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UKRAINIAN MINISTRY OF PUBLIC HEALTH
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ANALYTICAL CHEMISTRY

PART II

QUANTITATIVE ANALYSIS

The manual for foreign students of pharmaceutical higher schools and pharmaceutical departments of medical higher schools of the III – IV accreditation levels

Translation from Ukranian by Foreign Languages department, edited by prof. M. V. Lubieva

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The manual created at the Analytical Chemistry department of National University of Pharmacy corresponds to the modern level of development of theory and practice in the analysis of substances, their mixtures, including medicines.

This part of the manual is devoted to quantitative analysis of substances. The manual consists of theoretical basis, laboratory works, theoretical and control questions for students, situational tasks, examples of the decision of typical exercises.

For foreign students of pharmaceutical higher schools and pharmaceutical departments of medical higher schools of the III – IV accreditation levels.

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SUBJECT AND PROBLEMS OF QUANTITATIVE ANALYSIS

Quantitative analysis is the set of experimental methods allowing to determine the quantitative content (concentration) of individual components and impurities in the sample of material to be researched.

The aim of quantitative analysis is determination of quantitative ratios of chemical compounds, ions and elements, which are the part of substances to be researched.

Quantitative analysis solves various questions of modern science and production. With the help of quantitative analysis optimal conditions of carrying out various chemical and technological processes are determined, the quality of raw materials, the purity degree of manufactured products including medicines are controlled, the content of components in mixtures, the relation between the chemical composition and physical properties of substances are determined.

CLASSIFICATION OF QUANTITATIVE ANALYSIS METHODS

The quantitative analysis methods are divided into three groups:

- chemical methods;
- physical methods;
- physical and chemical methods.

Chemical methods are based on using the various types of chemical reactions proceeding quantitatively in solutions, melts, solids or gases. These methods are divided into:

- *gravimetric* (weight) methods of analysis based on the exact mass measurement of the component to be analysed in the substance to be researched;
- *titrimetric* (volumetric) methods of analysis, in which the quantitative composition of the sample to be researched is determined by the exact

volume measurement of a reagent solution with the known concentration (titrant), which interacts with the substance to be determined in the equivalent quantities;

- *gas* analysis based on measurement of the gas volume, which is formed or absorbed due to a chemical reaction.

Chemical methods of analysis are often called classical methods. These are the most developed methods of analysis, which continue being developed. They are exact, simple in performance, do not require special equipment. But their application is sometimes bound up with some difficulties (isolation of components of complex mixtures, etc.) and a comparatively low limit of sensitivity.

Physical methods of analysis are based on sizes measurement of physical parameters of substances to be analysed or their solutions, on conditions that physical parameters are the function of substances quantitative composition. The methods based on size measurement of the refractive index (refractometry), the optical rotation (polarimetry), the fluorescence intensity (fluorimetry), etc., belong to them. Physical methods are characterized by rapidity, low limit of detection, objectivity of results, possibility of process automation. But they are not always specific, because physical size is influenced not only by concentration of the substance to be researched, but also by the presence of other substances and impurities. Their use often requires application of complex equipment.

Physical and chemical methods of quantitative analysis are based on sizes measurement of physical parameters of the system to be analysed, appearing or changing as a result of carrying out chemical reactions. These methods are characterized by low limit of detection and rapidity of their performance.

Physical and physical and chemical methods are called instrumental methods as they require application of definite devices.

GRAVIMETRIC METHOD OF ANALYSIS

Gravimetric method of quantitative analysis (weight analysis) is based on the exact mass measurement of the substance to be researched or the mixture component, separated in the chemically pure state or in the form of chemical compounds with the exactly known composition.

Gravimetric analysis is conditionally divided into three groups of methods: precipitation, volatilization and particulate methods.

PRECIPITATION METHODS

In precipitation methods the component to be determined is quantitatively precipitated in chemical ways in the form of a slightly soluble chemical compound with the constant composition.

The sample of the substance to be investigated is dissolved in a suitable solvent, and then the certain component is quantitatively precipitated in the form of a slightly soluble compound. A precipitate is called «the precipitated form». It is exposed to the analytical processing, that is separated by filtering, washed out, dried, ignited and then it is weighed with the help of the analytical balance. Such precipitate is called the gravimetric or the weighed form.

The precipitated form can both coincide (1) and differ (2) from the gravimetric form in the chemical formula:

$$Ba^{2+} + SO_4^{2-} \rightleftharpoons BaSO_4\downarrow \xrightarrow{\Delta} BaSO_4 \qquad (1)$$

Ba^{2+} – is the component to be determined;
SO_4^{2-} – is the precipitant;
$BaSO_4\downarrow$ – is the precipitated form;
$BaSO_4$ – is the gravimetric form.

$$Ca^{2+} + C_2O_4^{2-} \rightleftharpoons CaC_2O_4\downarrow \xrightarrow{\Delta} CaO + CO_2\uparrow + CO\uparrow \qquad (2)$$

Ca^{2+} – is the component to be determined;
$C_2O_4^{2-}$ – is the precipitant;
$CaC_2O_4\downarrow$ – is the precipitated form;
CaO – is the gravimetric form.

The gravimetric and precipitated forms should satisfy a number of requirements:

– the precipitated form should be slightly soluble (in case of binary electrolytes precipitation completeness is reached at $K_S^0 = 10^{-8}$); the precipitate should be macrocrystalline; the precipitated form should quantitatively transfer in the gravimetric one;
– the composition of the gravimetric form should correspond exactly to its chemical formula; the gravimetric form should be chemically stable, and the content of the component to be analysed in it should be as small as possible to reduce the error of determination. Therefore, the molecular mass of the gravimetric form should be as large as possible.

Precipitation gravimetric methods allow to determine quantitatively almost all of the most important cations and anions of the inorganic nature, as well as a number of organic compounds, including medicinal ones. So, lactose in dairy products, salicylates in medicinal substances, nicotine in insecticides, cholesterol in blood serum, etc., are determined by the precipitation gravimetric method.

VOLATILIZATION METHODS

In volatilization gravimetric methods the component to be analysed is isolated from the sample to be analysed and quantitatively volatilized as a volatile compound. Volatilization method is called a direct one if the mass of the volatilized product is measured directly. In the cases when the mass is calculated by the difference of the sample masses before and after volatilization, it is called the indirect method. As the first method example it

is possible to use CO_2 determination after calcium carbonate sample decomposing and CO_2 absorption by a tube with sodium hydroxide:

$$CaCO_3\downarrow + 2H^+ \rightarrow CO_2\uparrow + Ca^{2+} + H_2O$$
$$CO_2 + 2\ NaOH \rightarrow Na_2CO_3 + H_2O.$$

The CO_2 mass is calculated by mass increase of the absorption tube previously weighed with the help of the analytical balance.

The indirect volatilization method allows to determine the rest mass after the complete isolation of a definite component. For example, determination of the crystalline water content in sodium tetraborate is carried out according to the following scheme:

$$Na_2B_4O_7 \cdot 10H_2O \xrightarrow{\Delta} Na_2B_4O_7 + 10\ H_2O.$$

The indirect volatilization method is applied mainly for determination of moisture in medicines, sometimes for determination of carbonates, sulphides and sulphites content after the sample processing by an acid, and it is carried out by the drying method with subsequent ignition.

PARTICULATE METHODS

In gravimetric particulate methods the component to be analysed or the mixture component are quantitatively isolated in a free state and weighed with the help of the analytical balance.

Particulate method is applied, for example, for quality evaluation of medicines by determination of the substance content in them. The total ash is determined by ignition of a weighed medicine previously weighed with the help of the analytical balance in a platinum or porcelain crucible. After processing the residue by hydrochloric acid the ash, which is insoluble in hydrochloric acid, is determined. Besides, the sulphated ash obtained after heating and ignition of the analyte sample processed preliminary by concentrated sulphuric acid is also determined.

BALANCE AND WEIGHING TECHNIQUE

Balance is used as the basic device in the gravimetric method of analysis.

Weighing with the accuracy of ± 0.01 g is carried out with the help of the pharmacy (hand) or the technochemical balance.

Weighing with the accuracy of ± 0.0001 – 0.0002 g is carried out with the help of the analytical balance.

When weighing with the help of the *technochemical* or the *technical balance* the subject to be analysed is placed on the left-hand pan of the arrested balance, and counterpoising weights are placed on the right-hand pan. Weighing process is finished when the balance pointer is in the middle position after free damping the balance beam oscillation.

When weighing with the help of the *pharmacy balance* the central ring is held by the thumb and forefinger of the left hand leaning by elbow against the laboratory bench. The place of subjects to be weighed on this or that pan of the balance is strictly discussed. Damping the balance beam oscillation can be accelerated by a light touch of the balance pans bottom to the surface of the laboratory bench.

The *analytical balance* is put in specially intended laboratory premises (weighing rooms) on special monolithic tables-supports. To prevent the influence of air oscillations, dust and moisture the balance is protected by special glass cases.

When working with the analytical balance it is necessary to follow such requirements and rules:

- the balance state is tested and the zero point is set before each weighing;
- substances to be weighed are placed into a special container (weighing bottle, watch glass, crucible, test-tube);
- the temperature of the substances to be weighed is adjusted to the balance temperature in the weighing room for 20 minutes;
- the balance should not be loaded over the fixed limit load.

The analytical balance possesses a high degree of sensitivity in order to give the true weight of samples (weight in this context being synonymous with mass). Factors affecting these requirements are:

- the length of the balance arms;
- co-planarity of the knife edges;
- the weight of the beam;
- the position of the gravity centre of the beam in relation to the central knife edge or pivot.

The influence of these factors is shown by considering the hypothetical balance beam ABC (fig. 1) of weight W with knife edges at A, B and C and gravity centre at G. Fig. 1 shows the position of the beam when loads W_1 and W_2 have caused a small deflection θ.

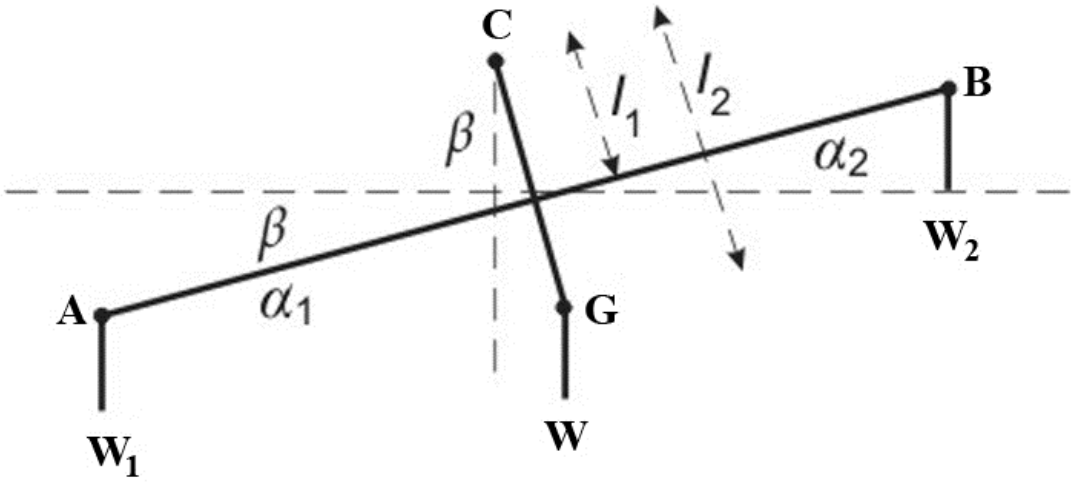


Fig. 1. The hypothetical balance beam

At equilibrium, it may be shown that

$$\tan\theta = \frac{W_1 a_1 - W_2 a_2}{(W_1 + W_2) l_1 - W l_2} \qquad (3)$$

When equal weights are on each arm, the balance beam should be horizontal, i. e. $\theta = 0$; this applies when the lengths (a_1 and a_2) of the arms are equal. If they are not, a true weight may be obtained by weighing the sample first on one pan to give an apparent weight W_3 and then on the other

pan to give an apparent weight W_4. The true weight is calculated from the formula:

$$\text{True Weight} = \sqrt{(W_3 \cdot W_4)} \, .$$

The sensitivity of a balance can be defined as the deflection of a pointer caused by a standard difference of weight between the two sides, e. g. the deflection, in scale divisions, per mg weight difference. For small deflections, tan θ may be taken as θ expressed in radians and, incorporating the condition of equal balance arms in eq. (3), the sensitivity is proportional to

$$\frac{\theta}{W_1 - W_2} = \frac{a}{(W_1 + W_2)l_1 + Wl_2} \qquad (4)$$

where a represents the length of a balance arm. Increasing the length of each arm will increase the sensitivity of the balance only if it can be done without too great increase in weight W of the beam.

Sensitivity can be increased by reducing the magnitude of the denominator in (4) and manufacturers eliminate l_1 by making all three knife edges co-planar. Under this condition, the sensitivity is now proportional to a/Wl_2 and should remain constant with increase in load. If this co-planarity is lost due to excessive load and distortion of the beam, the sensitivity will decrease with increase in load. If, on the other hand, the central knife edge is below the other two, the sensitivity will increase with increase in load. The position of the gravity centre can also be varied by means of a sensitivity bob. In this way G can be made to approach C and, hence, l_2 will be reduced leading to increased sensitivity. In the limit, when G coincides with C, a horizontal position of equilibrium is possible, but the slightest additional weight on one side causes the beam to swing to an extreme position; the balance is now unstable.

The ordinary technique in weighing is to determine the weight of sample by difference and, hence, inequality of balance arms and loss of co-planarity of knife edges under load, with concomitant variations in sensi-

tivity, may give rise to small errors. To avoid these errors, weighing by substitution has received considerable attention and is likely to achieve much wider use with the advent of synthetic sapphire for planes and knife edges. This hard material meets the objection of excessive wear on bearing surfaces at high loads when «softer» materials are used. The technique involves both balance pans being fully loaded, and when a sample is placed upon the left-hand pan, weights must be taken off until equilibrium is attained.

Application and care of the balance

It is presumed that the student is already well acquainted with the principles of the balance and its use in weighing. The following points are intended to draw attention to certain important practical details using a simple analytical balance, which requires manual addition of weights.

1) Material spilled on the balance pans or base must be cleaned up immediately.
2) The balance should be tested to see that it swings freely and is in adjustment before each weighing is made.
3) Sample must not be weighed directly upon the balance pans. A stoppered container must be used for weighing liquids and volatile, deliquescent or hygroscopic solids.
4) Hot objects must be cooled to room temperature before introduction into the balance case.
5) The balance door must be closed when the final weighing is made.
6) The arrestment of the beam must be lowered slowly when setting the balance swinging.
7) The beam must be raised and the pans arrested before an object or weight is added to or removed from the pans.
8) The object to be weighed is usually placed on the left-hand pan and weights on the right-hand one.
9) All weights must be handled with forceps and not with the fingers. The forceps are manipulated with the right hand and the balance arrestment with the left hand. The heavy weight should be placed towards the centre of the balance pan.

10) Before recording a weight, check the empty spaces in the box of weights, as well as the weights on the balance pan.
11) The balance must not be overloaded (maximum load usually 200g).
12) When a weighing has been completed, a check should be made to see that the beam is arrested, the weights are in their correct places in the box of weights, the «rider» is on the sliding hook and the balance-case and box of weights are closed.

Weighing the sample

An accurate weight of a sample may be obtained either by «weighing by difference» or by «weighing by addition».

Weighing by difference

Method A. Place sufficient sample for several analyses in a stoppered weighing bottle and weigh accurately. Take the bottle from the balance with the tips of a clean dry thumb and finger and remove the stopper (left hand), holding the bottle over the mouth of the vessel, in which the sample is to be placed. Pour out the correct amount of the substance estimated by carefully tilting the bottle from the horizontal and rotating it. While it is still over the receiving vessel, tilt the bottle towards the upright position and rotate the bottle about its vertical axis. Tap the bottle lightly with the finger so that sample remaining on the inside of the bottle lip slides back in, and that on the outside falls into the receiving flask. Insert the stopper slowly and carefully to prevent powder being blown out of the bottle. Reweigh the bottle and contents. The difference between the two weighings gives the weight of the sample.

The disadvantage of this method lies in the difficulty of estimating the correct amount to be tipped out of the bottle. Since it is inadmissible to return any sample to the weighing bottle after it has been introduced into the receiving vessel, a number of additions of small portions are frequently required before the correct sample weight is obtained. The British Pharmacopoeia states that in assays «the quantity actually used must not deviate by more than 10 per cent from that stated in the method». The following (Method B) is, therefore, recommended, despite the fact that it involves four accurate weighing to obtain two analytical sample portions instead of three accurate weighings, which would be required by Method A.

Method B. Weigh the weighing bottle approximately to the nearest 0.01 g. (The approximate weight of the students' own bottle should be known). Introduce into the

bottle slightly more than the specified amount of the sample. Alternatively, if the material to be weighed is stable, weigh slightly more than the specified amount on a rough balance and then introduce into the weighing bottle. Weigh the bottle and contents accurately. Tip out the contents of the bottle into the receiving vessel using the technique described under Method A. When most of the solid has been transferred (no attempt should be made to transfer the last few particles, which adhere to the inside of the bottle), replace the stopper, taking the precautions mentioned above, and reweigh the bottle and remaining contents accurately.

General precautions for weighing the sample

1) If the material is deliquescent or hygroscopic, exposure to the atmosphere should be reduced to a minimum and method B is applied.
2) If the sample is being transferred to a conical flask or other vessel with a narrow aperture, which is not narrow enough to require the use of a funnel, it is necessary to ensure that the mouth of the vessel is dry because of the possibility of contact with the weighing bottle. A funnel should not to be used when transferring a solid from a weighing bottle to a conical flask in the «weighing by difference» procedure.
3) A record of the weighings must be made in the laboratory register immediately, in ink.
4) Analytical samples of liquids should not be weighed by difference but by the method of «weighing by addition», as outlined below.

Weighing by addition

The empty dry vessel is first weighed accurately. The vessel can be a clock-glass, a weighing bottle, a small beaker, a small conic flask, a crucible, etc., depending upon the weight and nature of the material to be weighed. The sample is then introduced into the vessel and the container and the sample is weighed again accurately. It is essential that the vessel should not be too large as changes due to adsorption of moisture and electrification during weighing may be minimised. Solids require slightly different weighing procedures from those used for liquids and the general methods are outlined below.

Method A. Solids (as in the preparation of standard solutions). Weigh the vessel (clock-glass, watch-glass or weighing bottle) accurately. Introduce the solid in portions until the correct weight has been added. Weigh the vessel and contents accurately.

Hold the vessel over the receiver (beaker, or funnel in the mouth of the flask) and incline slightly so that the solid slides down slowly into the receiver. Wash the weighing vessel thoroughly with a jet of water, collecting all the washings in the receiver.

On the semi-micro scale, the solid can be weighed directly in the small conic flask or beaker, in which the titration or other subsequent treatment will be performed. Great care must be taken in weighing small quantities to ensure that the vessel, into which the sample is to be weighed directly, has been allowed to remain on the balance pan for some time so that a constant weight is obtained. The material to be weighed should be introduced directly into the weighed container while it remains on the balance pan and then the container and its contents reweighed accurately.

Method B. Water-miscible liquids. Weigh accurately an empty, clean, stoppered weighing bottle. Remove the stopper, placing it on the balance pan. Add the liquid carefully from a teat pipette until the correct weight has been added. Insert the stopper into the weighing bottle and weigh the latter and its contents accurately. The liquid should not come into contact with the ground glass portion of the bottle in order that the stopper is not wetted. Take the bottle from the balance and, holding it at the base between the tips of the fingers and the thumb of the right hand, remove the stopper with the left hand, and pour the liquid gently down a guiding rod (also in the left hand) into the receiving vessel. A funnel should only be used if the receiver has a narrow neck. While the bottle is upturned and still held over the receiving vessel, transfer it to the left hand and wash down the bottle and guide rod with a jet of water from a wash-bottle held in the right hand.

Method C. Water-immiscible liquids. If the titration (or other treatment) of the sample requires the use of a large flask or other container, the sample is usually weighed in a small vessel, e. g. a sample tube or other special container with a flattened end.

Weigh the small vessel empty, introduce the sample and then accurately weigh the vessel and its contents. Introduce the weighing vessel and its contents into the larger vessel, in which the determination is to be carried out.

If the determination can be carried out in a small vessel, and a liquid is non-volatile, the liquid may be weighed directly into the vessel.

Accuracy of weighings

It is not necessary to weigh a sample with a degree of accuracy, which is appreciably greater than that can be attained in the subsequent steps of the analysis.

In volumetric work, if the accuracy of the apparatus is ±0.2% and 1 g of sample is required for a particular assay, it would be unnecessary to weigh the sample to ±0.0001 g since it would constitute an error of only ±0.01% in the weighing. For samples of such size in volumetric work, it is not necessary to weigh closer than ±0.0005 g. In gravimetric work, however, all weighings should be with the accuracy of ±0.0002 g. The British and European Pharmacopoeias adopt a convention whereby the degree of precision required is indicated by the number of significant figures stated e. g. 1 g, 0.50 g, or 0.500 g.

Constant weight

In practice, it is unusual for two consecutive weighings of the same object to be completely identical. This is particularly true where the object has been submitted to some physical treatment, such as heating and cooling between weighings. In gravimetric analysis, an object or sample is said to be at constant weight when two consecutive weighings after heating and then cooling in the desiccator differ by not more than 0.0003 g. The British Pharmacopoeia defines the term «constant weight» used in relation to the determination of loss on drying or loss on ignition as meaning that two consecutive weighings do not differ by more than 0.5 mg per g of the substance or a residue for the determination, the second weighing being made after an additional hour of drying or after further ignition.

EQUIPMENT AND TECHNIQUE OF CARRYING OUT THE BASIC OPERATIONS

Gravimetric determination of one or another component of the substance to be analysed is carried out by performing a series of practical operations, their enumeration and sequence depend on the method of gravimetric analysis. So, in the precipitation gravimetric method the following operations are distinguished: sampling the substance to be analysed, taking the sample, dissolving in a suitable solvent, precipitation, analytical processing the precipitate, weighing the gravimetric form, content calculation of the substance to be analysed.

In volatilization gravimetric methods the following operations are distinguished: sampling the substance to be analysed, taking the sample, carrying out the volatilization process, weighing either volatilization product (direct volatilization method) or mass of the substance to be analysed after carrying out the volatilization, content calculation of the substance to be analysed.

Let us consider general operations, which are characteristic for all methods of gravimetric analysis.

A sample coming for analysis should represent the average composition of the materials to be analysed.

The purpose of *average sampling* is obtaining a relatively small amount of the initial substance, in which quantitative content of all components should be equal to their quantitative content in the whole mass of the substance to be analysed.

There are special procedures for correct sampling of such sample, which permit to minimize the possible errors of this operation.

Taking the sample. When calculating a sample weight it is necessary to take into account that weight of the gravimetric form (or of the component to be determined) must be sufficient for weighing with the help of the analytical balance with the respective accuracy and suitable for practical operation. The sample weight calculations, as well as the content of the substance or the component to be determined will be considered below. Taking the exact weight of an average sample is carried out with the help of the analytical balance.

Dissolution of the taken sample is carried out taking into account solubility of the substance to be analysed in the corresponding solvent.

Carrying out the gravimetric analysis by precipitation method requires choosing a precipitant. The precipitant is chosen so that formed precipitates must be either macrocrystalline or densely amorphous. In case of possible choosing a precipitant the preference should be given to that one, excess of which is removed easier.

