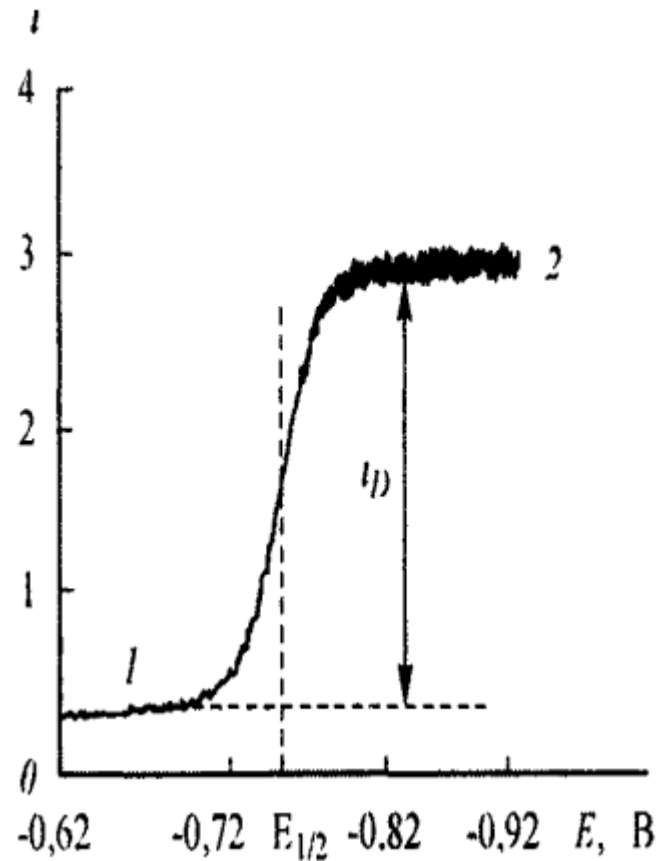
- ▶ The analyzed solution contains, in addition to the substance being determined, also an indifferent background electrolyte (background), the ions of which are not discharged on the electrodes under conditions of polarographic analysis, but serve as conductive particles to maintain a certain amount of electric current in the cell when the substance being determined is not yet restored on the microcathode.

POLAROGRAPHIC CELL WITH MERCURY DROPPING ELECTRODE CIRCUIT AND MERCURY ANODE (A) OR SATURATED CALOMEL ELECTRODE (B):



1 — mercury drop electrode; 2 — mercury anode; 3— analyzed solution; 4- vessel with liquid mercury; 5 — conductors to outer direct current source; 6 saturated calomel electrode; 7 — porous glass plug

POLAROGRAPHIC OF AQUEOUS ALKALINE 0.0005 MOL/L LEAD NITRATE SOLUTION AT 25 °C (i -CURRENT, E - POTENTIAL)



- ▶ 1 - residual current,
 - ▶ 2 - maximum current.
- Potential values are given with respect to the saturated calomel electrode;
- ▶ I_D — diffusion current,
 - ▶ $E_{1/2}$ — half-wave potential

Classical polarographic analysis

- ▶ The substance discharged at the microcathode is called a depolarizer, polarographically active, electroactive. These names are conditional, since a substance can be polarographically inactive at one potential and polarographically active at a higher potential.
- ▶ Instead of the release potential, in practice, the half-wave potential $E_{1/2}$ is determined, corresponding to half the magnitude of the diffusion current.
- ▶ The resulting polarographic curve is called, as noted above, a subroutine, or a polarographic wave.

Classical polarographic analysis

- ▶ When using a dripping mercury electrode, current oscillations are observed on the polarogram (its periodic slight increase and decrease). Each such oscillation corresponds to the appearance, growth and separation of a mercury droplet from the microcathode capillary.
- ▶ In some modern polarographs, the electric current is measured only at the end of droplet formation, which eliminates oscillations on the polarogram.
- ▶ On the mercury dripping microcathode, there is a constant resumption of mercury droplets, on the surface of which the discharge of cations is carried out. The surface of such an electrode is constantly being updated due to new mercury droplets, which eliminates changes in its properties due to electrochemical processes occurring on it and is one of the main advantages of using a mercury dripping electrode.

Classical polarographic analysis

- ▶ In qualitative and quantitative polarographic analysis, two parameters obtained when considering iolarograms are used: the half-wave potential $E_{1/2}$ and the magnitude of the diffusion current i (D) (height h of the polarographic wave).
- ▶ The value of the half-wave potential of the opened or determined cation should be less than the value of the ion discharge potential of the background electrolyte.

Classical polarographic analysis

- ▶ The half-wave potential of $E_{1/2}$ depends on:
- ▶ The nature of the regenerating substance itself
- ▶ The nature of the solvent
- ▶ Background electrolyte
- ▶ Composition and pH of the analyzed solution
- ▶ The presence of complexing agents
- ▶ Temperatures.

Quantitative polarographic analysis

- ▶ Quantitative polarographic analysis is based on the measurement of the diffusion current as a function of the concentration of the polarographically active depolarizer substance being determined in the polarographed solution.
- ▶ When analyzing the obtained routines, the concentration of the substance to be determined is found by methods of a calibration schedule, standard additives, and standard solutions.

Conditions for conducting polarographic analysis

- ▶ To maintain the necessary electrical conductivity of the analyzed solution, a background electrolyte is introduced into it, for example, potassium chloride or nitrate, ammonium chloride, tetraalkylammonium salts, etc. The ions of the background electrolyte should be discharged on a mercury dripping micro-electrode at higher signs of the applied potential than the polarographed substance.