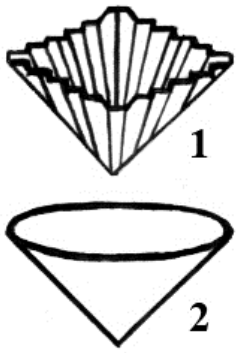


Fig. 2. Ashless paper filters: 1 – folded; 2 – smooth

Operation of *precipitation* is carried out in beakers, the substance to be determined is precipitated from the hot diluted solution. The precipitant is carefully added on the beaker wall continuously shaking the solution by the glass stick, watching the solution does not splash and the glass stick should be rotated untouching the beaker bottom and walls. After finishing the operation of precipitation the completeness of precipitation is checked by adding 3 – 5 drops of the precipitant. Crystalline precipitates are being kept with a glass stick in a beaker for a while for maturing the precipitate, and amorphous precipitates are filtrated and washed out.

Precipitates *filtering* and *washing out* significantly influence on the accuracy of gravimetric analysis results. When filtering ashless filters are used (fig. 2), which after ignition give ashes weight smaller than the analytical balance weighing error, owing to it is possible to neglect this weight.

Ashless filters have different density required for work with crystalline and amorphous precipitates, and are marked by colour of a paper strip belting a filter package (a red strip – for coarse-grained and amorphous precipitates, a white one – for precipitates of an average grain size, a blue one – for fine-grained precipitates). For filtering of the most of precipitates the filters of an average density (a white strip) are more convenient, a red strip is for some amorphous precipitates, a blue strip is for microcrystalline ones.

To carry out the operation of filtering a paper filter, a glass funnel, a glass stick, a beaker and the support with a ring are used.

A smooth paper filter is put in a dry funnel so that its edge is 1 cm lower than the funnel edge, then it is moistened with distilled water and pushing the filter to the funnel walls air bubbles are removed. The funnel with the filter is put in the ring of the support, the beaker is placed under it; a bevel edge of the funnel is pressed to the beaker wall.

Then the glass stick is taken out from the beaker with a precipitate, and the liquid is carefully poured out along this stick without shaking the precipitate (fig. 3). The liquid level on the filter should be 5 mm below the filter edge.

Filtering is continued until all liquid, which was in the beaker above the precipitate, is poured out. Then the precipitate is washed out by decantation several times and transferred quantitatively on the filter.

Washing out the precipitate on the filter is carried out until impurities are completely removed.

Choosing the washing liquid depends on the precipitate properties and its further processing. The most typical washing liquids are distilled water, diluted solutions of any electrolytes (solution of volatile acids or ammonium salts), solutions of the substance inhibiting the precipitate hydrolysis. The operation of washing out, as a rule, is carried out firstly by decantation and then on the filter. For this purpose washing bottles, which allow to bring purposefully necessary portion of the washing liquid into the beaker or on the filter, are used (fig. 4).

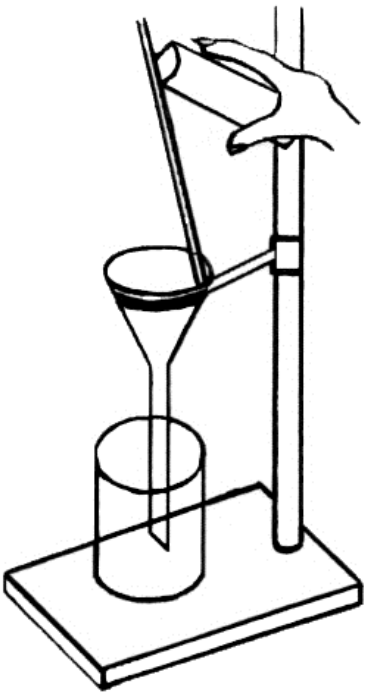


Fig. 3. Filtering through the smooth filter

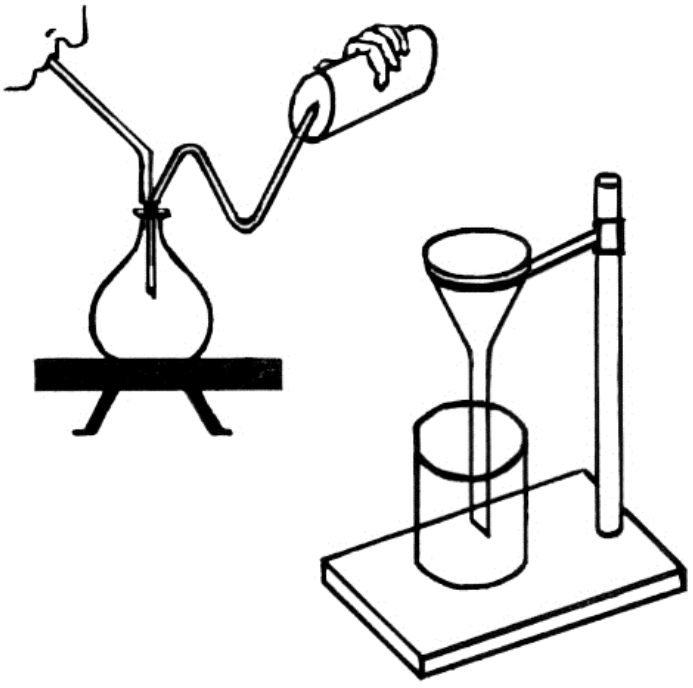


Fig. 4. Processing with a washing bottle

In the gravimetric method of analysis while operating with precipitates the methods of drying, ignition and ashing is used.

While *drying* precipitates the filter with a precipitate is transferred into the crucible and dried out in the drying-cabinet at 95 – 100°C.

When working by the volatilization method precipitates are put into the drying-cabinet in a glass weighing bottle with the open cork or on the filter in the funnel, covered by a sheet of filter paper wetted by distilled water (fig. 5).

Precipitates *ashing* is carried out in a porcelain or platinum crucibles in the burner flame or in the electrical muffle furnace watching the paper or the substance must smoulder but not burn.

Precipitates *ignition* in crucibles is carried out at the temperature of about 500°C in the muffle furnace. The crucibles and weighing bottles with precipitates are transferred only with the help of the crucible tongs. Cooling, storing and transferring the dried and ignited precipitates are carried out with the help of the desiccators (fig. 6).

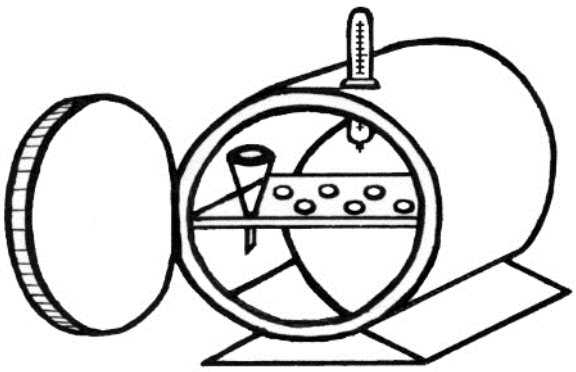


Fig. 5. Drying of a precipitate in the drying-cabinet

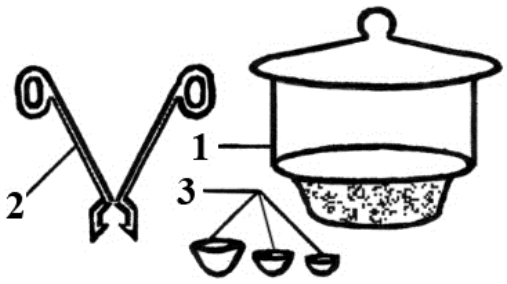


Fig. 6. Equipment in the gravimetric analysis: 1 – desiccator; 2 – crucible tongs; crucibles

Special features of analytical operations in gravimetry depend not only on the method of gravimetric analysis, but also on the nature of the object to be analysed.

CALCULATIONS IN GRAVIMETRIC METHODS OF ANALYSIS

Calculating the sample mass of the substance to be investigated

When calculating the sample of the substance to be determined in the gravimetric method of analysis it is recognized that the mass of the gravimetric form obtained while weighing with the help of the analytical balance should not exceed the relative error of the method (±0.2%). Taking into account specificity of analytical processing the precipitates in gravimetry sample masses suitable for the work have been determined experimentally: for crystalline precipitates – 0.5 g, for amorphous ones – 0.1 g.

Generally calculation of the sample mass is carried out according to the formulae:

– *in precipitation of crystalline precipitates:*

$$m = \frac{0.1 \cdot F \cdot 100}{\omega},$$

– *in precipitation of amorphous precipitates:*

$$m = \frac{0.5 \cdot F \cdot 100}{\omega},$$

where m – is the sample mass of the substance to be analysed, g;

F – is the gravimetric (analytical) factor, which is equal to the ratio of the molar mass of the compound to be determined to the molar mass of the gravimetric form;

ω – is the approximate percentage of the substance to be determined, %;

0.5 and 0.1 – are the minimal masses of the gravimetric form, which can be weighed with the help of the analytical balance with the respective accuracy (±0.2%), g.

Calculating the volume of the precipitant solution

The formula is generally used when calculating the volume of the precipitant solution following:

$$V_{pr} = \frac{1.5 \cdot m \cdot F \cdot 100}{\rho \cdot w},$$

where V_{pr} – is the volume of the precipitant solution, cm^3;

1.5 – is the factor of the precipitant excess practically determined relative to the one theoretically calculated;

w – is the concentration of the precipitant solution, %;

ρ – is the density of the precipitant solution, g/cm^3;

F – is the gravimetric factor;

m – is the sample mass of the substance to be determined, g.

Calculating the results of determinations

– *by the precipitation method*

$$\omega, \% = \frac{m_{g.f.} \cdot F \cdot 100}{m},$$

where ω – is the percentage of the substance to be analysed, %;

$m_{g.f.}$ – is the mass of the gravimetric form, g;

F – is the gravimetric factor;

m – is the sample mass of the substance to be analysed, g.

– *by the direct volatilization method*

$$\omega, \% = \frac{m_{g.f.} \cdot 100}{m},$$

where ω – is the percentage of the substance to be analysed, %;

m – is the sample mass of the substance to be analysed, g;

$m_{g.f.}$ – is the mass of the gravimetric form determined by increase of the mass of the absorbing device, g.

– *by the indirect volatilization method*

$$\omega, \% = \frac{(m - m_{g.f.}) \cdot 100}{m},$$

where ω – is the percentage of the substance to be analysed, %;

m – is the sample mass of the substance to be analysed, g;

$m_{g.f.}$ – is the mass of the dried or ignited substance to be determined after removing of volatile components, g.

– *by the particulate method*

$$\omega, \% = \frac{m_{g.f.} \cdot 100}{m},$$

where ω – is the percentage of the substance to be analysed, %;

m – is the sample mass of the compound, which composition contains the substance to be analysed, g;

$m_{g.f.}$ – is the mass of the gravimetric form of the substance to be analysed, g.

LABORATORY WORKS

LABORATORY WORK № 1
DETERMINATION OF THE PERCENTAGE OF SULPHATE-IONS IN MAGNESIUM (II) SULPHATE BY THE PRECIPITATION GRAVIMETRIC METHOD

REAGENTS

Hydrochloric acid, 10% solution;

barium (II) chloride, 1 mole/dm^3 solution.

PROCEDURE OF CARRYING OUT THE WORK

Taking the sample. With the help of the hand balance weigh the previously calculated sample of the substance to be determined, transfer it in-

to a test tube and weigh with the help of the analytical balance. Transfer the sample carefully into the beaker prepared, and weigh the empty test tube again with the help of the analytical balance. Determine the sample mass (m) as difference of two weighings:

$$m = m_1 - m_2 ,$$

where m_1 – is the mass of the test tube with the substance to be determined, g;

m_2 – is the mass of the test tube, g;

m_s – is the mass of the sample, g.

Precipitation. Dissolve the sample of the medicine in 30 cm^3 of distilled water, add 2 cm^3 of 10% hydrochloric acid solution.

Measure the calculated quantity (3 – 5 cm^3) of 1 mole/dm^3 of barium (II) chloride solution and 50 cm^3 of distilled water into the conic flask. Heat the beaker and the flask with the solutions simultaneously on the water bath to 50 – 60°C. Then add the solution of barium (II) chloride to $MgSO_4$ solution slowly, drop by drop, while mixing continuously by a glass stick. When the liquid above the precipitate become lighter, check the completeness of precipitation. For this purpose add to the solution with the precipitate some drops of barium (II) chloride solution. If there is no residue in the place of drops falling, the completeness of precipitation is reached.

Cover the beaker with the precipitate and the glass stick with filtering paper to exclude the ingress of dust, and allow the precipitate to mature until the next classwork.

Bringing a crucible to the mass constant value. Place a clean dry porcelain crucible with the help of crucible tongs in the muffle furnace for 15 – 20 minutes at 800°C. Open the muffle furnace, take by crucible tongs and transfer in the desiccator. Leave the desiccator cover opened for 1 – 2 minutes, then close and move it aside from time to time to give the opportunity for the excess of hot air leaving the desiccator. Transfer the desiccator (fixing the cover with hands) to the weighting room. Weigh the crucible after its cooling for 20 – 30 minutes.

Repeat all operations on bringing the crucible weight to the constant value until two reproducible results of weighings are obtained ($\Delta m = \pm 0.0005$ g).

Filtering and washing out the precipitate. After maturing the precipitate of barium (II) sulphate wash out several times with decantation using distilled water, transfer it quantitatively on «a blue label» filter and wash out again to the complete separation of chloride-ions.

Measure volume of the washing liquid and calculate the precipitate losses from solubility when washing out.

Drying the filter with the precipitate, ashing the filter. Dry the filter with the precipitate and the funnel in the drying-cabinet (105°C) not allowing the paper to be overdried. Take out the filter from the funnel by means of a needle, roll it up and transfer it into the crucible brought to the mass constant value. Place the crucible on a porcelain triangle. Burn the filter heating the crucible slowly on a small flame of a burner. If the filter flashes, the burner should be immediately put aside (do not put the flame out, as the precipitate losses are possible). Ashing can be carried out in the open muffle furnace.

Bringing the crucible with the precipitate to the mass constant value. After the filter stops smoking, transfer the crucible with the precipitate with the help of crucible tongs in the muffle furnace and ignite it at 800 – 900°C. Meanwhile oxidation of barium (II) sulphide is taking place; it is the product of partial reduction of barium (II) sulphate by carbon, which has formed during combustion of the filter according to the equations of the chemical reactions:

$$BaSO_4\downarrow + 4\ C \rightarrow BaS\downarrow + 4\ CO\uparrow$$
$$BaS\downarrow + 2\ O_2 \rightarrow BaSO_4\downarrow$$

The temperature in the muffle furnace should not exceed 800 – 900°C, because increasing of the temperature can lead to decomposition of barium (II) sulphate:

$$BaSO_4\downarrow \rightarrow BaO\downarrow + SO_3\uparrow$$

Carry out bringing the crucible with the precipitate to the mass constant value until two reproducible results of weighings are obtained.

Calculate the percentage of sulphate-ions in $MgSO_4$ medicine.

LABORATORY WORK № 2
DETERMINATION OF THE PERCENTAGE OF IRON (II) IONS IN MOHR'S SALT BY THE PRECIPITATION GRAVIMETRIC METHOD

REAGENTS

Ammonium chloride, chemically pure;
nitric acid, concentrated;
ammonium hydroxide, 12% aqueous solution.

PROCEDURE OF CARRYING OUT THE WORK

Taking the sample. Dissolve the calculated exact sample of Mohr's salt in 20 – 25 cm^3 of distilled water in a beaker, add 3 g of ammonium chloride. Heat the solution almost to boiling. Add 1 – 2 cm^3 of the concentrated HNO_3 drop by drop while stirring and continue heating for more 3 – 5 minutes. Then while stirring pour $NH_3 \cdot H_2O$ solution till the odour of ammonium appears and add 100 – 150 cm^3 of hot water. In 5 minutes filter the precipitate and wash it out. Use filters of a mean density («a white label» type).

Measure the volume of the washing liquid in the beaker and calculate the precipitate losses from solubility.

Dry the filter with the precipitate and transfer it into a crucible brought to the mass constant value, burn the filter (see laboratory work № 1).

Bringing the crucible with the precipitate to the mass constant value. Ignite the crucible with the precipitate in the muffle furnace at 800 – 900°C for 10 – 15 minutes (during a long-term ignition the partial reduction of iron (III) ions by carbon to Fe_3O_4 takes place).

The next operations are similar to the ones described in laboratory work № l.

Calculate the percentage of iron (II) ions in Mor's salt.

LABORATORY WORK № 3

DETERMINATION OF THE PERCENTAGE OF MOISTURE BY THE INDIRECT VOLATILIZATION GRAVIMETRIC METHOD

PROCEDURE OF CARRYING OUT THE WORK

Bringing a weighing bottle to the mass constant value. Weigh a glass or metal weighing bottle with the help of the analytical balance, place it in the drying-cabinet previously heated to 150°C for 30 minutes. Then transfer the weighing bottle by crucible tongs into the desiccator. Half-open the desiccator cover (by moving it aside) and allow it to stay at the room temperature for 3 minutes. After that close the desiccator and carefully transfer it to the weighting room, where it is kept for 30 minutes.

Take out the weighing bottle from the desiccator, place it on the left-hand pan of the analytical balance and weigh.

Repeat the process of drying the weighing bottle in the drying-cabinet until reproducible results of weighings are obtained. After bringing the weighing bottle to the mass constant value, place it into the desiccator.

Taking the sample of the substance to be analysed and its drying. Weigh the calculated sample of the substance to be analysed (maltose, lactose, glucose, analgin) with the help of the hand balance and transfer it, as much as possible, into the weighing bottle brought to the mass constant value.

Weigh the weighing bottle with the sample with the help of the analytical balance and place it in the drying-cabinet for 2 hours. Repeat all operations on bringing the weighing bottle with the sample to the mass constant value, keeping it in the drying-cabinet for 15 minutes each time, until the reproducible results of weighings (±0.0005 g) are obtained.

Calculate the percentage of moisture in the substance to be analysed.

LABORATORY WORK № 4
DETERMINATION OF THE PERCENTAGE OF MOISTURE IN KAOLIN BY THE INDIRECT VOLATILIZATION GRAVIMETRIC METHOD

PROCEDURE OF CARRYING OUT THE WORK

Bringing a crucible to the mass constant value. (See laboratory work № 1).

Taking the sample of the medicine and its ignition. Weigh the calculated sample of kaolin with the help of the hand balance and transfer it into the crucible brought to the mass constant value. Weigh the crucible with the sample with the help of the analytical balance and place it with the help of crucible tongs into the muffle furnace for 20 minutes.

Repeat all operations on bringing the crucible with kaolin to the mass constant value, keeping it in the muffle furnace at 400 – 500ºC for 10 minutes each time, until the reproducible results of weighings are obtained.

Calculate the percentage of moisture in kaolin.

LABORATORY WORK № 5
DETERMINATION OF THE PERCENTAGE OF THE TOTAL ASH IN MEDICINAL PLANT RAW MATERIAL BY THE PARTICULATE GRAVIMETRIC METHOD

REAGENTS

Ammonium nitrate, the saturated solution.

PROCEDURE OF CARRYING OUT THE WORK

Bringing a crucible to the mass constant value. (See laboratory work №1).

Taking the sample of the raw material. Weigh the calculated sample of the plant raw material with the help of the hand balance, then with the help of the analytical ones. Transfer it into the crucible brought to the mass constant value.

Burning the substance. Place the crucible on a porcelain triangle and carefully heat it on a small flame of a burner. After the complete combustion of coal parts increase the flame.

In the case of the incomplete combustion of coal parts, cool the rest, moisten it with water or with the saturated solution of ammonium nitrate, evaporate it on a water bath and ignite it again.

Ignition of ash in the crucible. Bringing the crucible with ash to the mass constant value. Place the crucible with the precipitate after combustion of the substance in the desiccator and then transfer it with the help of crucible tongs in the muffle furnace and ignite for 20 minutes at the temperature of about 500°C, periodically observing and not allowing the ash to sinter on crucibles walls.

Carry out bringing the crucible with ash to the mass constant value, as described in Laboratory work №4.

Calculate the percentage of the total ash in the plant raw material.

LABORATORY WORK № 6
DETERMINATION OF THE PERCENTAGE OF THE ASH, INSOLUBLE IN HYDROCHLORIC ACID, IN MEDICINE BY THE PARTICULATE GRAVIMETRIC METHOD

REAGENTS

Hydrochloric acid, 10% solution;
silver nitrate, 0.5 mole/dm^3 solution;
ammonium hydroxide, the concentrated solution.

PROCEDURE OF CARRYING OUT THE WORK

Bringing a crucible to the mass constant value. (See laboratory work № 1).

Taking the sample and burning the substance. Take and burn the calculated sample of the medicine (activated coal), as described in Laboratory work № 5.

Treating the dry rest. Add 15 cm^3 of 10% hydrochloric acid solution to the dry rest obtained the crucible after burning. Cover the crucible with

a watch glass and heat it for 10 minutes on a boiling water bath in the hood.

After that add 5 cm^3 of hot distilled water to the content of the crucible washing a watch glass. Then transfer the liquid from the crucible quantitatively on a prepared filter of «a white label» type. Wash out the rest on the filter by the portions of 10 cm^3 of hot water to the negative chloride-ions reaction. Neglect losses from solubility.

Drying the filter with the precipitate. Burning the filter and ignition of the ash in the crucible. Bringing the crucible with the ash to the mass constant value. Transfer the filter with the precipitate washed out to the same crucible and dry it in the drying-cabinet at the temperature of about 105°C.

After drying the filter transfer the crucible with the help of crucible tongs in the muffle furnace, burn the filter and then ignite at 500°C for about 20 minutes. Carry out bringing crucible with ash to the mass constant value, as described in Laboratory work №4.

Calculate the percentage of the ash, which is insoluble in hydrochloric acid.

LABORATORY WORK № 7
DETERMINATION OF THE PERCENTAGE OF THE SULPHATED ASH IN MEDICINE BY THE PARTICULATE GRAVIMETRIC METHOD

REAGENTS

Sulphuric acid, concentrated.

PROCEDURE OF CARRYING OUT THE WORK

Bringing a crucible to the mass constant value. (See laboratory work № 1).

Taking the sample of the substance. Take the calculated sample of the substance (glucose, phtalazole, novocaine, phenolphthalein), as described in Laboratory work № 5.

Treating the sample and ignition. Carefully add 1 cm^3 of the concentrated sulphuric acid to the exact sample of the medicine in a porcelain crucible brought to the mass constant value. Heat the crucible with its content on a water bath in the hood till sulphuric acid evaporation completes.

Ignition of sulphated ash in the crucible. Bringing the crucible with sulphated ash to the mass constant value. Transfer the crucible with sulphated ash with the help of crucible tongs from the water bath in the muffle furnace and ignite it at 500°C for 20 minutes.

Carry out bringing crucible with the sulphated ash to the mass constant value, as described in Laboratory work № 4.

Calculate the percentage of the sulphated ash in the medicine.

CONTROL QUESTIONS FOR IN-CLASS AND OUT-OF-CLASS WORK OF STUDENTS

1. Describe gravimetric determination by the precipitation method for each of the given ions : Ba^{2+}, Ca^{2+}, Mg^{2+} (HPO_4^{2-}; hydroxyquinoline), Pb^{2+}, Fe^{3+}, Al^{3+} ($NH_3 \cdot H_2O$, 8-hydroxyquinoline), SO_4^{2-}, Cl^-, PO_4^{3-}. While explaining you should answer the following questions.
   1) Write the equations of precipitation reactions for the ion to be determined and transformation of the precipitated form into the gravimetric one.
   2) Calculate the minimal weight, which can be weighed with the help of the balance with the accuracy of ±0.2%, if its grating period is 5 mg.
   3) Write the required value of the sample and the gravimetric form weight if they have been weighed with the help of the analytical balance. Compose the formula for calculating the percentage of the ion to be determined in the solution to be analysed with the help of these numbers and explain it.
   4) Calculate the result and write it down according to the significant numbers.
2. Calculate the precipitant volume (0.2 mole/dm^3 $H_2C_2O_4 \cdot 2H_2O$ solution) for gravimetric determination of Ca^{2+}-ion in 0.1825 g of $CaCl_2$.

3. How is the sample weight in the precipitation gravimetric method calculated?
4. How many times is it necessary to wash out the $BaSO_4$ precipitate by the washing liquid equal portions of 10 cm^3 to decrease the impurity content in 70 times if with each washing the precipitate retains 3.5 cm^3 of the washing liquid?
5. What case will the precipitate be washed out better in: if it is washed out 2 times by the washing liquid with the portions of 50 cm^3 or 5 times with the portions of 20 cm^3 of this liquid?
6. While carrying out the gravimetric determination of the moisture content in glucose the following results of the weighing bottle with sample weighings have been obtained:

   1. m_s = 7.3142 g 4. m_s = 6.9061 g
   2. m_s = 7.2518 g 5. m_s = 6.9067 g
   3. m_s = 6.9084 g 6. m_s = 6.9063 g

   Is it necessary to carry out the further drying the sample? If it is not necessary, then why? What results should be taken for calculations in this case?
7. Calculate the percentage of the hygroscopic moisture in kaolin if the substance sample of 0.5037 g after ignition has decreased to 0.4528 g.
8. To determine the moisture the sample of dandelion roots of 5.1123 g is dried in the weighing bottle to the constant weight of 0.4284 g. Calculate the moisture of the medicinal raw material in percents.
9. Calculate the loss due to solubility when washing out 0.4811 g of Ag_2CrO_4 precipitate by 250 cm^3 of water.

TITRIMETRIC METHODS OF ANALYSIS

Titrimetric (volumetric) methods of the quantitative analysis are based on the accurate measurement of the volume of the reagent solution (titrant), which reacts with the substance to be determined. The titrant concentration should be exactly known.

During titration the titrant solution is added to the solution of the substance to be determined by small portions. While adding a new portion of the titrant the concentration of the substance to be determined decreases, and the concentration of the reaction products increases.

The moment when the titrant is added in the quantity equivalent to the substance to be determined is known as *the equivalence point*.

In practice, the point of the reaction termination or the end-point of titration, which approximates to the equivalence point to a certain extent, is more often fixed.

In chemical methods of analysis it is visually determined by the analytical effect (changes of colour, turbidity of solution, etc.). Often to determine the equivalence point auxiliary substances – indicators are added into the reaction mixture. In physicochemical methods of analysis the end-point of titration is determined by sharp changing the physical value measured (pH, electrical conductivity, etc.) in the process of titration.

Chemical reactions applied in the titrimetric analysis should meet such requirements:

- the reaction should proceed fast enough and be practically irreversible;
- interaction between the substance to be determined and the titrant should occur stoichiometrically, fixing accurately the end-point of titration;
- in the solution there should not be any substances, which interfere the course of the main reaction or fixation of the end-point of titration.

Advantages of titrimetric methods of analysis are: the rate of determination, equipment simplicity, high accuracy, possibility of the analysis process automation.

Titrimetric methods are classified according to the reaction types underlied in basis of the method and according to the way of titration.

CLASSIFICATION OF TITRIMETRIC METHODS OF ANALYSIS ACCORDING TO TYPES OF CHEMICAL REACTIONS

1. *Methods of the acid-base titration*

These methods are based on using the neutralization reaction. They are applied to determine the acids, bases and salts, which create an acid or an alkaline medium reaction after hydrolysis.

2. *Methods of the precipitation titration*

In these methods the substance to be determined while interacting with the titrant is isolated from the solution in the form of a slightly soluble compound.

3. *Methods of the complex formation titration*

Methods of the complex formation titration are based on formation of complexes of the titrant with the substance to be determined.

4. *Methods of the oxidation-reduction titration (redox methods*)

They are based on the oxidation-reduction reactions, which take place between the substance to be determined and the titrant.

CLASSIFICATION OF TITRIMETRIC METHODS ACCORDING TO THE WAY OF TITRATION

1. *Direct titration*

The way of direct titration is that the titrant is added drop by drop to the definite volume of the solution of the substance to be determined in the presence of the indicator to reach the end-point of titration.

2. *Back titration*

The excess of the auxiliary titrant accurately measured and interacted with the substance is added to the solution of the substance to be determined. After completing the reaction the excess of the unreacted titrant is determined by direct titration with another titrant. The method is used in cases when the reaction proceeds slowly, the substance to be determined is volatile or it is impossible to choose an indicator for direct titration.

For example, the concentration of ammonia solution is determined by back titration because of its volatility. The excess of the hydrochloric acid

standard solution is added to the definite volume of the ammonia solution, then its rest is titrated with the sodium hydroxide standard solution.

3. *Displacement titration (indirect titration, substitution titration)*

An auxiliary reagent is added to the solution of the substance to be determined with which it forms a new compound (a substituent) in the equivalent quantity to the substance to be determined. A substituent concentration is determined by direct titration. This method is used when the substance to be determined does not react with the titrant or reacts with it non-stoichiometrically.

For example, potassium dichromate reacts with the titrant $Na_2S_2O_3$ non-stoichiometrically. Therefore, the reagent KI is added to the solution of the substance to be determined ($K_2Cr_2O_7$), then the equivalent quantity of iodine liberated from it is determined by the subsequent titration with the sodium thiosulphate standard solution.

TECHNIQUE AND ACCURACY OF ANALYSIS

The basic operations in titrimetric analysis are weighing the sample of the substance to be determined and measuring the titrant volume. Usually a relative error of titrimetric analysis is ±0.2%. So, the operations mentioned above should be carried out with no less accuracy. An absolute error of volumes measuring with the help of macroburettes (25.00; 50.00 cm^3) with the grating period of 0.1 cm^3 is ±0.04 cm^3. Hence, the minimum volume *X*, which can be measured with the error not exceeding ±0.2%, is calculated:

$$X = \frac{\Delta X}{A} \cdot 100,$$

where ΔX – is an absolute error of measuring, cm^3;

A – is a relative error of measuring, %;

$$X = \frac{\pm 0.04}{\pm 0.2} \cdot 100 = 20\ cm^3.$$

This volume is further specified as $V_{min.}$

Preparing the titrants

The basic solution in titrimetric analysis is the standard (titrated) solution – titrant, with the help of which the substance content in the sample to be examined is determined.

Preparation of titrant solutions requires the compliance of special rules, thoroughness and exactness in work.

The method of the titrant preparation depends on properties of the initial substance, from which the standard solution is prepared. There are some methods of preparing titrated solutions.

Preparation of primary standard solutions. The simplest way is the following one: the exact sample of the substance is weighed with the help of the analytical balance; it is dissolved in the measuring flask and is diluted to the volume by distilled water. The solution prepared in this way is known as the primary standard solution or the solution with the prepared titre. Primary standard solutions are prepared only from standard substances, which should satisfy the following requirements:

- the substance should be easily obtained in the chemically pure form, have a known structure, conformed exactly to the chemical the formula;
- the substance should be stable while storing, both in a dry state and in the solution;
- the substance should be readily soluble in water (or in other solvent);
- the substance should have, as far as possible, a high molar mass value that decreases errors when weighing the sample.

In this way it is possible to prepare titrated solutions from chemically pure substances: $K_2Cr_2O_7$, $KBrO_3$, $H_2C_2O_4$, $Na_2B_4O_7$, etc.

Preparation of secondary standard solutions. It is difficult to obtain some substances in a pure state due to their volatility, high hygroscopicity, interaction with the air oxygen or ability to absorb carbon (IV) oxide from the air.

For example, alkalis (NaOH, KOH) besides hygroscopic moisture contain impurities of respective carbonates (Na_2CO_3, K_2CO_3) due to absorption CO_2 from the air. In this case a solution is prepared with the approximate concentration, which is somehow greater than required by cal-

culations. The concentration of the solution obtained is determined against standard substances or with the help of other standard solutions.

The titrant solution prepared in this way is known as the secondary standard solution or the solution with the determined titre.

There are two ways of determining the exact concentration of a secondary standard:

– the method of separate samples;
– the pippeting method.

The method of separate samples. The sample of the standard substance is calculated by the corresponding the formula. Separate, almost equal samples of the standard substance are weighed with the help of the analytical balance (about 20 cm^3 of the standard solution should be spent for titration of each of them), are dissolved in the volume of water suitable for titration (20 – 25 cm^3) and are titrated with the solution which is being standardized. The method of separate samples is more exact, but it demands great expenses of time.

The pippeting method. The calculated sample of the standard substance is weighed with the help of the analytical balance, quantitatively transferred into the measuring flask, dissolved in distilled water and diluted to the volume by distilled water. The aliquot of the solution prepared in this way is transferred by a pipette into a conic flask and titrated with the solution, which is being standardized.

Preparation of titrants from «fixanals». «Fixanals» are often used for preparation of titrated solutions. «Fixanal», or the standard-titre, is a sealed glass ampoule, which contains the amount of the substance exactly known in a dry form or in solution. More often there is 0.1 mole of the substance in the ampoule. To prepare the titrated solution the ampoule is broken, its content is quantitatively transferred into a measuring flask of the required volume, diluted by fresh boiled and cooled distilled water, dilute to the volume and mixed thoroughly.

MEASURING THE VOLUMES OF SOLUTIONS

For accurate measurements of the solutions volumes a special glassware for measuring: burettes, pipettes and measuring flasks are used. For approximate volume measurements cylinders and beakers are used.

The burette is a long cylindrical volumetric tube with a tap or other clip (fig. 7). With the help of it the accurate volume of the solution, which is spent for titration is measured. The solution volume is determined as a difference of levels before and after titration. In the laboratory practice when working by the macromethod burettes with the capacity of 25.00; 50.00 cm^3 are applied. Graduation of a burette begins from the top where there is a reference point – zero point. The large division of the burette is 1 cm^3, the small one is 0.1 cm^3. When reading the hundredths of cm^3 are also estimated; a distance between the neighbouring divisions is mentally divided into five parts. For accurate reading the eye level should be at the level of the liquid meniscus. If there is a colourless or slightly coloured solution in the burette, reading is taken by the bottom edge of the meniscus, if there is a coloured solution, reading is taken by the upper edge (fig. 8). The results of readings with the accuracy of the hundredths of the volume (cm^3) are written down in the laboratory register.

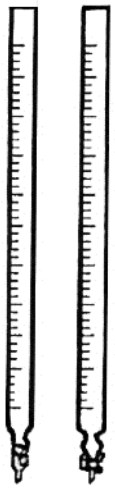


Fig. 7. Burettes

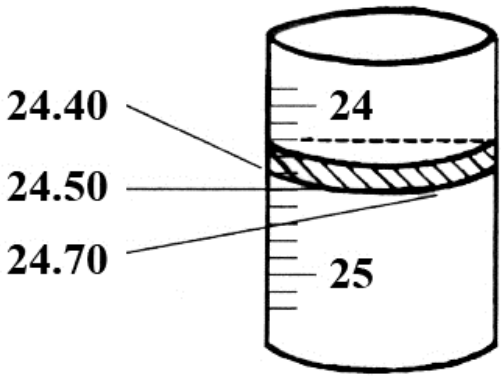


Fig. 8. Reading the volume of the solution by a burette (24.50 is the correct value)

Before using a burette should be thoroughly washed, so that while its washing water moistens the internal surface of the burette evenly, without rests of drops. A burette washed by distilled water is rinsed up three times with a small quantity of the titrant solution to remove the rests of water, which change the concentration of the titrant solution due to its dilution. After that the burette is vertically fixed in a rack. Before each titration the

burette is filled with the solution to the zero point. It is necessary that the narrowed end of the burette should not contain air bubbles and it must be completely filled by the solution. To remove air a rubber clip is bended, the end of the burette is lifted upwards and a ball is compressed or a clip is opened and an air bubble is squeezed out by the solution.

The burette is filled by means of a glass funnel. The level of the liquid is adjusted a little above the zero point, after that the funnel is immediately taken out of the burette. The zero point level is placed on the eye level, and the liquid is letted out from the burette until the suitable edge of meniscus coincides with the zero point.

During titration a liquid from the burette should be letted out slowly, and the reading should be taken in 20 – 30 seconds after completing the titration, enabling all the liquid to drain down the walls of the burette. To prevent splashing the liquid to be titrated or losses of the standard solution the end of the burette should be lowered on 1 – 2 cm into the neck of the flask for titration. To read the results a screen made of a firm white paper or a cardboard with the lower part shaded by black ink (5×5 cm^2) is placed behind the burette. The meniscus is more distinct on the black background. Reading by the burette is taken with the accuracy of ±0.02 cm^3. The volume of the solution, which is spent for titration, should not be too small (not less than 20 cm^3) and should not exceed the capacity of the burette. Titration is carried out several times until the reproducible results are obtained, that is the results of parallel determinations, each of which differs one from another not more than ±0.04 cm^3 for colourless titrants and ±0.05 cm^3 for coloured ones.

Pipettes. These are narrow long tubes with a bulb in the middle. On the top of the narrow part of the pipette tube there is the mark, which limits the certain volume. The capacity and temperature of calibration is specified on the pipette (fig. 9). Cylindrical pipettes graduated like burettes are also used.

Before work a clean pipette washed out by distilled water is rinsed out three times with the solution, the volume of which will be measured. Then the upper part of the pipette is held by the thumb and the middle finger of the right hand, the lower end of the pipette is lowered deep into the liquid.

The liquid is carefully taken through the upper part of the pipette (in case of poisonous and volatile substances it is necessary to use a rubber bag or a syringe).

The pipette lowing is carried out deeply enough for preventing the ingress of air bubbles. The solution is taken a little above the mark, and then the upper part of the pipette is quickly closed by the forefinger. Holding the pipette vertically the forefinger is slightly lifted, allowing the liquid to drain down slowly until the bottom edge of meniscus is on the level of the mark. Meanwhile an eye should be at the mark level.

The upper part of the pipette is closed tightly by the forefinger not letting the liquid to drain down, a pipette is transferred into a flask for titration. The finger is lifted from its upper part and the liquid is allowed to drain down; when all the liquid is drained down, the pipette end is touched to the vessel wall and wait for 10 – 15 seconds until the rests drain down. The liquid remained in the pipette end must not be blown or shaken out, because it was considered during the pipette graduation.

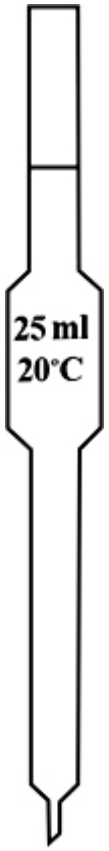


Fig. 9. Pipettes

Measuring flasks. They are flasks with long narrow necks. All round the neck the mark is made to indicate the level, to which the flask should be filled. The volume and the calibration temperature are indicated on the flask. Measuring flasks differ according to their capacity: 5; 10; 25; 50; 100; 200; 250; 500; 1000; 2000 cm^3 (fig. 10).

A measuring flask must be washed thoroughly before use and rinsed out by a suitable solvent.

A measuring flask is filled by the liquid with the help of a funnel. When the level of liquid is below the mark of 0.5 cm, the funnel is taken out and the liquid is added with the help of a drop pipette until the bottom edge of meniscus is at the level of the flask mark (eye should be at the mark level). Then the flask is closed by a cork, and the solution is thoroughly mixed turning slowly over 15 – 20 times.

It is not recommended to heat measuring flasks because of the glass deformation that leads to changing the measuring flask capacity.

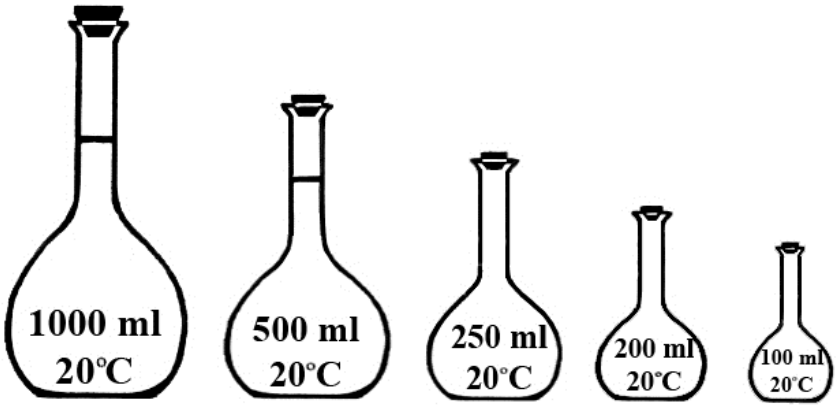


Fig. 10. Measuring flasks

Titration technique

The most suitable vessels for general work are conic flasks. Beakers are not recommended. If the latter are used, a stirring rod must also be employed to mix solutions during the titration. With a conic flask this can be done safely and easily by gently shaking the flask during the titration. The titration vessel should be kept well polished in order that the end-point may be seen clearly. The solution being titrated is generally viewed against a white background (a white tile).

Near the end-point, it is advisable to split the drops of titrant. Partially open the tap so that a fraction of a drop flows out and remains attached to the burette tip. Touch the liquid against the inside of the flask and wash the small volume of a titrant into the bulk of the liquid with a few drops of water. In any event the upper internal portion of the flask should be washed down with some water just before the end-point.

When it is considered that the end-point has been reached, note the burette reading and then, add a further drop of the titrant, when a further distinct colour or other change should occur, unless the indicator changes to colourless. (Note: this cannot be done if the solution is required for subsequent titration when the excess titrant would interfere.)

If the colour change at the end-point is gradual, it is useful to have a comparison solution available. For example, if methyl orange is being used as indicator and the end-point is gradual, two flasks containing the same volume of the solution of approximately the same composition as the liquid being titrated can be prepared, one is slightly acidic (a red solution) and an-

other is slightly alkaline (a yellow solution). These reference solutions will assist in deciding the colour change, which indicates the end-point.

Any solution remaining in the burette after a series of titrations should be rejected and must not be returned to the stock solution. The burette is then washed out with distilled water after use and allowed to drain.

CALCULATIONS IN TITRIMETRIC METHODS OF ANALYSIS

GENERAL STATEMENTS OF TITRIMETRY

Let us specify the basic terms and concepts applied in calculations in the quantitative analysis.

According to the International System of Units of Physical Sizes (SI) *mole* is the amount of a substance, which contains as many real or conditional particles as there are atoms in 0.012 kg of carbon-12 isotope. Thus, this is a physical value, which characterizes the number of structural elements in the given substance as in the system. Therefore, using the concept of *mole* it is necessary to specify what exactly real or conditional particles are born in mind. Real particles are atoms, ions, electrons or molecules. Conditional particles are parts of molecules, ions, etc. For example, 1/6 of $K_2Cr_2O_7$ molecule; 1/2 of $H_2C_2O_4$ molecule; 1/5 of $KMnO_4$ molecule, etc. The amount of the substance (ν) is written down as follows:

$$\nu\ (NaOH) = 1\ \text{mole},$$
$$\nu\ (1/6\ K_2Cr_2O_7) = 1\ \text{mole}.$$

Molar mass of the substance *X* is the mass of 1 mole of the substance, it is written down by letter *M(X)*:

$$M(X) = \frac{m(X)}{\nu(X)},$$

where *m(X)* – is the mass of the substance, g;

ν(X) – is the quantity of moles of the substance X, mole.

A basic unit for molar mass of the substance in SI system is kg/mole, however, in practice g/mole dimension is used more often. For example, molar mass of Fe^{2+}-ion, HCl, 1/2 of I_2 molecules are $M(Fe^{2+})$ = 55.847 g/mole; M(HCl) = 36.461 g/mole; M(1/2 I_2) = 126.9096 g/mole, respectively.

Equivalent is a real or conditional particle (c. p.), which can add, release or interact with one hydrogen atom (ion) or a hydroxide ion, or with other univalent element, or with one electron in oxidation-reduction reactions. Using the term «equivalent» it is necessary to specify the reaction, which it is calculated for.

The factor of equivalence $f_{eqv}(X)$ is a number, which specifies what part of the substance *X* real particle is equivalent to one atom (ion) of an univalent element in this reaction or to one electron in this oxidation-reduction reaction. The factor of equivalence is not a constant value and depends on the exact reaction, in which the substance takes part. For example, in semi-reactions:

$$MnO_4^- + 4\ H^+ + 3\ \bar{e} \rightarrow MnO_2\downarrow + 2\ H_2O$$
$$f_{eqv}(KMnO_4) = 1/3;$$
$$MnO_4^- + 8\ H^+ + 5\ \bar{e} \rightarrow Mn^{2+} + 4\ H_2O$$
$$f_{eqv}(KMnO_4) = 1/5.$$

It should be noted that when calculating f_{eqv} it should be taken into account all reactions, which take place in the process of titration. For example, KIO_3 reacts with KI in the acid medium according to the equation:

$$KIO_3 + 5\ KI + 6\ HCl \rightarrow 3\ I_2 + 6\ KCl + 3\ H_2O$$

Iodine liberated during the given reaction is titrated with sodium thiosulphate:

$$I_2 + 2\ S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2\ I^-$$

It follows from comparing the equations of these two reactions:

$$KIO_3 \equiv 3\ I_2 \equiv 6\ I^-$$

As $3\ I_2 + 6\ \bar{e} = 6\ I^-$, $f_{eqv}(KIO_3) = 1/6$.

If only the first equation is used for $f_{eqv}(KIO_3)$ calculation, $f_{eqv}(KIO_3)$ = 1/5, and it is not true.

Such value of f_{eqv} would be correct if the first reaction was carried out potentiometrically with registration of the iodine amount that is being liberated.

Molar mass of the equivalent substance E(X) is the mass of one mole of the equivalents of this substance, which equals to the product of the factor of equivalence and the molar mass of this substance:

$$E = f_{eqv}(X) \cdot M(X)$$

THE EXPRESSION WAYS OF SOLUTIONS CONCENTRATION

Molar concentration of a dissolved substance (c(X)) is the amount of the dissolved substance contained in 1 dm^3 (1 l) of the solution. Molar concentration of the dissolved substance *X* is calculated as the ratio of the amount of the dissolved substance *ν(X)* and the volume of this solution (dimension is mole/dm^3 or mole/l).

The basic unit for molar concentration in the SI system is mole/m^3, however, in practice mole/dm^3 or mole/l are used. According to SPhU molar concentration of solutions is written down as the quantity of the substance moles with the letter M.

Molar concentration of the substance *X* in the solution is written down by *c(X)* symbol and is determined as the ratio of the substance amount *ν(X)* to the volume *V* of the solution:

$$c(X) = \frac{\nu(X)}{V} = \frac{m(X)}{M(X) \cdot V}.$$

Names of solutions with the different molar concentration of a dissolved substance are:

c = 1 mole/dm^3 = 1 M is a monomolar solution;

c = 0.1 mole/dm^3 = 0.1 M is a decimolar solution;

c = 0.01 mole/dm^3 = 0.01 M is a centimolar solution;

c = 0.001 mole/dm^3 = 0.001 M is a millimolar solution.

It is not recommended to use the term «molarity of a solution» instead of the term «molar concentration», although this term is used in SPhU.

The equal volumes of solutions of different substances with the equal molar concentration contain the equal quantity of molecules. It facilitates the volumes calculations of solutions, which take part in the reaction.

Molar concentration of the equivalent substance in a solution is also widely used in practice. It is the ratio of the amount of the equivalent substance $\nu[f_{eqv}(X)X] = \nu(E)$ to the volume of this solution *(V)*:

$$c(f_{eqv}(X)X) = \frac{\nu[f_{eqv}(X)X]}{V} = \frac{\nu(E)}{V}.$$

Dimension unit for molar concentration of the equivalent substance is mole/m^3, however, in practice mole/dm^3 or mole/l are used.

If the solution contains 1 mole of the equivalent substance in 1 dm^3, it is called normal. Instead of designation of the measuring unit mole/dm^3 or mole/l abbreviation of «n» or «N» can be used.

A solution with $c(f_{eqv}(X)X) = 0.1$ N is called a decinormal, 0.01 N – is a centinormal, 0.001 N – is a millinormal.

It is necessary to specify f_{eqv} on glasses with solutions, which are marked in units of normal concentration, for example, 0.1 N KIO_3 ($f_{eqv} = 1/6$) or 0.1 N (1/6 KIO_3).