Conditions for conducting polarographic analysis

- ▶ Before conducting a polarographic analysis, the oxygen dissolved in the analyzed solution must be removed. This is achieved most often by passing a current of an inert gas (e.g. nitrogen) through the solution for ~ 15 minutes before polarography begins.
- ▶ To suppress the current maxima, additives of gelatin or other surfactants (agar-agar, methyl red, fuchsin, etc.) are introduced into the solution, which change the surface tension of the mercury droplet and prevent the movement of the surface layers of the mercury droplet.
- ▶ It is necessary to thermostatize the polarographic cell, keeping the temperature constant with an accuracy of ± 0.5 ° C.

Application of polarographic analysis

- ▶ For the determination of small amounts of inorganic and organic substances. Methods for the polarographic determination of almost all metal cations, a number of anions (bromate, iodate, nitrate, permanganate ions), organic compounds of various classes containing diazo groups, carbonyl, peroxide, epoxy groups, double carbon-carbon bonds, as well as carbon-halogen, nitrogen-oxygen, sulfur-sulfur.
- ▶ It is used to determine salicylic acid, norsulfazole, vitamin B1 alkaloids, folic acid, kellin in powder and tablets, nicotinamide, pyridoxine hydrochloride, arsenic preparations, cardiac glycosides, as well as oxygen and various impurities in pharmaceuticals.

Advantages of the method

- ▶ High sensitivity (up to 10^{-5} – 10^{-6} mol/l); selectivity; comparatively good reproducibility of results (up to -2%); wide range of applications; allows you to analyze mixtures of substances without separation, colored solutions, small volumes of solutions (the volume of a polarographic cell can be only 1 ml); conduct analysis in the solution stream; automation carrying out

Disadvantages of the method

- ▶ The toxicity of mercury, its fairly easy oxidizability in the presence of oxidizing substances, the relative complexity of the equipment used.

Amperometric titration

- ▶ Amperometric titration (potentiostatic polarization titration) is a type of voltammetric method.
- ▶ It is based on measuring the magnitude of the current between the electrodes of an electrochemical cell. to which some voltage is applied, as a function of the volume of the added titrant.
- ▶ The equivalence point is fixed by a sharp change in the drop or increase in the diffusion current, which corresponds to the end of the reaction of the titrated substance with the titrant.

Amperometric titration

- ▶ There is an amperometric titration with one polarizable electrode, also called current limit titration, polarographic or polarimetric titration, and amperometric titration with two identical polarizable electrodes, or titration "until the current stops completely", biamperometric titration.

Amperometric titration with one polarizable electrode

- ▶ It is based on measuring the current in a polarographic cell depending on the amount of added titrant at a constant external potential on a microelectrode slightly exceeding the half-wave potential on the volt-ampere curve of the titrated substance X or titrant T. Usually the selected external potential corresponds to the region of the limiting current on the polarogram X or T. Titration is carried out on an installation consisting of a direct current source with an adjustable a voltage to which a galvanometer and a polarographic titration cell are connected in series.

Amperometric titration with one polarizable electrode

- ▶ The working (indicator) electrode of the cell can be a mercury dripping electrode, a stationary or rotating platinum or graphite electrode. When using solid electrodes, mixing of the solution during titration is necessary. Chlorine- silver or calomel electrodes are used as a reference electrode. The background is, depending on the conditions, various polarographically inactive electrolytes at a given potential.

Amperometric titration with two polarizable electrodes (biamperometric titration).

- ▶ It is based on measuring the current between two identical electrodes (made of platinum or gold) of an electrochemical cell, on which a small potential difference is imposed. A current flows in the cell when there is a reversible redox pair in the solution, at such concentrations of the oxidizer and reducing agent at which it is possible to carry out cathodic and anodic processes. When one of the components of a reversible redox pair disappears in the system or when a reversible redox pair appears, the current in the fuel cell is abruptly interrupted or appears instantly.

Coulometry

- ▶ It is based on the use of the dependence between the mass t of a substance that reacted during electrolysis in an electrochemical cell and the amount of electricity that passed through the electrochemical cell during electrolysis of only this substance.
- ▶ Coulometric analysis is performed either in an amperostatic (galvanostatic) mode, i.e. with a constant electric current, or with a controlled constant potential of the working electrode (potentiostatic coulometry), when the electric current changes (decreases) during electrolysis.
- ▶ There are direct coulometry and indirect coulometry (coulometric titration).

Direct coulometry

- ▶ Direct coulometry at direct current is rarely used. Coulometry with a controlled constant potential of the working electrode or direct potentiostatic coulometry is more often used.
- ▶ In direct potentiostatic coulometry, a directly detectable substance is electrolyzed. The amount of electricity spent on the electrolysis of this substance is measured, and then the mass of the substance to be determined is calculated.

Direct coulometry

Advantages of direct coulometry:

- ▶ high selectivity, sensitivity, reproducibility (up to 1-2%), allows you to determine the content of trace impurities.

Disadvantages of direct coulometry:

- ▶ the complexity and duration of the analysis, the need for expensive equipment.

Application of direct coulometry

- ▶ To determine — during cathodic reduction — metal ions, organic nitro and halogen derivatives; during anodic oxidation - chloride, bromide, iodide, thiocyanate anions, metal ions in lower oxidation states when they are transferred to higher oxidation states.
- ▶ In pharmaceutical analysis, direct coulometry is used to determine ascorbic and picric acids, novocaine, and oxyquinoline.

Coulometric titration

- ▶ The detectable substance X , which is in solution in an electrochemical cell, reacts with the "titrant" T — a substance continuously formed (generated) on the generator electrode during the electrolysis of an auxiliary substance also present in the solution. The end of titration is the moment when all the detectable substance X fully reacts with the generated "titrant" T , is fixed either visually with an indicator metal, introducing into the solution an appropriate indicator that changes color near TE, or using instrumental methods — potentiometrically, amperometrically, photometrically.