The advantages of using solutions with normal concentration are that solutions with equal normal concentrations react in equal volumes.

If normal concentrations differ, the following equation is correct:

$$c_1 \cdot V_1 = c_2 \cdot V_2 .$$

The titre of a solution is the mass of the dissolved substance expressed in grams in 1 cm^3 of the solution. Titre *T(X)* is calculated as the ratio of the dissolved substance mass *m(X)* to the volume of the solution in cm^3 (dimension is g/cm^3):

$$T(X) = \frac{m(X)}{V} .$$

The titre of a titrant by the substance to be determined T(Y/X) is the mass of the substance to be determined *(X)* expressed in grams, which is equivalent to 1 cm^3 of the titrant *(Y)* with theoretical molar concentration of the equivalent substance (dimension is g/cm^3):

$$T\,(Y/X) = \frac{c_{theor} \cdot E}{1000},$$

where c_{theor} – is theoretical molar concentration of the equivalent substance of the titrant (Y), $mole/dm^3$ or mole/l (for example, 0.01 M);

E – is the molar mass of the equivalent substance to be determined, g/mole.

The mass fraction of the dissolved substance (ω(X)) is the ratio of the mass of the dissolved substance *m(X)* to the mass of the solution m_s:

$$\omega(X) = \frac{m(X)}{m_s}.$$

The mass fraction is expressed as decimal fraction or as percentage (% is the hundredth part), or as per thousand (‰ is the thousandth part), ppm (mln^{-1} is the quantity of particles per million), ppb (bln^{-1} is the quantity of particles per billion).

If percentage of sodium chloride in the solution equals 20%, it means that 100 g of the solution contains 20 g of sodium chloride. If the substance contains 5 ppm of the impurity, it means $5{:}10^6 = 5 \cdot 10^{-4}$% of the impurity or 5 mkg/g of the impurity. If the substance contains 5 ppb of the impurity, it means $5{:}10^9 = 5 \cdot 10^{-7}$% or 5 ng/g.

THE CALCULATION FORMULAE IN TITRIMETRIC ANALYSIS

The method of separate samples

1. According to the molar mass of the equivalent substance:

- *the sample mass of chemically pure substances* used for titrants standardization is calculated according to the formula:

$$m = \frac{c \cdot V_{min} \cdot E}{1000},$$

where V_{min} – is the volume of the titrant solution, which equals approximately 20 cm^3;

- *the sample mass of the substance to be determined* is calculated according to the formula:

$$m = \frac{c \cdot V_{min} \cdot E \cdot 100}{1000 \cdot \omega},$$

where V_{min} – is the volume of the titrant solution, which equals approximately 20 cm^3;

ω – is the percentage of the substance to be determined in the sample;

- *the molar concentration of the equivalent substance of the titrant* is calculated according to the formula:

$$c = \frac{m \cdot 1000}{E \cdot V},$$

where V – is the volume of the titrant solution used for the sample titration, cm^3;

- *the percentage of the substance to be determined in the sample to be analysed* is calculated according to the formulae:

$$\omega, \% = \frac{c \cdot V \cdot E \cdot 100}{1000 \cdot m}, \qquad \text{(direct and substitution titration)}$$

where V – is the volume of the titrant solution used for the sample titration, cm^3;

$$\omega, \% = \frac{(c_1 V_1 - c_2 V_2) \cdot E \cdot 100}{1000 \cdot m}, \qquad \text{(back titration)}$$

where V_1 – is the volume of the titrant solution 1 added in excess, cm^3;

V_2 – is the volume of the titrant solution 2 used for titration, cm^3.

2. According to the titre of the titrant by the substance to be determined:

- *the percentage of the substance to be determined in the sample to be analysed* is calculated according to the formulae:

$$\omega,\% = \frac{T \cdot K \cdot V \cdot 100}{m}, \qquad \text{(direct and substitution titration)}$$

$$\omega,\% = \frac{T_1 \cdot (K_1 V_1 - K_2 V_2) \cdot 100}{m}, \qquad \text{(back titration)}$$

where T – is the titre of the titrant by the substance to be determined in direct and substitution titration, g/cm^3;

T_1 – is the titre of the titrant 1, which reacts directly with the substance to be determined, by the substance to be determined in back titration, g/cm^3;

K, K_1, K_2 – are correction coefficients for the molar concentration of the appropriate titrant solutions:

$$K = \frac{c_{pract}}{c_{theor}} = \frac{V_{pract}}{V_{theor}}.$$

For example, if c_{pract} equals 0.1082, K equals 0.1082/0.1000 = 1.082.

The pippeting method

1. According to the molar mass of the equivalent substance:

- *the sample mass of chemically pure substances* used for titrants standardization is calculated according to the formula:

$$m = \frac{c \cdot V_{min} \cdot E \cdot V_{m.f.} \cdot}{1000 \cdot V_{p.}},$$

where V_{min} – is the volume of the titrant solution, which equals approximately 20 cm^3;

$V_{m.f.}$ – is the volume of the measuring flask, in which the c. p. substance sample is dissolved, cm^3;

$V_{p.}$ – is the volume of the pipette, which is used for measuring the solution aliquot, cm^3.

- *the sample mass of the substance to be determined* is calculated according to the formula:

$$m = \frac{c \cdot V_{min} \cdot E \cdot V_{m.f.} \cdot 100}{1000 \cdot V_{p.} \cdot \omega},$$

where V_{min} – is the volume of the titrant solution, which equals approximately 20 cm^3;

$V_{m.f.}$ – is the volume of the measuring flask, in which the c. p. substance sample is dissolved, cm^3;

$V_{p.}$ – is the volume of the pipette, which is used for measuring the solution aliquot, cm^3;

- *the molar concentration of the equivalent substance of the titrant* is calculated according to the formula:

$$c = \frac{m \cdot V_{p.} \cdot 1000}{E \cdot V_{m.f.} \cdot V},$$

where V – is the volume of the titrant solution used for titration of the aliquot of the standard substance solution, cm^3;

- *the percentage of the substance to be determined in the sample to be analysed* is calculated according to the formulae:

$$\omega,\% = \frac{c \cdot V \cdot E \cdot V_{m.f.} \cdot 100}{1000 \cdot m \cdot V_{p.}}, \quad \text{(direct and substitution titration)}$$

where V – is the volume of the titrant solution used for the sample titration, cm^3;

$$\omega,\% = \frac{(c_1V_1 - c_2V_2) \cdot E \cdot V_{m.f.} \cdot 100}{1000 \cdot m \cdot V_{p.}}, \qquad \text{(back titration)}$$

where V_1 – is the volume of the titrant solution 1 added in excess, cm^3;

V_2 – is the volume of the titrant solution 2 used for titration, cm^3.

2. According to the titre of the titrant by the substance to be determined:

- *the percentage of the substance to be determined in the sample to be analysed* is calculated according to the formulae:

$$\omega,\% = \frac{T \cdot K \cdot V \cdot V_{m.f.} \cdot 100}{m \cdot V_{p.}}, \quad \text{(direct and substitution titration)}$$

$$\omega,\% = \frac{T_1 \cdot (K_1V_1 - K_2V_2) \cdot V_{m.f.} \cdot 100}{m \cdot V_{p.}}, \qquad \text{(back titration)}$$

where T – is the titre of the titrant by the substance to be determined in direct and substitution titration, g/cm^3;

T_1 – is the titre of the titrant 1, which reacts directly with the substance to be determined, by the substance to be determined in back titration, g/cm^3;

K, K_1, K_2 – are correction coefficients for the molar concentration of the appropriate titrant solutions.

When determining the molar concentration of the titrant by titration with the solution of the known concentration the calculations are carried out according to the formula:

$$c_2 = \frac{c_1 \cdot V_1}{V_2},$$

where c_1 – is the molar concentration of the known solution, $mole/dm^3$;

V_1 – is the volume of the solution of the known molar concentration, cm^3;

V_2 – is the volume of the solution, which molar concentration must be determined, cm^3.

When determining the substance mass in grams in the volume of measuring flask the calculations are carried out according to the formulae:

1. According to the molar mass of the equivalent substance:

$$g/V_{m.f.} = \frac{c \cdot V \cdot E \cdot V_{m.f.}}{1000 \cdot V_{p.}}, \qquad \text{(direct and substitution titration)}$$

$$g/V_{m.f.} = \frac{(c_1V_1 - c_2V_2) \cdot E \cdot V_{m.f.}}{1000 \cdot V_{p.}}, \qquad \text{(back titration)}$$

2. According to the titre of the titrant by the substance to be determined:

$$g/V_{m.f.} = \frac{T \cdot V \cdot K \cdot V_{m.f.}}{V_{p.}}, \qquad \text{(direct and substitution titration)}$$

$$g/V_{m.f.} = \frac{T_1 \cdot (K_1V_1 - K_2V_2) \cdot V_{m.f.}}{V_{p.}}, \qquad \text{(back titration)}$$

Calculations in the titrimetric analysis when using the titrant solutions with the molar concentration differ from calculations, in which the molar concentration of the equivalent substance is used.

In all calculation the formulae, which are mentioned above with the molar concentration of the equivalent substance, E value should be replaced by the product $s \cdot M(X)$, where s is the stoichiometric ratio determined according to the equation of the reaction, $M(X)$ is the molar mass of the substance to be determined X.

The stoichiometric ratio shows what amount of the substance to be determined reacts with one mole of the substance of the titrant solution.

For example, when titrating the solution of Fe^{2+}-ion salt with the titrant solution of $KMnO_4$ the process is described by the equation:

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

In this case $s = 5/1 = 5$ (there are 5 Fe^{2+}-ions for one mole of MnO_4^--ions). The percentage of Fe^{2+}-ions in the sample to be determined should be calculated according to the formula:

$$\omega,\% = \frac{c \cdot V \cdot 5 \cdot M(Fe^{2+}) \cdot 100}{1000 \cdot m}.$$

To calculate the titre of the titrant $KMnO_4$ by Fe^{2+}-ions the following the formula is used:

$$T = \frac{c \cdot 5 \cdot M(Fe^{2+})}{1000}.$$

It should be taken into account that solutions with the equal molar concentration react in equal volumes only in case if the stoichiometric ratio s equals 1. For example, it is observed when 0.1 mole/dm^3 NaOH and HCl solutions interact. When 0.1 mole/dm^3 NaOH and H_2SO_4 solutions interact the process is described by the equation:

$$2\ NaOH + H_2SO_4 = Na_2SO_4 + 2\ H_2O$$

In this case two volumes of 0.1 mole/dm^3 NaOH solution will be spent for one volume of 0.1 mole/dm^3 H_2SO_4 solution (in the case of titration of NaOH solution with H_2SO_4 standard solution $s = 2/1 = 2$, and in opposite case $s = 1/2$).

In this connection for analytical aims 0.1 mole/dm^3 NaOH solution and 0.05 mole/dm^3 H_2SO_4 solution are prepared. These solutions react in equal volumes.

The factor mentioned above should be paid a special attention to while carrying out back titration, when the difference between volumes of two titrants solutions is used in calculations. In this case solutions, which react in equal volumes, should be used or the stoichiometric ratio should be taken into account.

In the standardization of NaOH solution by titration with H_2SO_4 standard solution the stoichiometric ratio should be also taken into account. Using the equation $c_1 \cdot V_1 = c_2 \cdot V_2$ for calculating the molar concen-

tration of NaOH solution (c_2) is not correct (c_1 and V_1 – are the molar concentration and the volume of H_2SO_4 standard solution, respectively). In this case the following equation should be used: $s \cdot c_1 \cdot V_1 = c_2 \cdot V_2$, where $s = \frac{c_2}{c_1} = \frac{2}{1} = 2$, from which $c_2 = \frac{s \cdot c_1 \cdot V_1}{V_2} = \frac{2 \cdot c_1 \cdot V_1}{V_2}$.

It should be also mentioned that in spite of differences between the numerical values of titrant solutions concentrations, which are expressed by the molar concentration and the molar concentration of the equivalent substance, which are applied in the analysis, the titres of these solutions coincide. For example, the titres of 0.1 M (1/2 H_2SO_4) and 0.05 M (H_2SO_4) are equal:

$$T\ 0.1M(1/2\ H_2SO_4) = \frac{0{,}1000 \cdot 49{,}037}{1000} = 0.004904\ \text{g/ml},$$

$$T\ 0.05M(H_2SO_4) = \frac{0{,}0500 \cdot 98{,}07}{1000} = 0.004904\ \text{g/ml},$$

$$T\ 0.02M(KMnO_4) = T\ 0.1M(1/5\ KMnO_4) = 0.0031608\ \text{g/ml}.$$

It is not difficult to show that between the molar concentration of the equivalent substance (c_{eqv}) in the solution and its molar concentration there is the following connection:

$$c = c_{eqv} \cdot f_{eqv}.$$

THE GENERAL RULES OF FILLING THE LABORATORY REGISTER

A student notes each work performed in the laboratory register. It is recommended to do notes in the following succession:

1. Date of carrying out a work.
2. The title of the work.
3. The brief description of the method's essence.

4. Then the equations of chemical reactions in a molecular form, conditional particles, which take part in the reaction, their molar masses must be specified.
5. Calculation of the minimal sample weight.
6. The brief description of the procedure of carrying out a work.
7. The table with the results obtained.
8. The calculations according to the molar mass of the equivalent substance and according to SPhU.
9. Statistical processing of the analysis results.
10. Conclusions.

LABORATORY WORKS

LABORATORY WORK № 1
CALIBRATION OF MEASURING VESSELS

When calibrating measuring vessels by manufacturers errors may appear. Therefore, while working with measuring vessels it is necessary to check up the correctness of calibration, i. e. to determine its actual capacity.

Meanwhile it is necessary to take into account that calibration is carried out in two ways:

– calibration «on pouring out» (pipettes, burettes);
– calibration «on pouring in» (measuring flasks).

Therefore, calibration checking is carried out by determining the weight of water, which contains in a measuring vessel or pours out from it. It should be taken into account a number of corrections concerning:

– the change of water density with the change of temperature;
– the change of matter weight according to the Archimedes's principle when weighing on air;
– the change of the flask capacity with the change of temperature.

When checking of capacity of measuring vessels with the volume less than 50 cm^3 weighings are performed with the help of the analytical balance, but with the accuracy of 0.001 g. If measuring vessels have greater

capacity, weighings are performed with the help of the technical balance with the accuracy of 0.02 g.

1.1. Checking the capacity of a measuring flask with the volume 100 cm^3

PROCEDURE OF CARRYING OUT THE WORK

Measuring flasks are calibrated «on pouring in», i. e. on the content of the certain volume of liquid in them. Flasks calibration with the capacity of 100 cm^3 is carried out with the help of the technical balance. To avoid a mistake of weighing because of asymmetrical beam the displacement method is used.

Measure the temperature of the distilled water used for flask filling. (It should not differ from the temperature of the ambient air more than 1°C). Place dry flask thoroughly washed on the left-hand pan of the technical balance, place there the weight of 100 g. Place a container for balancing (metal chips, dry sand or weights) on the right-hand pan. Arrest the balance and take the weight of 100 g off. Fill the flask with the distilled water up to the mark, wipe outside with a towel and delete drops of water from the internal surface of the flask neck with the strips of filtered paper. Then place the flask filled with water on the left-hand pan of the balance again and balance it by adding the weights on left-hand or on the right-hand pan.

In this case three variants are possible:

1. Balance of the technical balances is not broken, it means that the mass of water in the flask is 100.00 g:

$$m_{act.} = 100.00 \text{ g} .$$

2. Balance is broken, it is necessary to add the weight with the mass m (g) on the left-hand pan of the balance. Thus, the mass of water in the flask weights less than 100.00 g on the weight added on the left-hand pan of the balance:

$$m_{act.} = 100.00 – m .$$

3. Balance is broken, it is necessary to add the weight with the mass m (g) on the right-hand pan of the balance. Thus, the mass of water in the flask weights more than 100.00 g on the weight added on the right-hand pan of the balance:

$$m_{act.} = 100.00 + m .$$

Then determine theoretical mass of water m_{theor} taking into account various corrections (A, B, C) at the given temperature, that is the mass of water, which contains in the glass measuring flask, its capacity at the standard temperature (20°C) is equal 100 cm^3.

$$m_{theor} = 100.00 – (A + B + C),$$

find m_{theor} of water at this temperature in reference literature. Find the actual volume of the measuring flask ($V_{fact.}$) according to the formula:

$$V_{act.} = \frac{V_{theor.} \cdot m_{theor.}}{m_{act.}} .$$

Measurement of the measuring flask volume is carried out several times till obtaining the reproducible results, meanwhile the results of weighings should not differ more than ±0.1 g.

1.2. Checking the pipette capacity (of 10.00 – 25.00 cm^3)

PROCEDURE OF CARRYING OUT THE WORK

Measure the temperature of the distilled water used for pipette calibration. Weigh a dry weighing bottle closed by a cork with the accuracy of 0.001 g with the help of the analytical balance. Rinse the thoroughly washed pipette with the distilled water twice, fill the pipette by water to the mark and pour out water into the weighing bottle keeping to the rules of work with pipettes. Close the weighing bottle with the cork and weigh. Find the mass of water contained in the weighing bottle. Calculate the capacity of the pipette exactly as described for measuring flasks.

Repeat the experiment until the reproducible results, which should not differ more than ±0.001 g, are obtained.

1.3. Checking the burette capacity

PROCEDURE OF CARRYING OUT THE WORK

Measure the temperature of the distilled water used for burette calibration. Determine the mass of a dry weighing bottle closed by a cork with the accuracy of 0.001 g with the help of the analytical balance. Wash the burette thoroughly, rinse it with the distilled water twice and fill the burette by water to the mark. Pour out water into the weighing bottle from the burette in the range of 0 – 5 cm^3, 0 – 10 cm^3, 0 – 15 cm^3, etc., each time filling the burette to the zero mark, and weigh the weighing bottle with water. Calculate the capacity of the burette as described for measuring flasks.

Repeat the experiment until the reproducible results are obtained. The results of weighings should not differ more than ±0.001 g. Then make the correction table to the burette volume.

THE ACID-BASE TITRATION (THE NEUTRALIZATION METHOD)

The neutralization reaction underlies in the basis of the acid-base titration method:

$$H^+ + OH^- \rightleftharpoons H_2O$$
$$H_3O^+ + OH^- \rightleftharpoons 2\ H_2O$$

Standard solutions (titrants) of the method are 0.1 mole/dm^3 solutions of HCl, H_2SO_4, NaOH, KOH. Substances, which these solutions are prepared from, are not standard, because alkalis absorb CO_2 from the air and contain impurities of the corresponding carbonates, but concentrated acids solutions are volatile substances, that is why secondary standard solutions are prepared from them. The exact concentration (molarity) of titrants is found against standard substances or by titration with solutions of the known concentration.

Standardization of acids solutions is carried out:

- against standard substances: against borax $Na_2B_4O_7 \cdot 10H_2O$ or sodium carbonate Na_2CO_3;
- by titration with standard solutions of alkalis NaOH and KOH;

Standardization of alkalis solutions is carried out:

- against standard substances: against oxalic acid $H_2C_2O_4$ or succinic acid $H_2C_4H_4O_4$;
- by titration with standard solutions of HCl, H_2SO_4.

Depending on the object to be determined different ways of the acid-base titration: direct titration, back titration, displacement titration are used.

Determination of the end-point of titration

The end-point of titration in the neutralization method is determined with the help of acid-base (pH) indicators, as well as without an indicator – by changing the medium pH (potentiometric titration) or electrical conductance of the solution (conductometric titration).

Choosing the pH-indicators is carried out in two ways: by the products of the reaction and by plotting the titration curves.

Choosing an indicator by the products of the reaction is carried out taking into account medium pH of the solution in the end-point of titration. If the pH of medium is more than 7, the indicator with the transition interval in the alkaline range of pH values is suitable. For example:

$$H_2C_2O_4 + 2\ NaOH \rightleftharpoons Na_2C_2O_4 + 2\ H_2O$$

The product of the reaction (sodium oxalate) is hydrolyzed and forms the alkaline medium:

$$Na_2C_2O_4 + HOH \rightleftharpoons NaHC_2O_4 + NaOH$$
$$NaHC_2O_4 + HOH \rightleftharpoons H_2C_2O_4 + NaOH$$

Therefore, phenolphthalein is used for the given determination (the indicator transition interval is between 8.2 and 10.0 units of pH).

If the product of the reaction forms the acid medium (pH < 7) in the end-point of titration, the indicator with the transition interval in the acid range of pH values is suitable. For example:

$$NaHCO_3 + HCl \rightleftharpoons H_2CO_3 + NaCl$$

To determine the end-point of titration it is possible to use methyl orange (the indicator transition interval is between 3.1 and 4.0 units of pH).

The choice of the indicator by the titration curves is the most exact. With this purpose the titration curve, which represents graphically the change of the solution pH during titration, is plotted.

Indicators with the transition interval, which is completely or partially within the range of titration leap, that is indicators with pT value, which is within the range of titration leap, are suitable for titration.

By the acid-base titration method it is possible to determine:

- strong acids and strong bases;
- weak acids and weak bases (K_i is not less than $5 \cdot 10^{-7}$);
- salts formed from a weak base with $K_B \leq 5 \cdot 10^{-7}$ or a weak acid with $K_A \geq 5 \cdot 10^{-7}$;
- organic compounds with acid or basic properties.

By this method it is possible to determine not only individual substances, but also the mixtures of acids (bases) of various strength, the mixtures of hydrolyzed salts, as well as the mixtures of salts and acids (bases).

Titration of polybasic acids (bases), mixtures of acids (bases), mixtures of hydrolyzed salts is carried out taking into account the stepwise ionisation of polybasic acids (bases) or stepwise hydrolysis of salts, the strength of acids K_A and the strength of bases K_B, it enables to carry out differential titration with fixation of several equivalence points.

Polybasic acids (bases) can be considered as mixtures of acids (bases) of various strength owing to their stepwise ionisation. If acids (bases) significantly differ in strength and the ratio of ionisation constants $\frac{K_1}{K_2} \geq 10^4$, each of acids (bases) will be titrated separately. At first, the strongest acid (base) will be titrated, then the weakest one. Thus, the titration curve has two titration leaps. If $\frac{K_1}{K_2} \leq 10^4$, both acids (bases) will be titrated simultaneously, and the titration curve will have one titration leap.

LABORATORY WORKS

LABORATORY WORK № 1
PREPARATION OF 0.1 mole/dm^3 SODIUM HYDROXIDE AND HYDROCHLORIC ACID SOLUTIONS

$$E(\text{NaOH}) = M(\text{NaOH}) \cdot f_{eqv}; f_{eqv} = 1;$$
$$E(\text{HCl}) = M(\text{HCl}) \cdot f_{eqv}; f_{eqv} = 1.$$

REAGENTS

Sodium hydroxide, chemically pure (c. p.);
hydrochloric acid, concentrated.

PROCEDURE OF CARRYING OUT THE WORK

Preparation of 0.1 mole/dm^3 sodium hydroxide solution. Weigh the sample calculated for preparing the certain volume of sodium hydroxide

solution in a porcelain cup or in a glass weighing bottle with the help of the technical balance, transfer it into the volumetric glass, dissolve in water, dilute to the volume, mix thoroughly, pour into the vessel for storing the solution.

Preparation of 0.1 mole/dm^3 hydrochloric acid solution. Measure the density of the concentrated hydrochloric acid with the help of the areometer. Determine the concentration of this solution in mole/dm^3 and calculate the volume of the concentrated acid, which is necessary for preparation of the certain volume of 0.1 mole/dm^3 solution. Measure the calculated volume of the concentrated acid by measuring cylinder, place in the volumetric glass with small volume of the distilled water, dilute to the volume, mix thoroughly, pour into the vessel for storing the solution.

LABORATORY WORK № 2
STANDARDIZATION OF THE HYDROCHLORIC ACID SOLUTION AGAINST SODIUM TETRABORATE

Such equations of reactions are in the basis of the determination:

$$Na_2B_4O_7 \rightarrow 2\ Na^+ + B_4O_7^{2-} \qquad K_a = 5.8 \cdot 10^{-10}$$

$$B_4O_7^{2-} + 2\ H_2O \rightleftharpoons H_2B_4O_7 + 2\ OH^-$$

$$H_2B_4O_7 + 5\ H_2O \rightleftharpoons 4\ H_3BO_3$$

$$B_4O_7^{2-} + 7\ H_2O \rightleftharpoons 4\ H_3BO_3 + 2\ OH^-$$

$$2\ OH^- + 2\ H^+ \rightleftharpoons 2\ H_2O$$

$$B_4O_7^{2-} + 5\ H_2O + 2\ H^+ \rightleftharpoons 4\ H_3BO_3$$

$$Na_2B_4O_7 + 5\ H_2O + 2\ HCl \rightleftharpoons 4\ H_3BO_3 + 2\ NaCl$$

$$E(Na_2B_4O_7 \cdot 10H_2O) = M(Na_2B_4O_7 \cdot 10H_2O) \cdot f_{eqv};\ f_{eqv} = 1/2.$$

REAGENTS

Sodium tetraborate, c. p.
hydrochloric acid, 0.1 mole/dm^3 solution;
methyl orange, 0.1% solution.

PROCEDURE OF CARRYING OUT THE WORK

Transfer the calculated exact sample of sodium tetraborate through a dry funnel into the measuring flask. Wash off the rests of the substance from the funnel into the measuring flask by small portions of warm water (70 – 80°C). Add water approximately up to the half of the measuring flask. Cool the solution to the room temperature, dilute the solution to the volume with water and mix thoroughly.

Take the aliquot of the solution prepared for titration into a conic flask with the help of the measuring pipette, add 1 – 2 drops of methyl orange and titrate with the hydrochloric acid solution until the change of the colour from yellow to orange after addition of one drop of the titrant. Repeat the titration until the reproducible results are obtained.

Calculate the molar concentration of the equivalent substance of hydrochloric acid in the solution and the correction coefficient (K).

LABORATORY WORK № 3
DETERMINATION OF THE MOLAR CONCENTRATION OF THE EQUIVALENT SUBSTANCE OF SODIUM HYDROXIDE IN THE SOLUTION BY THE HYDROCHLORIC ACID STANDARD SOLUTION

Such equation of reaction is in the basis of the determination:

$$HCl + NaOH \rightleftharpoons NaCl + H_2O$$

REAGENTS

Hydrochloric acid, 0.1 mole/dm^3 solution;
methyl orange, 0.1% solution.

PROCEDURE OF CARRYING OUT THE WORK

Place the volume of the hydrochloric acid solution accurately measured by burette within the range of 20.00 – 25.00 cm^3 into a conic flask, add 1 – 2 drops of the methyl orange solution and titrate with the sodium

hydroxide solution until the change of the colour from red to yellow after addition of one drop of the titrant. For the purpose of avoiding an error take different volumes of the acid for titration within the given range.

Repeat the titration until the reproducible results are obtained. To estimate the reproducibility recalculate the results of all titrations for 20.00 cm^3 of the acid solution.

Calculate the molar concentration of the equivalent substance of sodium hydroxide in the solution and the correction coefficient (K).

LABORATORY WORK № 4
DETERMINATION OF THE OXALIC ACIDPERCENTAGE

Such equation of reaction is in the basis of the determination:

$$H_2C_2O_4 + 2\ NaOH \rightleftharpoons Na_2C_2O_4 + H_2O$$

$$E(H_2C_2O_4 \cdot 2H_2O) = M(H_2C_2O_4 \cdot 2H_2O) \cdot f_{eqv};\ f_{eqv} = 1/2.$$

REAGENTS

Sodium hydroxide, 0.1 mole/dm^3 solution;
phenolphthalein, 0.1% solution in 60% ethanol.

PROCEDURE OF CARRYING OUT THE WORK

Transfer the calculated exact sample of oxalic acid through a dry funnel into a 100.00 cm^3 measuring flask, dissolve in the distilled water, which does not contain CO_2, dilute the solution to the volume and mix thoroughly.

Take the aliquot of the oxalic acid solution for titration into a conic flask with the help of the measuring pipette, add 8 – 10 drops of phenolphthalein and titrate with 0.1 mole/dm^3 sodium hydroxide solution until a pink colour, which is kept for about 30 seconds, appears.

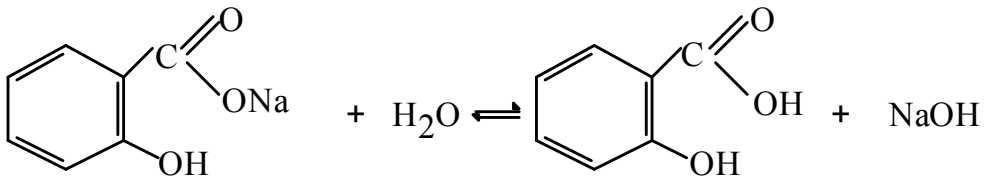
Repeat the titration until the reproducible results are obtained.

Calculate the percentage of oxalic acid.

LABORATORY WORK № 5

DETERMINATION OF THE PERCENTAGE OF SODIUM SALICYLATE

Such equations of reactions are in the basis of the determination:



$$NaOH + HCl \rightleftharpoons NaCl + H_2O$$

$$E(C_7H_5O_3Na) = M(C_7H_5O_3Na) \cdot f_{eqv}; f_{eqv} = 1.$$

REAGENTS

Hydrochloric acid, 0.1 mole/dm^3 solution;
diethyl ether*, c. p.;
methyl orange, 0.1% solution;
methylene blue**, 0.1% solution.

* Diethyl ether extracts salicylic acid insoluble in water, which is formed during titration and can influence on colour of the indicator.

** Methylene blue creates a background for more precise fixation of changing the colour of methyl orange.

PROCEDURE OF CARRYING OUT THE WORK

Dissolve the exact sample of sodium salicylate in 10 cm^3 of water, add about 25 cm^3 of diethyl ether, 2 drops of methyl orange and 1 drop of methylene blue. Titrate with the standard hydrochloric acid solution until the change of the water layer colour from green to violet appears.

Repeat the titration until the reproducible results are obtained.

Calculate the percentage of sodium salicylate.

LABORATORY WORK № 6

DETERMINATION OF THE PERCENTAGES OF SODIUM HYDROXIDE AND SODIUM CARBONATE IN THE MIXTURE

Such equations of reactions are in the basis of the determination:

1. $NaOH + HCl \rightleftharpoons H_2O + NaCl$

   $pH = 7$

2. $CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$

   $OH^- + H^+ \rightleftharpoons H_2O$

   $Na_2CO_3 + HCl \rightleftharpoons NaHCO_3 + NaCl$ (the 1-st equivalence point)

   $pH = 11.8$ $pH = 8.3$

3. $HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$

   $OH^- + H^+ \rightleftharpoons H_2O$

   $NaHCO_3 + HCl \rightleftharpoons H_2CO_3 + NaCl$ (the 2-nd equivalence point)

   $pH = 8.3$ $pH = 3.8$

$$E(NaOH) = M(NaOH) \cdot f_{eqv}; f_{eqv} = 1.$$

$$E(Na_2CO_3) = M(Na_2CO_3) \cdot f_{eqv}; f_{eqv} = 1/2.$$

REAGENTS

Hydrochloric acid, 0.1 mole/dm^3 solution;
phenolphthalein, 0.1% solution in 60% ethanol;
methyl orange, 0.1% solution.

PROCEDURE OF CARRYING OUT THE WORK

Transfer the calculated exact sample of the mixture into the conic flask for titration, dissolve in the volume of water suitable for titration, add 8 – 10 drops of the phenolphthalein solution and titrate with hydrochloric acid till decolouration of the solution takes place. Then add 1 – 2 drops of the methyl orange solution to this solution and continue titration until the

change of the colour from yellow to orange after addition of one drop of the titrant.

V_1 – is the volume of HCl spent for titration with phenolphthalein ($NaOH + 1/2\ Na_2CO_3$ are being titrated), cm^3;

V_2 – is the volume of HCl spent for titration with phenolphthalein and methyl orange ($NaOH + Na_2CO_3$ are being titrated), cm^3;

V_3 – is the volume of HCl spent for titration of Na_2CO_3,

$V_3 = 2\ (V_2 - V_1)$, cm^3;

V_4 – is the volume of HCl spent for titration NaOH,

$V_4 = V_2 - V_3$, cm^3.

Calculate the percentages of sodium hydroxide and sodium carbonate in the mixture according to the corresponding formulae.

LABORATORY WORK № 7
DETERMINATION OF THE PERCENTAGES OF SODIUM HYDROXIDE AND SODIUM HYDROCARBONATE IN THE MIXTURE

Such equations of reactions are in the basis of the determination:

1. $NaOH + HCl \rightleftharpoons NaCl + H_2O$

pH = 7 (the 1-st equivalence point)

2. $HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$

$OH^- + H^+ \rightleftharpoons H_2O$

$NaHCO_3 + HCl \rightleftharpoons H_2CO_3 + NaCl$

pH = 8.3 pH = 3.8 (the 2-nd equivalence point)

$$E(NaOH) = M(NaOH) \cdot f_{eqv}; f_{eqv} = 1.$$

$$E(NaHCO_3) = M(NaHCO_3) \cdot f_{eqv}; f_{eqv} = 1.$$

REAGENTS

Hydrochloric acid, 0.1 mole/dm^3 solution;

phenolphthalein, 0.1% solution in 60% ethanol;

methyl orange, 0.1% solution.

PROCEDURE OF CARRYING OUT THE WORK

Dissolve the calculated exact sample of the mixture in water in a conic flask for titration, add 8 – 10 drops of phenolphthalein solution and titrate with hydrochloric acid till decolouration of the solution, then add 1 – 2 drops of the methyl orange solution to this solution and continue titration until the change of the colour from yellow to orange after addition of one drop of the titrant.

V_1 – is the volume of HCl spent for titration with phenolphthalein (NaOH is being titrated), cm^3;

V_2 – is the volume of HCl spent for titration with phenolphthalein and methyl orange (NaOH + $NaHCO_3$ are being titrated), cm^3;

V_3 – is the volume of HCl spent for titration of $NaHCO_3$,

$V_4 = V_2 - V_1$, cm^3;

Calculate the percentages of sodium hydroxide and sodium hydrocarbonate in the mixture according to the corresponding formulae.

LABORATORY WORK № 8
DETERMINATION OF THE PERCENTAGES OF SODIUM CARBONATE AND SODIUM HYDROCARBONATE IN THE MIXTURE

Such equations of reactions are in the basis of the determination:

1. $CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$

   $OH^- + H^+ \rightleftharpoons H_2O$

   $Na_2CO_3 + HCl \rightleftharpoons NaHCO_3 + NaCl$ (the 1-st equivalence point)

   pH = 11.8 pH = 8.3

2. $HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$

   $OH^- + H^+ \rightleftharpoons H_2O$

   $NaHCO_3 + HCl \rightleftharpoons H_2CO_3 + NaCl$ (the 2-nd equivalence point)

   pH = 8.3 pH = 3.8

$$E(Na_2CO_3) = M(Na_2CO_3) \cdot f_{eqv}; f_{eqv} = 1/2.$$

$$E(NaHCO_3) = M(NaHCO_3) \cdot f_{eqv}; f_{eqv} = 1.$$

REAGENTS

Hydrochloric acid, 0.1 mole/dm^3 solution;
phenolphthalein, 0.1% solution in 60% ethanol;
methyl orange, 0.1% solution.

PROCEDURE OF CARRYING OUT THE WORK

Transfer the calculated exact sample of the mixture into a conic flask for titration, dissolve in the volume of water suitable for titration, add 8 – 10 drops of phenolphthalein solution and titrate with hydrochloric acid till decolouration. Then add 1 – 2 drops of the methyl orange solution to this solution and continue titration until the change of the colour from yellow to orange after addition of one drop of the titrant.

V_1 – is the volume of HCl spent for titration with phenolphthalein (1/2 Na_2CO_3 is being titrated), cm^3;

V_2 – is the volume of HCl spent for titration with phenolphthalein and methyl orange ($NaHCO_3$ + Na_2CO_3 are being titrated), cm^3;

V_3 – is the volume of HCl spent for titration of Na_2CO_3,
$V_3 = 2\ V_1$, cm^3;

V_4 – is the volume of HCl spent for titration $NaHCO_3$,
$V_4 = V_2 - V_3$, cm^3.

Calculate the percentages of sodium carbonate and sodium hydrocarbonate in the mixture according to the corresponding formulae.

LABORATORY WORK № 9
DETERMINATION OF THE MASS-VOLUME FRACTION OF AMMONIA IN THE SOLUTION (BACK TITRATION)

Such equations of reactions are in the basis of the determination:

$$NH_3 \cdot H_2O + HCl \rightleftharpoons NH_4Cl + H_2O$$
$$\text{excess } HCl + NaOH \rightleftharpoons NaCl + H_2O$$

$$E(NH_3) = M(NH_3) \cdot f_{eqv}; f_{eqv} = 1.$$

REAGENTS

Hydrochloric acid, 0.1 mole/dm^3 solution;
sodium hydroxide, 0.1 mole/dm^3 solution;
methyl orange, 0.1% solution.

PROCEDURE OF CARRYING OUT THE WORK

Measure 35.00 – 40.00 cm^3 of the standard hydrochloric acid solution in a conic flask by a burette, add 15.00 cm^3 of the ammonia solution to be determined by a measuring pipette, add 1 – 2 drops of the methyl orange solution. Titrate the excess of the acid, which has not reacted with ammonia, with the standard sodium hydroxide solution until the change of the colour from red to yellow after addition of one drop of the titrant.

Repeat the titration until the reproducible results are obtained.

Calculate the mass-volume fraction of ammonia in the solution.

LABORATORY WORK № 10
DETERMINATION OF THE MASS-VOLUME FRACTION OF ACETIC ACID IN THE SOLUTION (BACK TITRATION)

Such equations of reactions are in the basis of the determination:

$$CH_3COOH + NaOH \rightleftharpoons CH_3COONa + H_2O$$
$$\text{excess } NaOH + HCl \rightleftharpoons NaCl + H_2O$$

$$E(CH_3COOH) = M(CH_3COOH) \cdot f_{eqv}; f_{eqv} = 1.$$

REAGENTS

Hydrochloric acid, 0.1 mole/dm^3 solution;
sodium hydroxide, 0.1 mole/dm^3 solution;
phenolphthalein, 0.1% solution in 60% ethanol.

PROCEDURE OF CARRYING OUT THE WORK

Measure 35.00 – 40.00 cm^3 of the standard sodium hydroxide solution in a conic flask by a burette, add 15.00 cm^3 of the acetic acid solution to be

determined by a measuring pipette, add 8 – 10 drops of the phenolphthalein solution. Titrate the excess of the base, which has not reacted with acetic acid, with the standard hydrochloric acid solution till decolouration.

Repeat the titration until the reproducible results are obtained.

Calculate the mass-volume fraction of acetic acid in the solution.

CONTROL QUESTIONS FOR IN-CLASS AND OUT-OF-CLASS WORK OF STUDENTS

1. The essence and classification of titrimetric methods of analysis.
2. Requirements to reactions in titrimetric methods of analysis.
3. Standard substances and requirements to them. Standard solutions, their preparation and standardization.
4. Acid-base indicators. The index of titration and the indicator transition interval, relationship between them.
5. Rules of choosing an indicator by reaction products and by plotting the titration curves.
6. Direct and back titration, cases of their application.
7. The possibility of determination of hydrolyzed salts by the acid-base titration method.
8. The possibility of determination of acids (bases) mixtures by the acid-base titration method.
9. How many cm^3 of the concentrated HCl should be taken to prepare 1 dm^3 of 0.1 mole/dm^3 HCl solution (ρ = 1.19 g/cm^3)?
   Answer: 8.0 cm^3.
10. Calculate the volume of 0.0924 mole/dm^3 NaOH solution spent for titration of 20.00 cm^3 of 0.1012 mole/dm^3 HCl solution.
    Answer: 21.90 cm^3.
11. Determine the percentage of $H_2C_2O_4 \cdot 2H_2O$ in 0.1582 g of the medicine if 21.37 cm^3 of 0.1093 mole/dm^3 KOH solution has been spent for the sample titration.
    Answer: $\omega(H_2C_2O_4 \cdot 2H_2O) = 87.53\%$.

TITRIMETRIC METHODS OF PRECIPITATION (THE PRECIPITATION TITRATION)

Titrimetric methods of precipitation are based on using when titrating the reactions accompanied by formation of slightly soluble compounds. The essence of methods is in that the equivalent quantity of the precipitant in the form of the standard solution is added to the solution of a certain substance. Precipitation titration reactions should satisfy the following requirements:

- the precipitate formed must be practically insoluble ($K_S^0 \approx 10^{-10}$ for binary electrolytes; $K_S^0 \approx 10^{-12}$ for precipitates of other composition);
- the precipitation reaction should proceed quickly, quantitatively, stoichiometrically, without formation of oversaturated solutions;
- the results of titration should not be appreciably misrepresented by the processes of co-precipitation.

It is necessary to add the titrant slowly close to the equivalence point and mix the solution intensively to remove the adsorption effect.

Argentometry (the Mohr method, the adsorptive indicators method of Fajans-Khodakov); thiocyanatometry and mercurometry are the most widely applied methods in analytical practice.

ARGENTOMETRY

The argentometric methods are based on using the standard solutions of silver (I) nitrate as a precipitant, and they are used mainly for quantitative determination of halogenide-, thiocyanate-ions and silver (I)-ions:

$$Ag^+ + HaL^- \rightarrow AgHaL\downarrow$$

The main standard solutions are 0.05 mole/dm^3 or 0.1 mole/dm^3 $AgNO_3$ solutions, which are more often prepared as secondary standard solutions with the further standardization against chemically pure KCl, NaCl or by titration with standard solutions of these salts.

$AgNO_3$ solutions are photosensitive and are stored in vessels made of a dark glass.

THE MOHR METHOD

The method titrant is 0.05 mole/dm^3 or 0.1 mole/dm^3 $AgNO_3$ solution. The indicator is K_2CrO_4 solution, its application is based on fractional precipitation of halogenide- and chromate-ions.

When titrating Cl^--ions by the Mohr method in the presence of CrO_4^{2-}-ions chloride-ions are precipitated at first:

$Ag^+ + Cl^- \rightarrow \downarrow AgCl$ (white)

$K_S^0(AgCl) = 1.78 \cdot 10^{-10}$ $\quad$ $S(AgCl) = 1.33 \cdot 10^{-5}$ mole/dm^3

After complete precipitation of chloride-ions the excess drop of $AgNO_3$ solution causes formation of a brick-red Ag_2CrO_4 precipitate:

$2\ Ag^+ + CrO_4^{2-} \rightarrow \downarrow Ag_2CrO_4$ (brick-red)

$K_S^0(Ag_2CrO_4) = 2.1 \cdot 10^{-12}$ $\quad$ $S(Ag_2CrO_4) = 8.1 \cdot 10^{-5}$ mole/dm^3

In the end-point of titration the precipitates are coloured in a brick-red colour.

Conditions of titration by the Mohr method are:

- titration is carried out in the neutral or weak alkaline medium (pH = 6.3 – 10.5);
- silver (I) chromate is dissolved in the acid medium:

$$2\ Ag_2CrO_4\downarrow + 2\ H^+ \rightarrow 4\ Ag^+ + Cr_2O_7^{2-} + H_2O;$$

- decomposition of the titrant occurs in the alkaline medium at pH ≥ 10:

$$2\ Ag^+ + 2\ OH^- \rightarrow 2\ AgOH\downarrow \rightarrow Ag_2O\downarrow + H_2O;$$

- Pb^{2+}, Ba^{2+}, Hg_2^{2+}, Bi^{3+} and other ions, which form precipitates with chromate-ion, as well as PO_4^{3-}-, CO_3^{2-}-, $C_2O_4^{2-}$-, AsO_4^{3-}- and other anions, which precipitate silver (I)-ion, should be absent in the solution.

The Mohr method is applied for determination of chloride- and bromide-ions. Determination of iodide-ions is difficult due to their powerful adsorption on the surface of AgI precipitate.

Some salt of haloid acids and weak bases are not determined by the Mohr method, because their aqueous solutions have the acid medium as the result of hydrolysis.

The main methodical error in titration by the Mohr method will be the indicator error, because the solution is consciously overtitrated.

LABORATORY WORKS

LABORATORY WORK № 1
PREPARATION OF 0.1 mole/dm^3 SILVER (I) NITRATE SOLUTION

$$E(AgNO_3) = M(AgNO_3) \cdot f_{eqv}; f_{eqv} = 1$$

REAGENTS

Silver (I) nitrate, c. p.

PROCEDURE OF CARRYING OUT THE WORK

Weigh the calculated exact sample of $AgNO_3$ (recrystallized and dried at 220 – 250°C) with the help of the technical balance, transfer into the vessel for preparing the solution, dissolve in a required amount of water, then dilute the solution volume to 1 dm^3 with distilled water, mix and pour into the vessel for storing the solution.

LABORATORY WORK № 2
STANDARDIZATION OF 0.1 mole/dm^3 SILVER (I) NITRATE SOLUTION AGAINST SODIUM CHLORIDE

Such equations of reactions are in the basis of the determination:

$$AgNO_3 + NaCl \rightarrow AgCl\downarrow + NaNO_3$$
$$2\ AgNO_3 + K_2CrO_4 \rightarrow Ag_2CrO_4\downarrow + 2\ KNO_3$$

$$E(NaCl) = M(NaCl) \cdot f_{eqv}; f_{eqv} = 1.$$

REAGENTS

Sodium chloride, c. p.;
silver (I) nitrate, 0.1 mole/dm^3 solution;
potassium chromate, 5% solution.

PROCEDURE OF CARRYING OUT THE WORK

Transfer the exact sample of sodium chloride quantitatively calculated (recrystallized twice from water and slightly ignited in a crucible at 250 – 300°C) through a dry funnel into a measuring flask, dissolve in water, dilute the solution to the volume. Place the aliquot of the solution into a conic flask for titration by a measuring pipette, add 2 – 4 drops of K_2CrO_4 solution and titrate with $AgNO_3$ solution mixing it thoroughly until the precipitate formed becomes with a brick-red tint.

Repeat the titration until the reproducible results are obtained.

Calculate the molar concentration of the equivalent substance of silver (I) nitrate in the solution and the correction coefficient (K).

LABORATORY WORK № 3
DETERMINATION OF THE PERCENTAGE OF POTASSIUM BROMIDE BY THE MOHR METHOD

Such equations of reactions are in the basis of the determination:

$$KBr + AgNO_3 \rightarrow AgBr\downarrow + KNO_3$$
$$2\ AgNO_3 + K_2CrO_4 \rightarrow Ag_2CrO_4\downarrow + 2\ KNO_3$$

$$E(KBr) = M(KBr) \cdot f_{eqv}; f_{eqv} = 1.$$

REAGENTS

Silver (I) nitrate, 0.1 mole/dm^3 solution;

potassium chromate, 5% solution.

PROCEDURE OF CARRYING OUT THE WORK

Dissolve the calculated exact sample of potassium bromide in a conic flask in the volume of water suitable for titration, add 2 – 4 drops of K_2CrO_4 solution and titrate with the standard solution of silver (I) nitrate until a brick-red colour of precipitate formed appears.

Repeat the titration until the reproducible results are obtained.

Calculate the percentage of potassium bromide.

LABORATORY WORK № 4

DETERMINATION OF THE PERCENTAGE OF SODIUM CHLORIDE IN THE ISOTONIC SOLUTION

Such equations of reactions are in the basis of the determination:

$$NaCl + AgNO_3 \rightarrow AgCl\downarrow + NaNO_3$$
$$2\ AgNO_3 + K_2CrO_4 \rightarrow Ag_2CrO_4\downarrow + 2\ KNO_3$$

$$E(NaCl) = M(NaCl) \cdot f_{eqv}; f_{eqv} = 1.$$

REAGENTS

Silver (I) nitrate, 0.1 mole/dm^3 solution;
potassium chromate, 5% solution.

PROCEDURE OF CARRYING OUT THE WORK

Carry out the work by the semi-micromethod, which differs from the macromethod in the reduced volume of the solution of the substance to be determined and application of a semi-microburette with the capacity of 5.00 cm^3 and the grating period of 0.02 cm^3.

Transfer the aliquot of the isotonic solution into a flask for titration by a measuring pipette, add 4 – 5 drops of K_2CrO_4 solution and titrate with the standard solution of silver (I) nitrate until a brick-red colour of the precipitate formed appears.

Repeat the titration until the reproducible results are obtained.

Calculate the percentage of sodium chloride in the volume to be investigated of the isotonic solution.

THE FAJANS-KHODAKOV METHOD

The method is based on direct titration of halogenides (Cl^-, Br^-, I^--ions) and thiocyanate-ions with the standard solution of silver (I) nitrate in the presence of adsorption indicators. Adsorption indicators are weak organic acids, which dissociate according to the scheme:

$$HInd \rightarrow H^+ + Ind^-$$

The anions of these acids are able to be adsorbed by the surface of the precipitates formed near to the equivalence point, and it leads to changing the colour of the mixture to be titrated and allows to fix the end-point of titration.

Eosine, fluoresceine, dichlorfluoresceine, etc., are widely used as adsorption indicators in analytical practice. So, for example, at iodide-ions (KI) titration with silver (I)-ions ($AgNO_3$) the precipitate of AgI is able to form colloidal solutions:

$$Ag^+ + I^- \rightarrow AgI\downarrow$$

First of all, colloidal particles of AgI adsorb ions, which are into the composition of the precipitate on its surface. Till the moment of equivalence there is excess of I^--ions in the solution. They are adsorbed by the micelle centre m[AgI] and give it a negative charge: m[AgI]·$n I^-$ (the primary adsorptive layer). The structure of the micelle formed includes a certain quantity of counter-ions $(n - x)K^+$, which form the secondary (external) adsorptive micelle layer: $\{m[AgI]\cdot nI^-\cdot(n-x)K^+\}^{x-}$.

After reaching the moment of equivalence the excess of silver(I)-ions, which are adsorbed by the micelle centre: m[AgI]·$n Ag^+$ and give it a positive charge, appears in the solution. At this time as counter-ions are adsorbed nitrate-ions and form the secondary (external) micelle layer: $\{m[AgI]\cdot nAg^+\cdot(n-x)NO_3^-\}^{x+}$. Nitrate-ions do not form a precipitate with parts of the micelle, therefore, they are easy replaced with a coloured anion of the indicator, and it leads to the abrupt colour change on the surface of the precipitate in the equivalence point.

Conditions of titration by the Fajans-Khodakov method:

– titration is carried out at different pH values, for example, titration with fluoresceine at pH = 7...10 (determination of Cl^-, Br^-, I^-, SCN^--ions), with eosine at pH = 2 (determination of Br^-, I^-, SCN^--ions; when determining Cl^--ions eosine are not used because of the colour change of the precipitate proceeds before reaching the point of equivalence);

– the precipitate must have the maximal surface, that is look like colloidal particles, that is why the protective colloidal solution: starch, dextrin, etc., are added to the solution to be titrated;
– indicator ions must be adsorbed by the precipitate much less than the ions to be determined to avoid the results with conservative values.

LABORATORY WORKS

LABORATORY WORK № 1
DETERMINATION OF THE PERCENTAGE OF SODIUM CHLORIDE IN THE MEDICINE

Such equation of reaction is in the basis of the determination:

$$NaCl + AgNO_3 \rightarrow AgCl\downarrow + NaNO_3$$

$$E(NaCl) = M(NaCl) \cdot f_{eqv}; f_{eqv} = 1.$$

REAGENTS

Silver (I) nitrate, 0.1 mole/dm^3 solution;
fluoresceine, 0.5% solution.

PROCEDURE OF CARRYING OUT THE WORK

Transfer the calculated exact sample of sodium chloride into a measuring flask, dissolve in water and dilute the solution to the volume, mix. Transfer the aliquot of the solution into a flask for titration by a measuring pipette, add the volume of water approximately equal to aliquot, add 3 – 5 drops of the fluoresceine solution. Titrate the green solution obtained with the $AgNO_3$ standard solution while shaking continuously in diffused light till the colour of the precipitate becomes pink-red.

Repeat the titration until the reproducible results are obtained.

Calculate the percentage of sodium chloride.

LABORATORY WORK № 2

DETERMINATION OF THE PERCENTAGE OF POTASSIUM IODIDE IN THE MEDICINE

Such equation of reaction is in the basis of the determination:

$$KI + AgNO_3 \rightarrow AgI\downarrow + KNO_3$$

$$E(KI) = M(KI) \cdot f_{eqv}; f_{eqv} = 1.$$

REAGENTS

Silver (I) nitrate, 0.1 mole/dm^3 solution;
sodium eosinate, 0.1 mole/dm^3 solution;
acetic acid, 2 mole/dm^3 solution.

PROCEDURE OF CARRYING OUT THE WORK

Dissolve the calculated exact sample of potassium iodide, previously dried at 110°C for 4 hours, in a flask for titration in 15 – 20 cm^3 of water, add 2 cm^3 of the acetic acid solution, 5 drops of the sodium eosinate solution and titrate with the $AgNO_3$ standard solution till the colour of the precipitate changes from yellow to pink.

Repeat the titration until the reproducible results are obtained.

Calculate the percentage of potassium iodide.

Explain the necessity of adding the acetic acid in the solution.

THIOCYANATOMETRY (RODANOMETRY)
THE FOLGARD METHOD

The standard solutions in thiocyanatometry are 0.05 mole/dm^3 and 0.1 mole/dm^3 NH_4SCN or KSCN solutions; 0.05 mole/dm^3 and 0.1 mole/dm^3 $AgNO_3$ solutions.

Silver (I) nitrate and ammonium (potassium) thiocyanate in the presence of the indicator – Fe (III) salts in the form of $NH_4[Fe(SO_4)_2]\cdot 12H_2O$ are determined by direct titration of the Folgard method.

Determination of silver salts is based on the such reaction as:

$$Ag^+ + NCS^- \rightarrow AgNCS\downarrow \qquad K_S^0(AgNCS) = 1.1\cdot10^{-12}$$

After complete precipitation of Ag^+-ions the excess drop of the titrant reacts with Fe^{3+}-ions with forming the water-soluble complex ions with the various structure: $[Fe(NCS)]^{2+}$, $[Fe(NCS)_2]^+$, $[Fe(NCS)_3]$ ... $[Fe(NCS)_6]^{3-}$.

The indirect Folgard method provides direct titration of the ion to be determined by silver (I) nitrate solution, but the indicator and a little quantity (0.1 cm^3) of 0.1 mole/dm^3 NH_4SCN solution are added to the halogenide sample diluted in water and acidified by nitric acid, and the solution is titrated until the pink colour of the complex $[Fe(SCN)_3]$ formed with the interaction of Fe (III)- and thiocyanate-ions disappears.

Silver nitrate firstly reacts with halogenide-ions:

$$KI + AgNO_3 \rightarrow AgI\downarrow + KNO_3$$

The excess drop of $AgNO_3$ solution interacts with iron (III) thiocyanate owing to the solution above the precipitate becomes colourless:

$$[Fe(NCS)_3] + 3\ AgNO_3 \rightarrow 3\ AgNCS\downarrow + Fe(NO_3)_3$$

In case of back titration for halogenide-ions determination two standard solutions – $AgNO_3$ solution and NH_4SCN or KSCN solution are used.

To the halogenide solution analysed a definite excessive volume of $AgNO_3$ standard solution is added:

$$Ag^+ + HaL^- \rightarrow AgHaL\downarrow$$

The excess of silver (I) nitrate, which has not reacted, is titrated with the standard NH_4SCN solution in the presence of the indicator $NH_4[Fe(SO_4)_2]\cdot12H_2O$.

$$Ag^+ + NCS^- \rightarrow AgNCS\downarrow$$
$$Fe^{3+} + 3\ NCS^- \rightarrow [Fe(NCS)_3]$$

In the end-point of titration the solution above the precipitate is coloured in a red colour.

Conditions of titration by the Folgard method are:

- titration is carried out in the acid medium, which prevents the hydrolysis of Fe(III)-ions. The method is used for titration in acid solutions because AgSCN is not dissolved in acids. It favourably distinguishes it from the Mohr method and the Fajans-Khodakov method when determining Ag^+ and halogenide-ions in a strong acid medium;
- Hg^{2+}-salts prevent the titration, because they form a precipitate with NCS^--ions, as well as F^--ions, which form a strong complex with salts of Fe(III):

$$Fe^{3+} + 6\ F^- \rightarrow [FeF_6]^{3-};$$

- the silver (I) thiocyanate precipitate is able to adsorb Ag^+-ions on its surface, it increases the determination error, therefore, it is necessary to carry out the titration with the intensive shaking;
- while determining iodide-ions the following reaction is possible:

$$2\ Fe^{3+} + 2\ I^- \rightarrow 2\ Fe^{2+} + I_2,$$

thus, the indicator should be added in the end of titration;

- when determining chloride-ions the exchange reaction is possible:

$$AgCl\downarrow + NCS^- \rightarrow AgNCS\downarrow + Cl^-,$$

thus, to prevent the contact of AgCl particles with thiocyanate-ions 1 – 2 cm^3 of CCl_4, $CHCl_3$ or nitrobenzene in the solution to be titrated are added.

LABORATORY WORKS

LABORATORY WORK № 1
PREPARATION OF 0.1 mole/dm^3 AMMONIUM THIOCYANATE SOLUTION

$$E(NH_4NCS) = M(NH_4NCS) \cdot f_{eqv}; f_{eqv} = 1$$

REAGENTS

Ammonium thiocyanate, c. p.

PROCEDURE OF CARRYING OUT THE WORK

Weigh the calculated sample of NH_4SCN in a weighing bottle with the help of the technical balance (the salt is hygroscopic), transfer into a beaker for preparing the solution and dissolve in a small quantity of water, then dilute the solution volume to 1 dm^3; mix thoroughly and pour into a vessel for storing the solution.

LABORATORY WORK № 2
STANDARDIZATION OF 0.1 mole/dm^3 AMMONIUM THIOCYANATE SOLUTION BY THE SILVER (I) NITRATE STANDARD SOLUTION

Such equations of reactions are in the basis of the determination:

$$NH_4NCS + AgNO_3 \rightarrow AgNCS\downarrow + NH_4NO_3$$
$$3\ NH_4NCS + NH_4[Fe(SO_4)_2] \rightarrow [Fe(NCS)_3] + 2\ (NH_4)_2SO_4$$

$$E(NH_4NCS) = M(NH_4NCS) \cdot f_{eqv}; f_{eqv} = 1.$$

REAGENTS

Silver (I) nitrate, 0.1 mole/dm^3 solution;
nitric acid, 2 mole/dm^3 solution;
ammonium iron (III) sulphate, the saturated solution.

PROCEDURE OF CARRYING OUT THE WORK

Measure by a burette 20.00 cm^3 of the $AgNO_3$ standard solution in a flask for titration, add 50 cm^3 of water, 2 cm^3 of nitric acid, 2 cm^3 of $NH_4[Fe(SO_4)_2]\cdot 12H_2O$ saturated solution and titrate with the solution of ammonium thiocyanate when shaking vigorously till the pink colour of the solution above the precipitate appears.

Repeat the titration until the reproducible results are obtained.

Calculate the molar concentration of the equivalent substance of ammonium thiocyanate in the solution and the correction coefficient (K).

LABORATORY WORK № 3
DETERMINATION OF THE PERCENTAGE OF SILVER (I) NITRATE IN THE SAMPLE TO BE DETERMINED

Such equations of reactions are in the basis of the determination:

$$AgNO_3 + NH_4NCS \rightarrow AgNCS\downarrow + NH_4NO_3$$
$$3\ NH_4NCS + NH_4[Fe(SO_4)_2] \rightarrow [Fe(NCS)_3] + 2\ (NH_4)_2SO_4$$

$$E(AgNO_3) = M(AgNO_3) \cdot f_{eqv}; f_{eqv} = 1.$$

REAGENTS

Ammonium thiocyanate, 0.1 mole/dm^3 solution;
nitric acid, 2 mole/dm^3 solution;
ammonium iron (III) sulphate, the saturated solution.

PROCEDURE OF CARRYING OUT THE WORK

Dissolve the calculated exact sample of $AgNO_3$ in the flask for titration in 25 – 30 cm^3 of water, add 5 cm^3 of 2 mole/dm^3 nitric acid solution, 2 cm^3 of $NH_4[Fe(SO_4)_2]\cdot 12H_2O$ saturated solution and titrate with the standard solution of ammonium thiocyanate till the red colour of the solution above the precipitate appears.

Repeat the titration until the reproducible results are obtained.

Calculate the percentage of silver (I) nitrate.

LABORATORY WORK № 4

DETERMINATION OF THE PERCENTAGE OF TRIIODMETHANE (IODOFORM) IN MEDICINE

Such equations of reactions are in the basis of the determination:

$$CHI_3 + 3\ AgNO_3 + H_2O \rightarrow 3\ AgI\downarrow + 3\ HNO_3 + CO\uparrow$$

$$\text{excess of } AgNO_3 + NH_4NCS \rightarrow AgNCS\downarrow + NH_4NO_3$$

$$3\ NH_4NCS + NH_4[Fe(SO_4)_2] \rightarrow [Fe(NCS)_3] + 2\ (NH_4)_2SO_4$$

$$E(CHI_3) = M(CHI_3) \cdot f_{eqv}; f_{eqv} = 1/3.$$

REAGENTS

Silver (I) nitrate, 0.1 mole/dm^3 solution;
ammonium thiocyanate, 0.1 mole/dm^3 solution;
ammonium iron (III) sulphate, the saturated solution;
ethanol, 95%;
nitric acid, 2 mole/dm^3 solution.

PROCEDURE OF CARRYING OUT THE WORK

Transfer the exact sample of iodoform in a dry conic flask with the capacity of 250 – 300 cm^3, dissolve in 25 cm^3 of 95% ethanol, add 30.00 cm^3 of $AgNO_3$ standard solution (measure by a burette), 10 cm^3 of 2 mole/dm^3 nitric acid solution and heat with the reflux cooler on the water bath for 30 minutes (protect the reaction flask from light). Add 100 cm^3 of water through the cooler in the flask, remove the cooler and add 2 cm^3 of ammonium iron (III) sulphate saturated solution into the flask and titrate with NH_4SCN standard solution till the pink colour of the solution above the precipitate appears.

Simultaneously carry out the control experiment where all components, except the substance to be determined, are used.

Repeat the titration until the reproducible results are obtained.

Calculate the percentage of triiodmethane in the medicinal substance.

MERCUROMETRY

The mercurometric method of analysis is based on reactions of the halogenide-ions precipitation by salts of mercury (I)-cation:

$Hg_2^{2+} + 2\ Cl^- \rightarrow Hg_2Cl_2\downarrow$ $\qquad K_S^0 = 1.3 \cdot 10^{-18}$

$Hg_2^{2+} + 2\ Br^- \rightarrow Hg_2Br_2\downarrow$ $\qquad K_S^0 = 5.8 \cdot 10^{-23}$

$Hg_2^{2+} + 2\ I^- \rightarrow Hg_2I_2\downarrow$ $\qquad K_S^0 = 4.5 \cdot 10^{-29}$

The titrant of the method is 0.1 mole/dm^3 solution of $Hg_2(NO_3)_2$ in the diluted nitric acid (the solution of secondary standardization, because mercury(I)-salts are unstable and contain the impurity of Hg^{2+}-ions). That is why before standardization the titrant is kept above metallic mercury not less than twenty four hours, and it leads to reduction of Hg^{2+}-ions according to the equation:

$$Hg^{2+} + Hg \rightarrow Hg_2^{2+}$$

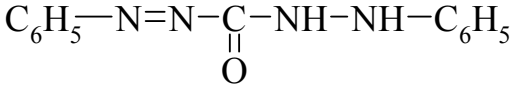
The following substances are used as indicators in the mercurometric method of analysis:

– *iron (III) thiocyanate* $Fe(NCS)_3$. The action of the indicator is based on the fact that after precipitation of halogenide-ions in the solution there is an excess of Hg_2^{2+}-ions, which react with NCS^--ions, and as a result, the red colour of the solution disappears:

$$3\ Hg_2^{2+} + 2\ [Fe(NCS)_3] \rightarrow 3\ [Hg_2(NCS)_2] + 2\ Fe^{3+}$$

Disadvantage of using iron (III) thiocyanate as an indicator is the necessity to carry out the control experiment, where the titrant volume used for the reaction with the indicator is determined. This volume of the solution is subtracted from the volume of the titrant solution spent for titration of halogenide-ions;

– *diphenylcarbazone* (1% solution in 95% ethanol)



The action of the indicator is based on the fact that after the complete precipitation of halogenide-ions the excess drop of the titrant forms either the precipitate of a dark blue colour (in a neutral or a weak acid medium) or the solution of a dark blue colour (in the medium of 6 mole/dm^3 HNO_3) with diphenylcarbazone.

The advantage of using diphenylcarbazone is the possibility of titration in a strong acid medium, as well as in the coloured or turbid solutions, also the possibility of back titration.

The mercurometric method of analysis has a number of advantages to argentometry:

- the application of an expensive titrant is excluded;
- salts of mercury(I)-cation are less soluble than the corresponding salts of silver, therefore, when titrating chloride-ions with $Hg_2(NO_3)_2$ solution a sharp leap of titration near to the point of equivalence is observed;
- in comparison with the thiocyanatometric method of the analysis it is possible to carry out the titration in the presence of peptized substances;
- some oxidants and reducers (MnO_4^--, CrO_4^{2-}-, NO_2^--, SO_3^{2-}-, S^{2-}-ions, H_2O_2) do not prevent the mercurometric determination of Cl^--ions.

LABORATORY WORKS

LABORATORY WORK № 1
PREPARATION OF 0.1 mole/dm^3 MERCURY (I) NITRATE SOLUTION

$$E(Hg_2(NO_3)_2 \cdot 2H_2O) = M(Hg_2(NO_3)_2 \cdot 2H_2O) \cdot f_{eqv}; f_{eqv} = 1/2$$

REAGENTS

Mercury (I) nitrate, c. p.;
nitric acid, 0.2 mole/dm^3 solution;
metallic mercury.

PROCEDURE OF CARRYING OUT THE WORK

Weigh the calculated sample of $Hg_2(NO_3)_2 \cdot 2H_2O$ with the help of the technical balance, transfer into a beaker for preparing a solution and dissolve while heating weakly in 1 dm^3 of 0.2 mole/dm^3 nitric acid solution. Add some (3 – 4) drops of metallic mercury to the solution obtained and mix. Pour into a vessel for storing the solution and allow it to stand not less than twenty four hours. It is necessary to protect the solution from the action of light.

ATTENTION! Salts of mercury (I) and metallic mercury are poisonous.

LABORATORY WORK № 2

STANDARDIZATION OF 0.1 mole/dm^3 MERCURY (I) NITRATE SOLUTION AGAINST SODIUM CHLORIDE

Such equation of reaction is in the basis of the determination:

$$Hg_2(NO_3)_2 + 2\ NaCl \rightleftharpoons Hg_2Cl_2\downarrow + 2\ NaNO_3$$

$$E(NaCl) = M(NaCl) \cdot f_{eqv}; f_{eqv} = 1.$$

REAGENTS

Mercury (I) nitrate, 0.1 mole/dm^3 solution;
sodium chloride, c. p.;
ammonium thiocyanate, 0.05 mole/dm^3 solution;
iron (III) nitrate, the saturated solution.

PROCEDURE OF CARRYING OUT THE WORK

Dissolve the calculated exact sample of NaCl in water in a measuring flask and dilute the solution to the volume by water. Transfer the aliquot of the solution prepared into a flask for titration by a measuring pipette, add 1 cm^3 of NH_4SCN solution and 2 – 3 cm^3 of $Fe(NO_3)_3$ saturated solution. Titrate the obtained mixture of red colour with $Hg_2(NO_3)_2$ solution while shaking vigorously till decolouration occurs. Simultaneously carry out the

control experiment. By the difference of titrant volumes in the basic and the control experiment calculate the volume of $Hg_2(NO_3)_2$ solution spent directly for titration of aliquots of the sodium chloride solution.

Repeat the titration until the reproducible results are obtained.

Calculate the molar concentration of the equivalent substance of mercury (I) nitrate in the solution and the correction coefficient (K).

LABORATORY WORK № 3
DETERMINATION OF THE PERCENTAGE OF POTASSIUM CHLORIDE IN THE MEDICINE

Such equation of reaction is in the basis of the determination:

$$2\ KCl + Hg_2(NO_3)_2 \rightleftharpoons Hg_2Cl_2\downarrow + 2\ KNO_3$$

$$E(KCl) = M(KCl) \cdot f_{eqv}; f_{eqv} = 1.$$

REAGENTS

Mercury (I) nitrate, 0.1 mole/dm^3 solution;
nitric acid, 2 mole/dm^3 solution;
diphenilcarbazone, 1 – 2% solution in ethanol.

PROCEDURE OF CARRYING OUT THE WORK

Dissolve the calculated exact sample of KCl in water in a flask for titration, add 5 – 6 drops of 2 mole/dm^3 nitric acid solution, which does not contain impurities of Cl^--ions. Then add 2 – 3 drops of the diphenylcarbazone solution and titrate drop by drop with $Hg_2(NO_3)_2$ standard solution while shaking vigorously. In the process of titrant addition the colour of the solution becomes gradually blue. Close to the equivalence point the colour becomes blue-violet. The results of the first titration are approximate because when adding diphenylcarbazone at the beginning of titration it is difficult to fix the moment of equivalence. Similarly carry out the second (exact) titration, but the indicator is added before 1 – 2 cm^3 the moment of equivalence is reached.

Calculate the percentage of potassium chloride.

CONTROL QUESTIONS FOR IN-CLASS AND OUT-OF-CLASS WORK OF STUDENTS

1. Which reactions are in the basis of titrimetric methods of precipitation? Requirements to these reactions.
2. Give the classification of titrimetric methods of precipitation according to titrants and indicators, which are used in quantitative analysis.
3. Which ways of preparing the titrant are used in argentometry? Substantiate your answer.
4. Give the comparative characteristic of the Mohr method and the Fajans-Khodakov method according to the scheme:
   - the reaction, which is in basis of the method;
   - the titrants of methods, its preparation, standardization, storage;
   - the indicators of the methods, their qualitative characteristics, the mechanism of action;
   - conditions of titration, their substantiation;
   - the objects of analysis, including medicines;
   - advantages and disadvantages of the methods.
5. Which titrants are used in the method of thiocyanatometry? Preparation and storage conditions of titrant solutions.
6. Give the chemical explanation of the mechanism of the indicator action and the conditions of carrying out analysis by the Folgard method.
7. Specify and substantiate possible mistakes when determining chloride- and iodide-ions by the indirect Folgard method. Which practical measures are used for their prevention?
8. Give the characteristic of the mercurometric method with the specification of the titrant, indicators of the method, conditions of titration.
9. Calculate the samples required for preparing 250 cm^3 of 0.1 mole/dm^3 $AgNO_3$ and NH_4SCN solutions.
10. How many grams of KCl are contained in 250 cm^3 of the solution, if 34.00 cm^3 of 0.1050 mole/dm^3 $AgNO_3$ solution are used for titrating 25.00 cm^3?
    Answer: 2.6620 g.

11. The solution containing 0.1918 g of sodium bromide was treated with 35.00 cm^3 of 0.1092 mole/dm^3 $AgNO_3$ solution. For back titration 25.45 cm^3 of 0.05 mole/dm^3 (K = 0.9200) solution of ammonium thiocyanate are used. Calculate the percentage of NaBr in the medicine.
Answer: 89.83%.
12. Calculate the molar concentration of $Hg_2(NO_3)_2$ solution if 18.06 cm^3 of the titrant are used for titration of 0.1350 g of KCl.
Answer: 0.1003 mole/dm^3.

METHODS OF COMPLEX FORMATION (COMPLEXOMETRY)

Complexometric methods of analysis are based on reactions of complex formation with inorganic and organic ligands. The greatest importance in titrimetric analysis has complex formation of metal-ions with halogenide- and pseudohalogenide-ions (SCN^-, CN^-), as well as with the group of aminopolycarboxylic acids, which are united under the general name «complexones».

The reactions used in complexometry should proceed quickly, stoichiometrically and quantitatively.

Stoichiometric proceeding the reaction depends on the coordination number of the complexing agent (it should be small) and on dentation of the ligand.

Generally inorganic ligands are mono dentate (Cl^-, CN^-, SCN^-, NH_3, etc.), in complexometry their use is limited because unlike polydentate ligands the complex formation with them generally proceeds non-stoichiometrically.

In analytical practice mercurimetric and complexonometric methods of analysis have the widest application.

MERCURIMETRIC TITRATION

The method is based on formation of stable complex compounds when mercury (II) nitrate solution interacts with Cl^-, Br^-, I^-, CN^--ions:

$$Hg^{2+} + 2\ Cl^- \rightleftharpoons [HgCl_2]$$

The titrant of the method is 0.1 mole/dm^3 solution of mercury (II) nitrate, it is prepared as the secondary standard solution with the further standardization against NaCl or KCl, or by their standard solutions. The following substances are used as indicators in mercurimetry:

– sodium nitroprusside solution, which forms a precipitate of a white colour ($K_S^{\,0} = 1.0 \cdot 10^{-9}$) with Hg^{2+} in the end-point of titration:

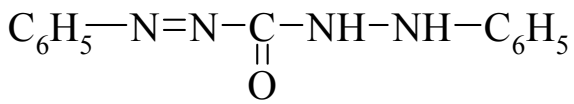
$$Na_2[Fe(CN)_5NO] \rightarrow 2\ Na^+ + [Fe(CN)_5NO]^{2-}$$
$$Hg^{2+} + [Fe(CN)_5NO]^{2-} \rightleftharpoons Hg[Fe(CN)_5NO]\downarrow,$$

however, the main methodical mistake arises when Hg^{2+}-ions interacts with $[HgCl_2]$ formed during titration of Cl^--ions:

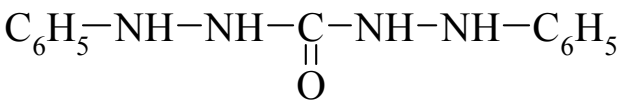
$$Hg^{2+} + [HgCl_2] \rightleftharpoons 2[HgCl]^+,$$

therefore, the necessity of introducing the correction coefficient to the equivalent titrant volume arises;

– the best indicators are diphenylcarbazide (1) solution and the product of its oxidation – diphenylcarbazone (2):



(1)



(2)

In the end-point of titration the excess drop of the titrant $Hg(NO_3)_2$ reacts with the indicator with formation of a complex compound of a dark blue colour.

– when determining iodide-ions it is possible mercurimetric titration without an indicator till the non-disappearing pink turbidity appears in the end-point of titration:

$$2\ I^- + Hg^{2+} \rightleftharpoons HgI_2\downarrow$$
$$HgI_2\downarrow + 2\ I^- \rightleftharpoons [HgI_4]^{2-}$$
$$Hg^{2+} + 4\ I^- \rightleftharpoons [HgI_4]^{2-}$$

The excess drop of the mercury (II) nitrate solution reacts with a complex ion $[HgI_4]^{2-}$ with appearance of HgI_2 precipitate of pink-orange colour:

$$[HgI_4]^{2-} + Hg^{2+} \rightleftharpoons 2\ HgI_2\downarrow$$

While determining iodide-ions the results with a slightly conservative values are obtained (dissociation of $[HgI_4]^{2-}$ complex), that is why the correction, which value is proportional to the total volume of the mixture being titrated, calculated in the following way: 0.35 cm^3 of the titrant volume per 20.00 cm^3 of the mixture, is added to the volume of $Hg(NO_3)_2$ solution used for titration.

The mercurimetric method of analysis has a number of advantages: it allows to determine a large group of anions, Hg^{2+}-ions, hydrohalogen salts of alkaloids and nitrogen bases by direct titration in the acid medium; titrate the mixture of halogenide in one sample. The presence of other ions does not influence on the results of the analysis; besides, salts of mercury(II)-ion can be easily regenerated.

However, the main disadvantage of the method is a high toxicity of the titrant that demands strict observance of rules of work with poisonous substances.

LABORATORY WORKS

LABORATORY WORK № 1
PREPARATION OF 0.1 mole/dm^3 MERCURY (II) NITRATE SOLUTION

$$E(Hg(NO_3)_2 \cdot H_2O) = M(Hg(NO_3)_2 \cdot H_2O) \cdot f_{eqv}; f_{eqv} = 1/2$$

REAGENTS

Mercury (II) nitrate, c. p.;
nitric acid, concentrated.

PROCEDURE OF CARRYING OUT THE WORK

Weigh the calculated sample of $Hg_2(NO_3) \cdot 2H_2O$ with the help of the technical balance, transfer into a beaker and dissolve in 2 cm^3 of the concentrated nitric acid and 50 cm^3 of water, then dilute the solution to the volume of 1 dm^3, mix thoroughly. Pour into a vessel for storing the solution.

LABORATORY WORK № 2

STANDARDIZATION OF 0.1 mole/dm^3 MERCURY (II) NITRATE SOLUTION AGAINST SODIUM CHLORIDE

Such equation of reaction is in the basis of the determination:

$$Hg(NO_3)_2 + 2\ NaCl \rightleftharpoons [HgCl_2] + 2\ NaNO_3$$

$$E(NaCl) = M(NaCl) \cdot f_{eqv}; f_{eqv} = 1.$$

REAGENTS

Sodium chloride, c. p.;
diphenilcarbazone, 1% solution in ethanol.

PROCEDURE OF CARRYING OUT THE WORK

Transfer the calculated exact sample of sodium chloride recrystallized twice from water and slightly ignited in a crucible at the temperature of 250 – 300°C in a conic flask, dissolve in 50 cm^3 of water, add 4 – 5 drops of the diphenylcarbazone solution and titrate with $Hg_2(NO_3)_2$ solution till the yellow colour of the solution changes to light violet.

Repeat the titration until the reproducible results are obtained.

Calculate the molar concentration of the equivalent substance of mercury (II) nitrate in the solution and the correction coefficient (K).

LABORATORY WORK № 3

DETERMINATION OF THE PERCENTAGE OF POTASSIUM IODIDE IN THE MEDICINE

Such equations of reactions are in the basis of the determination:

$$2\ KI + Hg(NO_3)_2 \rightleftharpoons HgI_2\downarrow + 2\ KNO_3$$

$$HgI_2\downarrow + 2\ I^- \rightleftharpoons [HgI_4]^{2-}$$

$$E(KI) = M(KI) \cdot f_{eqv}; f_{eqv} = 1.$$

REAGENTS

Mercury (II) nitrate, 0.1 mole/dm^3 solution.

PROCEDURE OF CARRYING OUT THE WORK

Dissolve the calculated exact sample of KI in a flask for titration in 25 – 30 cm^3 of water and titrate without the indicator with $Hg_2(NO_3)_2$ solution until of a non-disappearing pink turbidity appears.

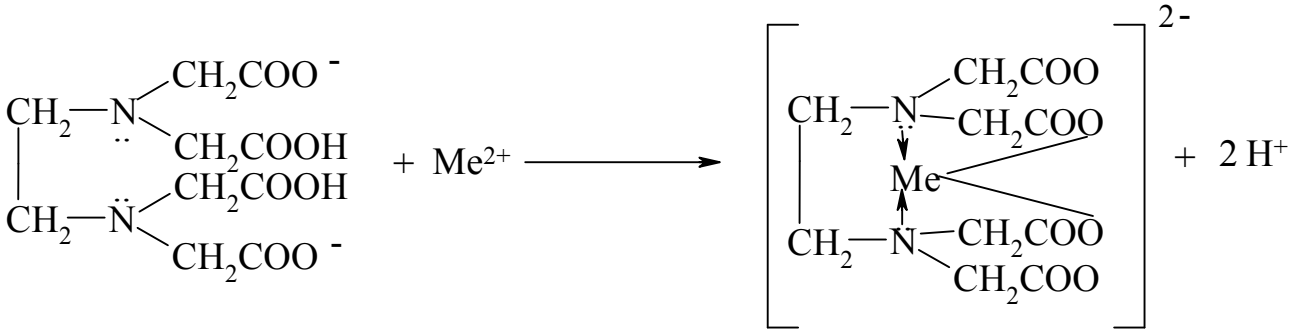
Repeat the titration until the reproducible results are obtained.

Calculate the percentage of potassium iodide subjected to the correction to the equivalent titrant volume.

COMPLEXONOMETRY (TRILONOMETRY)

The method is based on interaction of polydentate ligands-complexones with cations of alkaline-earth and heavy metals with formation of very stable, readily soluble in water, generally colourless, intracomplex (chelate) compounds.

Trilon B solutions (dihydrate of ethylenediamine-N,N,N',N'-tetraacetic acid disodium salt, disodium edetate) with 0.02 – 0.1 molar concentration, which forms complex compounds with cations of a number of metals in the ratio of 1:1, regardless of the metal ion valency, are used as the titrant:



H_2L^{2-} $[MeL]^{2-}$

or schematically:

$$H_2L^{2-} + Me^{2+} \rightleftharpoons [MeL]^{2-} + 2\ H^+$$
$$H_2L^{2-} + Me^{3+} \rightleftharpoons [MeL]^{-} + 2\ H^+$$
$$H_2L^{2-} + Me^{4+} \rightleftharpoons [MeL] + 2\ H^+$$

Stability of complex compounds of metal cations with Trilon B depends greatly on the nature of the metal and pH of the medium. For example, Fe^{3+}-ions with Trilon B form very stable complex compounds and can be determined in the acid medium. The majority of cations in these conditions form less stable complex compounds, therefore, their determination is carried out in the presence of the ammonia buffer solution (pH = 8 – 9), which binds hydrogen-ions formed owing to reactions.

To fix the end-point of titration metallochromic indicators – organic compounds forming in aqueous solutions with the ions determined the coloured complex compounds, which are less stable than a complex compound of a metal with Trilon B, are used in complexonometry.

$$Me^{2+} + H_2Ind^- \rightleftharpoons [MeInd]^- + 2\ H^+$$

After having reached the point of equivalence decomposition of the complex compound of a metal with an indicator occurs and the solution takes the colour of a free indicator:

$$[MeInd]^- + H_2L^{2-} \rightleftharpoons [MeL]^{2-} + H_2Ind^-$$

Fixing the moment of the equivalence in complexonometry can be carried out not only visually, but also potentiometrically.

In complexonometry various methods of titration – direct, back, substitution titration, oxidation-reduction, indirect alkalimetric titration are used.

In the method of *direct titration* the ions determined are titrated with Trilon B solution in the presence of a metallochromic indicator and a buffer solution. In this way hardness of water, Cu^{2+}-, Co^{2+}-, Pb^{2+}-, Ni^{2+}-, Zn^{2+}-, Fe^{3+}-, Al^{3+}-, Ba^{2+}-, Cr^{3+}-, Ca^{2+}-, Mg^{2+}-ions, etc. are determined (the factor of equivalence $f_{eqv} = 1$).

In case of *back titration* the exact excessive volume of the Trilon B standard solution, a buffer solution and an indicator are added to the ion to be determined; the mixture is heated before the reaction is over, then it is cooled and the excess of complexone is titrated with the standard solution of magnesium sulphate or zinc sulphate.

The colour of the solution in the end-point of titration is caused by formation of a complex compound of a metalloindicator with Mg^{2+}- або Zn^{2+}-ions:

$$Me^{2+} + H_2L^{2-} \rightleftharpoons [MeL]^{2-} + 2\ H^+$$
$$\text{excess of } H_2L^{2-} + Mg^{2+} \rightleftharpoons [MgL]^{2-} + 2\ H^+$$

The method of *substitution titration* is based on formation of a less stable complex compound of Mg^{2+}-ions with Trilon B in comparison with other cations ($K_{unstb.} = 2.7 \cdot 10^{-9}$), thus, the exchange reaction with the ion determined is possible:

$$Me^{2+} + [MgL]^{2-} \rightleftharpoons [MeL]^{2-} + Mg^{2+}$$

Liberated Mg^{2+}-ions are titrated in the presence of chromogen black indicator.

$$Mg^{2+} + [H_2L]^{2-} \rightleftharpoons [MgL]^{2-} + 2\ H^+$$

The method of indirect *alkalimetric titrations* is used taking into account that when the Trilon B solution interacts with cation, the equivalent quantity of hydrogen-ions, which is further titrated with alkali in the presence of the acid-base indicator (the factor of equivalence $f_{eqv} = 1/2$) is liberated:

$$Me^{2+} + [H_2L]^{2-} \rightleftharpoons [MeL]^{2-} + 2\ H^+$$
$$2\ H^+ + 2\ OH^- \rightleftharpoons 2\ H_2O$$

Complexonometric determination of organic compounds is based on quantitative liberation of the substance determined in the form of compounds with zinc(II)- or cadmium(II)-cations. Then Zn^{2+}- and Cd^{2+}-cations, which did not enter into the reaction, are titrated with the Trilon B solution in the presence of suitable indicators or their content in the precipitate is determined.

LABORATORY WORKS

LABORATORY WORK № 1
PREPARATION OF 0.05 mole/dm^3 TRILON B SOLUTION

$E(Na_2H_2C_{10}H_{12}O_8N_2) = M(Na_2H_2C_{10}H_{12}O_8N_2) \cdot f_{eqv}; f_{eqv} = 1$

REAGENTS

Ethylenediamine-N,N,N',N'-tetraacetic acid disodium salt dihydrate, disodium edetate (Trilon B), c. p.

PROCEDURE OF CARRYING OUT THE WORK

Weigh the calculated sample of ethylenediamine-N,N,N',N'-tetraacetic acid disodium salt dihydrate $Na_2H_2C_{10}H_{12}O_8N_2 \cdot 2H_2O$ with the help of the technical balance and dissolve in water in a beaker, dilute the volume to 1 dm^3, mix, filter through the paper filter into a vessel for storing the solution.

LABORATORY WORK № 2
STANDARDIZATION OF 0.05 mole/dm^3 TRILON B SOLUTION AGAINST METALLIC ZINC

REAGENTS

Metallic zinc;
sulphuric acid, 2 mole/dm^3 solution;
ammonia buffer solution, pH 9.5 ... 10;
eriochrome black T – the indicator mixture;
Trilon B, 0.05 mole/dm^3 solution.

PROCEDURE OF CARRYING OUT THE WORK

Dissolve the calculated exact sample of metallic zinc in 40 cm^3 of 2 mole/dm^3 sulphuric acid solution in a measuring flask and dilute the solution to the volume with water. Take the aliquot of the zinc(II) sulphate solution into a flask for titration by a measuring pipette, add 5 cm^3 of the ammonia buffer solution, 0.1 g of the eriochrome black T indicator mixture, 70 cm^3 of water, mix till complete dilution of the indicator and titrate

with the Trilon B solution until the violet colour changes to bright dark blue (without a violet tint).

Repeat the titration until the reproducible results are obtained.

Calculate the molar concentration of the equivalent substance of Trilon B in the solution and the correction coefficient (K).

LABORATORY WORK № 3
DETERMINATION OF THE TOTAL HARDNESS OF WATER

The total hardness of water is caused by the presence of calcium(II)- and magnesium(II)-cations, which total concentration is determined complexonometrically:

$$Ca^{2+} + H_2L^{2-} \rightleftharpoons [CaL]^{2-} + 2\ H^+$$
$$Mg^{2+} + H_2L^{2-} \rightleftharpoons [MgL]^{2-} + 2\ H^+$$

REAGENTS

Trilon B, 0.05 mole/dm^3 solution;
ammonia buffer solution, pH 9.5 ... 10;
eriochrome black T – the indicator mixture.

PROCEDURE OF CARRYING OUT THE WORK

Measure 40.00 – 50.00 cm^3 (the exact volume) of the tap water examined in a flask for titration by a burette, add 10 cm^3 of the ammonia buffer solution, 0.1 g of the eriochrome black T indicator mixture, titrate with the Trilon B standard solution until a dark blue colour appears.

Calculate the total hardness of water (X) according to the formula:

$$X = \frac{c \cdot V_1 \cdot 1000}{V_2},$$

where X – is the total hardness of water, mg-eqv/dm^3;

c – is the molar concentration of the Trilon B solution, mole/dm^3;

V_1 – is volume of the titrant, cm^3;

V_2 – is volume of water taken for analysis, cm^3.

LABORATORY WORK № 4

DETERMINING PERCENTAGES OF CALCIUM(II)- AND MAGNESIUM(II)-IONS WHEN COMBINED

$$E(Ca^{2+}) = M(Ca^{2+}) \cdot f_{eqv}; f_{eqv} = 1$$
$$E(Mg^{2+}) = M(Mg^{2+}) \cdot f_{eqv}; f_{eqv} = 1.$$

REAGENTS

Trilon B, 0.05 mole/dm^3 solution;
sodium hydroxide, 0.1 mole/dm^3 solution;
murexide, the indicator mixture;
ammonia buffer solution, pH 9.5 ... 10;
acid chrome dark blue, the indicator mixture.

PROCEDURE OF CARRYING OUT THE WORK

Transfer the exact sample of mixture of calcium and magnesium salts into a 100 cm^3 measuring flask, dissolve in water distilled twice, dilute the solution to the volume and mix thoroughly. Measure the aliquot of the solution into a flask for titration by a measuring pipette, add 50 cm^3 of water distilled twice, 10 cm^3 of NaOH solution, 0.1 g of the murexide indicator mixture until a pink colour appears and titrate slowly while mixing with the Trilon B standard solution until transition of a pink colour in violet occurs. Mark the titrant volume (V_1) by a burette. After that measure again by a measuring pipette into another flask for titration the aliquot of the solution determined, add 25 cm^3 of the ammonia buffer solution, 50 cm^3 of water distilled twice, 0.1 g of the acid chrome dark blue indicator mixture and titrate slowly while mixing with the Trilon B solution until the solution colour becomes dark blue. Mark the Trilon B volume (V_2) spent for titration of calcium and magnesium salts in the mixture. Determine the volume of Trilon B solution (V) spent for titration of magnesium salt by the difference $V_2 - V_1$.

Repeat the titration until the reproducible results are obtained.

Calculate the percentages of calcium(II)- and magnesium(II)-ions in the mixture.

CONTROL QUESTIONS FOR IN-CLASS AND OUT-OF-CLASS WORK OF STUDENTS

1. What is the essence and what are the possibilities of the mercurimetric method of analysis?
2. The characteristic of indicators used in mercurimetry.
3. The concept of complexones, their characteristic and properties.
4. What methods of complexonometric titration do you know? Their essence and possibilities.
5. Metallochromic indicators. The mechanism of their action.
6. Using the literature from the main list, give the characteristics of complexonometric determination features :
   1) Co^{2+}, Ni^{2+};
   2) Pb^{2+} from the precipitate $PbSO_4$;
   3) Mg^{2+} from the precipitate $Mg_2P_2O_7$;
   4) Ca^{2+} and Fe^{3+}.
7. Calculate the constant logarithm of magnesium with the Trilon B complex compound formation ($lg\beta$), if $\beta = 5.01 \cdot 10^{10}$.
8. Calculate the sample of Trilon B required for preparation of 200 cm^3 of 0.02 mole/dm^3 solution .
   Answer: 1.49 g.
9. 25.00 cm^3 of the solution containing 0.7200 g aluminium salts in 100 cm^3 was treated by 20.00 cm^3 of 0.1024 mole/dm^3 Trilon B solution. The excess of the reagent was titrated with 22.08 cm^3 of 0.0503 mole/dm^3 zinc sulphate solution. Determine the percentage of aluminium(III)-ions in the sample.
   Answer: 15.44%.

THE OXIDATION-REDUCTION TITRATION

Methods of oxidation-reduction titration are based on using reactions associated with electron transfer, i. e. oxidation-reduction processes. They are the most widespread and universal methods of titrimetric analysis and allow to determine directly and indirectly all inorganic substances. Besides, methods of oxidation-reduction titration are suitable for determination of many organic compounds, including medicines, overwhelming majority of them are potential reducers. Solutions of various oxidants or reducers are used as standard solutions.

Depending on properties of the titrant used there are:

– oxidimetry;
– reductometry.

Oxidimetry – is the method of reducers determination by their titration with standard solutions of oxidants. For example, in permanganatometry potassium permanganate solution is used as a titrant, in bromatometry – potassium bromate solution, in chromatometry – potassium chromate solution.

Reductometry – is the method of oxidants determination by their titration with standard solutions of reducers. For example, in hydrazinometry hydrazine hydrochloride solution as a titrant is used, in ascorbinometry – ascorbic acid solution, in ferrometry – iron (II) salts solutions.

The reactions applied in the methods of oxidation-reduction titration should satisfy the general requirements to reactions in titrimetric analysis, i. e. they should proceed quickly, quantitatively, stoichiometrically.

However, many oxidation-reduction reactions proceed slowly because of their multi-stage.

During the reaction of intermediates formation, radicals often takes place. The chemical activity of such compounds is usually higher than parent substances have, and quite often it is the cause of various side reactions. A stoichiometrical oxidation-reduction reaction is the sum of separate stages, and the speed of the total reaction will be determined by the slowest stage. The complex mechanism proceeding of redox reactions, the presence of intermediate products in the system open wide possibilities of

influence on their speed by changing the conditions of their carrying out: concentrations of reagents, temperature of the solution, introduction of catalysts.

First two factors influence also on the value of the real redox potential of the system calculated by the Nernst's equation:

$$E = E^0 + \frac{RT}{nF} ln \frac{a^A{}_{ox}}{a^B{}_{red}} \quad ,$$

where E – is a real redox potential of the system, V;

E^0 – is a standard redox potential of the system, V;

T – is the absolute temperature, K;

n – is a quantity of electrons, which take part in the oxidation-reduction process;

R – is the universal gaseous constant, which equals 8.312 J/mole·K;

F – is the Faraday's constant, which equals 96 500 C.

$a^A{}_{ox}$, $a^B{}_{red}$ – are activities of oxidated and reduced forms of a redox pair raised to their stoichiometrical coefficients powers, respectively, mole/dm^3.

If the oxidation-reduction reaction proceeds with participation of protons, its speed increases with increasing of their concentration according to the mass action law.

In this case the real redox potential of the system increases too. For example, for the system

$$+ 3\ e + MnO_4^- + 4\ H^+ \rightleftharpoons MnO_2\downarrow + 2\ H_2O \qquad (1)$$

$$E = E^0 + \frac{0.059}{3} \lg[MnO_4^-] \cdot [H^+]^4 \text{ (at 25°C)},$$

and for the system

$$+ 5\ e + MnO_4^- + 8\ H^+ \rightleftharpoons Mn^{2+} + 4\ H_2O \qquad (2)$$

$$E = E^0 + \frac{0.059}{5} \lg \frac{[MnO_4^-] \cdot [H^+]^8}{[Mn^{2+}]} \text{ (at 25°C)}$$

The value E depends greatly on the acid concentration, and in the presence of concentrated H_2SO_4 its value increases from +1.51 V to +1.9 V (for reaction 2).

The change of H^+ or OH^--ions concentration causes not only the change of the redox potential value, but, sometimes, the direction of the reaction course. Thus, interaction of arsenite-ions with iodine is possible only in the medium of sodium hydrocarbonate (pH = 9) according to the equation:

$-2\ e + AsO_2^- + 4\ OH^- \rightleftharpoons AsO_4^{3-} + 2\ H_2O$	1	$E^0 = -0.71$ V
$+2\ e + [I_3]^- \rightleftharpoons 3\ I^-$	1	$E^0 = 0.545$ V
$AsO_2^- + [I_3]^- + 4\ OH^- \rightarrow AsO_4^{3-} + 3\ I^- + 2\ H_2O$		

In the acid medium such interaction is impossible because $E^0_{H_3AsO_4/HAsO_2} = 0.56$ V, and it is more than $E^0_{[I_3]^-/3\ I^-} = 0.545$ V, and, therefore, the direction of the reaction course is changed:

$+2\ e + H_3AsO_4 + 2\ H^+ \rightleftharpoons HAsO_2 + 2\ H_2O$	1	$E^0 = 0.56$ V
$-2\ e + 3\ I^- \rightleftharpoons [I_3]^-$	1	$E^0 = 0.545$ V
$H_3AsO_4 + 3\ I^- + 2\ H^+ \rightarrow HAsO_2 + [I_3]^- + 2\ H_2O$		

Introduction of catalysts influences greatly on the speed of oxidation-reduction reactions. Both a foreign substance and one of the reaction products (autocatalysis) can be a catalyst. For example, the catalyst of the permanganate-ions reduction reaction by oxalic acid to Mn^{2+} is manganese(II)-cations that is the product of the reaction.

Proceeding completeness of oxidation-reduction reactions depends on the equilibrium constant value of the redox reaction, which is calculated by the equation:

$$K_p = 10^a, \text{ where}$$

$$a = \frac{n(E_1^{\ 0} - E_2^{\ 0})}{0.059} \text{ (at 25°C)},$$

where n – is the quantity of electrons, which take part in the process;

E^1_0, E^2_0 – are standard redox potentials of semi-reactions for the oxidant and the reducer, respectively, V.

The difference between E^1_0, and E^2_0 is marked as ΔE of the reaction; the reactions, where ΔE is more than 0.4 V, usually proceed quantitatively.

The stoichiometrical interaction between a titrant and a substance that is considered to be one of the conditions of reactions application in titrimetric analysis, in some cases is not fulfilled, and it is explained by proceeding the side, the so-called induced (conjugated), reactions.

The conjugated oxidation-reduction reactions are called the following two reactions, one of which proceeds spontaneously (the primary reaction), and second (the secondary one) reaction proceeds only if the primary reaction proceeds in this solution. The substance, which takes part in both reactions, is called the actor; the substance, which takes part only in the primary reaction, is called the inductor; the substance, which takes part only in the secondary reaction, is called the acceptor.

The conjugated oxidation-reduction reactions differ from catalystic ones. After the reaction has been completed, all three substances, which take part in it – the actor, the inductor, the acceptor, – turn into other products. It should be taken into account in analysis the possibility of proceeding conjugated reactions, for example, in permanganatometry.

In methods of oxidation-reduction titration direct, back and substitution titration are used.

Direct titration is used in cases when the reaction speed is great enough, and $\Delta E \geq 0.4$ V, it ensures the completeness of its proceeding.

Back titration is used if the reaction proceeds slowly and time is needed to complete it. It is also need for determination of volatile substances and those compounds, which do not react directly with a titrant.

For example, in iodometric determination of sulphide-ions the excess of the iodine standard solution exactly known is added to their solution. Its residue is titrated with the standard solution of sodium thiosulphate according to the equations:

$$\begin{array}{l|l} 1) - 2\,e + H_2S \rightleftharpoons S\downarrow + 2\,H^+ & 1 \\ \quad + 2\,e + [I_3]^- \rightleftharpoons 3\,I^- & 1 \\ \hline \quad H_2S + [I_3]^- \rightarrow S\downarrow + 2\,H^+ + 3\,I^- & \end{array}$$

$$\begin{array}{l|l} 2) - 2\ e + 2\ S_2O_3^{2-} \rightleftharpoons S_4O_6^{2-} & 1 \\ \quad + 2\ e + [I_3]^- \rightleftharpoons 3\ I^- & 1 \end{array}$$

$$[I_3]^- + 2\ S_2O_3^{2-} \rightarrow 3\ I^- + S_4O_6^{2-}$$

For back permanganatometric determination of calcium salts the known volume of the excess of the standard solution of ammonium oxalate is added to their solution (1), the solution is filtrated, the residue of ammonium oxalate is acidified by the H_2SO_4 solution (2) and titrated with the standard solution of $KMnO_4$ (3):

$$1)\ Ca^{2+} + C_2O_4^{2-} \rightleftharpoons CaC_2O_4\downarrow$$

$$2)\ C_2O_4^{2-} + 2\ H^+ \rightleftharpoons H_2C_2O_4$$

$$\begin{array}{l|l} 3) - 2\ e + H_2C_2O_4 \rightleftharpoons 2\ H^+ + 2\ CO_2\uparrow & 5 \\ \quad + 5\ e + MnO_4^- + 8\ H^+ \rightleftharpoons Mn^{2+} + 4\ H_2O & 2 \end{array}$$

$$5\ H_2C_2O_4 + 2\ MnO_4^- + 6\ H^+ \rightarrow 10\ CO_2\uparrow + 2\ Mn^{2+} + 8\ H_2O$$

Titration by the *substitution method* is used in cases when the substance to be determined does not react with a titrant or the reaction is not stoichiometrical. So, in iodometric determination of strong oxidants in the acid medium the excess of the standard solution of potassium iodide is added to their solution. Iodine liberated is titrated with the standard solution of sodium thiosulphate:

$$\begin{array}{l|l} 1) + 6\ e + Cr_2O_7^{2-} + 14\ H^+ \rightleftharpoons 2\ Cr^{3+} + & 1 \\ 7\ H_2O & \\ \quad - 2\ e + 3\ I^- \rightleftharpoons [I_3]^- & 3 \end{array}$$

$$Cr_2O_7^{2-} + 14\ H^+ + 9\ I^- \rightarrow 2\ Cr^{3+} + 3\ [I_3]^- + 7\ H_2O$$

$$\begin{array}{l|l} 2) - 2\ e + 2\ S_2O_3^{2-} \rightleftharpoons S_4O_6^{2-} & 1 \\ \quad + 2\ e + [I_3]^- \rightleftharpoons 3\ I^- & 1 \end{array}$$

$$[I_3]^- + 2\ S_2O_3^{2-} \rightarrow 3\ I^- + S_4O_6^{2-}$$

For permanganatometric determination of calcium salts by substitution titration the following operations are carried out: the standard solution

of ammonium oxalate is added to the solution of calcium salt until calcium oxalate is completely precipitated (1):

$$1)\ Ca^{2+} + C_2O_4^{2-} \rightleftharpoons CaC_2O_4\downarrow$$

The precipitate is filtered, washed out and treated by the sulphuric acid solution (2). Oxalic acid liberated in these conditions in the quantity, which is equivalent to calcium salt, is titrated with the standard solution of potassium permanganate (3):

$$2)\ CaC_2O_4 + 2\ H^+ + SO_4^{2-} \rightleftharpoons CaSO_4\downarrow + H_2C_2O_4$$

$$\begin{array}{l|l} 3) - 2\ e + H_2C_2O_4 \rightleftharpoons 2\ H^+ + 2\ CO_2\uparrow & 5 \\ \quad + 5\ e + MnO_4^- + 8\ H^+ \rightleftharpoons Mn^{2+} + 4\ H_2O & 2 \end{array}$$

$$5\ H_2C_2O_4 + 2\ MnO_4^- + 6\ H^+ \rightarrow 10\ CO_2\uparrow + 2\ Mn^{2+} + 8\ H_2O$$

Determination of the end-point of titration in redox methods is carried out by the method without the indicator or with the help of specific and redox indicators.

Methods without the indicator are used in that case when the titrant is coloured and the product of its reaction with the substance to be determined is colourless (permanganatometry), or in that case when the reaction product has an intensive colour (iodometry, bromatometry).

Starch used in iodometry and formed a compound of an intensively dark blue colour with iodine belong to *specific indicators*.

Reversible redox indicators are indicators, which distinctly and reversibly change their colour depending on change of the oxidation-reduction potential of the system. The range of the redox potential values, where the change of the redox indicator colour takes place, is called the transition interval. The transition interval of the redox indicator is within the range of:

$$E = E^0{}_{Ind} \pm \frac{0.059}{n} \quad \text{(at 25°C)},$$

where n – is the quantity of electrons, which take part in the reaction of the indicator oxidation-reduction.

Choosing the redox indicators is carried out by titration curves in conditions when the transition interval of the indicator is within the range of the titration leap. In that case when the titration curve is not built, redox indicators are chosen comparing to redox potentials of the system and the indicator.

In some methods reversible pH-indicators decomposed by the excess of the titrant are used, as a result their colour is irreversibly changed. For example, in bromatometry methyl orange or methyl red are used as indicators.

Besides internal indicators, in the methods of oxidation-reduction titration external and mixed indicators are used, for example, in the nitritometric method of analysis.

When calculating the results of analysis in the methods of oxidation-reduction titration the factor of equivalence is determined taking into account the number of accepted or given electrons (n): $f_{eqv} = 1/n$.

PERMANGANATOMETRY

Permanganatometry is the method based on using potassium permanganate as a titrant for determination of compounds with reducing properties.

Products of permanganate-ions reduction can be various depending on the medium pH:

– in a strong-acid medium:

$$+ 5\ e + MnO_4^- + 8\ H^+ \rightleftharpoons Mn^{2+} + 4\ H_2O \qquad E^0 = 1.51\ V;$$

– in a weak-acid or neutral medium:

$$+ 3\ e + MnO_4^- + 4\ H^+ \rightleftharpoons MnO_2\downarrow + 2\ H_2O \qquad E^0 = 1.69\ V;$$

– in an alkalescent medium:

$$+ 3\ e + MnO_4^- + 2\ H_2O \rightleftharpoons MnO_2\downarrow + 4\ OH^- \qquad E^0 = 0.60\ V.$$

The oxidation properties of MnO_4^--ions in the strong-acid medium are the most often used for the analysis because the product of MnO_4^--ions reduction in this case is colourless Mn^{2+}-ions (unlike the brown precipitate of MnO_2), on their background the colouration from the excessive drop of the titrant solution is clearly visible.

The necessary value of the medium pH is created with the help of the sulphuric acid solution. Other strong mineral acids are not used. So, nitric acid itself possesses oxidation properties and side reactions can proceed in its presence. In the hydrochloric acid solution (in the presence of Fe^{2+}-ions traces) the induced reaction of chloride-ions oxidation occurs:

$$\begin{array}{l|l} -2\,e + 2\,Cl^- \rightleftharpoons Cl_2\uparrow & 5 \\ +5\,e + MnO_4^- + 8\,H^+ \rightleftharpoons Mn^{2+} + 4\,H_2O & 2 \end{array}$$

$$2\,MnO_4^- + 16\,H^+ + 10\,Cl^- \rightarrow Mn^{2+} + 5\,Cl_2\uparrow + 8\,H_2O$$

Therefore, potassium permanganate is used both for oxidation of the substance to be determined and for oxidation of Cl^--ions, and the results of titration appear to be too high.

The titrant of the method is 0.1 mole/dm^3 (0.05 mole/dm^3) solution of potassium permanganate $KMnO_4$, it is prepared as a secondary standard solution and standardized against standard substances: oxalic acid, sodium oxalate, arsenic (III) oxide, Mohr's salt, etc.

Determination of the end-point of titration is carried out without an indicator (by colour from the permanganate-ions excess), potentiometric or amperometric methods.

It is possible to determine a number of reducers: H_2O_2, NO_2^-, $C_2O_4^{2-}$, Fe^{2+} etc., Ca^{2+} in various medicines by the permanganatometric method; MnO_2, PbO_2, $K_2Cr_2O_7$ and other oxidants – by back titration. The second standard solution in this case is the solution of a reducer (they are the most often solutions of oxalic acids or Mohr's salt).

LABORATORY WORKS

LABORATORY WORK № 1
PREPARATION OF 0.1 mole/dm^3 POTASSIUM PERMANGANATE SOLUTION

$$E(KMnO_4) = M(KMnO_4) \cdot f_{eqv};\ f_{eqv} = 1/5.$$

REAGENTS

Potassium permanganate, pure for analysis.

PROCEDURE OF CARRYING OUT THE WORK

Weigh 3.3 g of potassium permanganate with the help of the technical balance, transfer into a conic flask with the capacity of 2 dm^3, dissolve in 1 dm^3 of water, boil the solution for 10 minutes, then cover the flask with a glass cork. After two days filter the solution through the glass filter № 2 into a vessel for storing the solution.

LABORATORY WORK № 2
STANDARDIZATION OF THE POTASSIUM PERMANGANATE SOLUTION

Such equation of reaction is in the basis of the determination:

$-2\ e + C_2O_4^{2-} \rightleftharpoons 2\ CO_2\uparrow$	5	$E^0 = -0.49$ V
$+5\ e + MnO_4^- + 8\ H^+ \rightleftharpoons Mn^{2+} + 4\ H_2O$	2	$E^0 = 1.51$ V
$5\ C_2O_4^{2-} + 2\ MnO_4^- + 16\ H^+ \rightarrow 10\ CO_2\uparrow + 2\ Mn^{2+} + 8\ H_2O$		

$$E(KMnO_4) = M(KMnO_4) \cdot f_{eqv};\ f_{eqv} = 1/5.$$
$$E(Na_2C_2O_4) = M(Na_2C_2O_4) \cdot f_{eqv};\ f_{eqv} = 1/2.$$

REAGENTS

Potassium permanganate, 0.1 mole/dm^3 solution;
sulphuric acid, 1 mole/dm^3 solution;
sodium oxalate, pure for analysis.

PROCEDURE OF CARRYING OUT THE WORK

Transfer the calculated exact sample of sodium oxalate into a measuring flask with the capacity of 100.00 cm^3, dissolve in 80 cm^3 of 1 mole/dm^3 solution of sulphuric acid and dilute the solution to the volume with the acid. Mix the solution and transfer the aliquot of the solution (20.00 cm^3) into a conic flask for titration by a measuring pipette, heat to 70°C and titrate slowly with the potassium permanganate solution prepared until a light pink colour, which is stable not less than 15 s, appears.

Repeat the titration until the reproducible results are obtained.

Calculate the molar concentration of the equivalent substance of potassium permanganate and the correction coefficient (K).

LABORATORY WORK № 3
DETERMINATION OF THE MASS-VOLUME FRACTION OF HYDROGEN PEROXIDE IN THE MEASURING FLASK VOLUME

Such equation of reaction is in the basis of the determination:

$-2\ e + H_2O_2 \rightleftharpoons O_2\uparrow + 2\ H^+$	5	$E^0 = 0.682$ V
$+5\ e + MnO_4^- + 8\ H^+ \rightleftharpoons Mn^{2+} + 4\ H_2O$	2	$E^0 = 1.51$ V
$5\ H_2O_2 + 2\ MnO_4^- + 6\ H^+ \rightarrow 5\ O_2\uparrow + 2\ Mn^{2+} + 8\ H_2O$		

$$E(H_2O_2) = M(H_2O_2) \cdot f_{eqv};\ f_{eqv} = 1/2.$$

REAGENTS

Potassium permanganate, 0.1 mole/dm^3 solution;

sulphuric acid, 1 mole/dm^3 solution.

PROCEDURE OF CARRYING OUT THE WORK

Transfer the aliquot of the hydrogen peroxide solution to be determined into a measuring flask with the capacity of 100.00 cm^3, dilute the solution to the volume with water and mix. Transfer the aliquot of the solution obtained (20.00 cm^3) into a conic flask for titration by a measuring pipette, add 10 – 15 cm^3 of 1 mole/dm^3 solution of sulphuric acid and ti-

trate with 0.1 mole/dm^3 potassium permanganate solution until a light pink colour, which is stable not less than 15 s, appears.

Repeat the titration until the reproducible results are obtained.

Calculate the mass-volume fraction of hydrogen peroxide in the volume of the measuring flask.

LABORATORY WORK № 4
DETERMINATION OF THE PERCENTAGE OF IRON(II)-IONS IN MOHR'S SALT

Such equation of the reaction is in the basis of the determination:

$- e + Fe^{2+} \rightleftharpoons Fe^{3+}$	5	$E^0 = 0.77$ V
$+ 5 e + MnO_4^- + 8 H^+ \rightleftharpoons Mn^{2+} + 4 H_2O$	1	$E^0 = 1.51$ V
$5 Fe^{2+} + MnO_4^- + 8 H^+ \rightarrow 5 Fe^{3+} + Mn^{2+} + 4 H_2O$		

$$E(Fe^{2+}) = A(Fe^{2+}) \cdot f_{eqv};\ f_{eqv} = 1.$$

$$E((NH_4)_2Fe(SO_4)_2 \cdot 6H_2O) = M((NH_4)_2Fe(SO_4)_2 \cdot 6H_2O) \cdot f_{eqv};\ f_{eqv} = 1.$$

REAGENTS

Potassium permanganate, 0.1 mole/dm^3 solution;

sulphuric acid, 1 mole/dm^3 solution;

Mohr's salt, pure for analysis.

PROCEDURE OF CARRYING OUT THE WORK

Transfer the calculated exact sample of Mohr's salt $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ into a flask for titration, dissolve in 20 – 25 cm^3 of 1 mole/dm^3 solution of sulphuric acid and titrate with 0.1 mole/dm^3 potassium permanganate standard solution until a light pink colour, which is stable not less than 15 s, appears.

Repeat the titration until the reproducible results are obtained.

Calculate the percentage of iron(II)-ions in Mohr's salt.

LABORATORY WORK № 5

DETERMINATION OF THE PERCENTAGE OF CALCIUM LACTATE IN THE MEDICINE

Determination of calcium in various compounds, including medicines (for example, in calcium lactate $(CH_3CHOHCOO)_2Ca \cdot 5H_2O$), is carried out by the substitution method. It is based on precipitation of calcium in the form of a slightly soluble calcium oxalate, further dissolution of this precipitate in the diluted sulphuric acid and titration of oxalic acid liberated with the potassium permanganate solution:

$$Ca^{2+} + C_2O_4^{2-} \rightleftharpoons CaC_2O_4\downarrow$$

$$CaC_2O_4 + 2\ H^+ \rightleftharpoons Ca^{2+} + H_2C_2O_4$$

$-2\ e + H_2C_2O_4 \rightleftharpoons 2\ H^+ + 2\ CO_2\uparrow$	5	$E^0 = -0.49$ V
$+5\ e + MnO_4^- + 8\ H^+ \rightleftharpoons Mn^{2+} + 4\ H_2O$	2	$E^0 = 1.51$ V

$$5\ H_2C_2O_4 + 2\ MnO_4^- + 6\ H^+ \rightarrow 10\ CO_2\uparrow + 2\ Mn^{2+} + 8\ H_2O$$

$$E(C_6H_{10}CaO_6 \cdot 5H_2O) = M(C_6H_{10}CaO_6 \cdot 5H_2O) \cdot f_{eqv};\ f_{eqv} = 1/2.$$

REAGENTS

Potassium permanganate, 0.1 mole/dm^3 solution;
hydrochloric acid, concentrated;
sulphuric acid, 1 mole/dm^3 solution;
ammonia solution, 5%;
ammonium oxalate, 0.1% and 5% solutions;
methyl orange, 0.1% solution.

PROCEDURE OF CARRYING OUT THE WORK

Transfer the calculated exact sample of calcium lactate into a beaker and dissolve in 15 – 20 cm^3 of hot water. After cooling the solution 5 cm^3 of the hydrochloric acid concentrated solution, 2 drops of the methyl orange solution and 30 cm^3 of 5% solution of ammonium oxalate add to it. Heat the solution to 70 – 80°C and add the ammonia solution drop by drop while mixing until the solution changes its colour from red to yellow. Al-

low the precipitate to mature, keep the beaker on a sandy bath for 1 – 2 hours. Cool the solution and decant the liquid remained through the paper filter. Wash the precipitate out by decantation 3 – 4 times with 0.1% cold solution of ammonium oxalate until the negative chloride-ions reaction occurs. Then wash the precipitate off by water with the help of a washing bottle from the filter into the beaker. Treat the precipitate in the beaker by small portions of hot 1 mole/dm^3 solution of sulphuric acid till its complete dissolution. Heat the solution to 70 – 80°C and titrate slowly with the potassium permanganate standard solution until a light pink colour appears. After that place the filter into the solution and mix; if the solution becomes colourless, continue the titration to the stable (for not less than 15 s) light pink colour.

Calculate the percentage of calcium lactate in the medicine.

LABORATORY WORK № 6
DETERMINATION OF THE PERCENTAGE OF POTASSIUM NITRITE IN THE MEDICINE

Taking into account the nitrous acid volatility the back titration method is applied. The solution of sodium oxalate is used as the second standard solution. Such equations of reactions are in the basis of the determination:

$-2\ e + HNO_2 + H_2O \rightleftharpoons NO_3^- + 3\ H^+$	5	$E^0 = 0.94$ V
$+5\ e + MnO_4^- + 8\ H^+ \rightleftharpoons Mn^{2+} + 4\ H_2O$	2	$E^0 = 1.51$ V

$$5\ HNO_2 + 2\ MnO_4^- + H^+ \rightarrow 5\ NO_3^- + 2\ Mn^{2+} + 5\ H_2O$$

$-2\ e + H_2C_2O_4 \rightleftharpoons 2\ H^+ + 2\ CO_2\uparrow$	5	$E^0 = -0.49$ V
$+5\ e + MnO_4^- + 8\ H^+ \rightleftharpoons Mn^{2+} + 4\ H_2O$	2	$E^0 = 1.51$ V

$$5\ H_2C_2O_4 + 2\ MnO_4^- + 6\ H^+ \rightarrow 10\ CO_2\uparrow + 2\ Mn^{2+} + 8\ H_2O$$

$$E(KNO_2) = M(KNO_2) \cdot f_{eqv};\ f_{eqv} = 1/2.$$

REAGENTS

Potassium permanganate, 0.1 mole/dm^3 solution;
sodium oxalate, 0.1 mole/dm^3 solution*;
sulphuric acid, 1 mole/dm^3 solution.

* Preparation of the 0.1 mole/dm^3 sodium oxalate solution: weigh 1.68 g (it is the exact sample) sodium oxalate with the help of the analytical balance and transfer into a measuring flask with the capacity of 50.00 cm^3. Dissolve in a small quantity of water and dilute the solution to the volume with water. Calculate the exact concentration of the solution and the correction coefficient (K).

PROCEDURE OF CARRYING OUT THE WORK

Transfer the calculated exact sample of potassium nitrite into a measuring flask with the capacity of 100.00 cm^3, dissolve in water and dilute the solution to the volume with water. Fill two burettes with standard solutions: the first one with 0.1 mole/dm^3 potassium permanganate solution, the second one with 0.1 mole/dm^3 sodium oxalate solution.

Measure 30.00 cm^3 of 0.1 mole/dm^3 solution of $KMnO_4$ into a conic flask for titration from the burette, then add 10 cm^3 of a hot diluted (1:9) sulphuric acid, the aliquot of KNO_2 solution prepared to the solution and mix. After that add 10.00 cm^3 of the sodium oxalate solution (till decolouration) and titrate the excess of sodium oxalate with the potassium permanganate solution to the stable (for not less than 15 s) light pink colour. When calculating the whole volume of potassium permanganate is taken into account.

Repeat the titration until the reproducible results are obtained.

Calculate the percentage of potassium nitrite.

BROMATOMETRY

The method is based on using potassium bromate as a titrant-oxidant for determination of reducers:

$$+ 6\ e + BrO_3^- + 6\ H^+ \rightleftharpoons Br^- + 3\ H_2O \qquad E^0 = 1.45\ V$$

Bromate-ions liberate free bromine in the acid medium in the presence of bromide-ions:

$+ 10\ e + 2\ BrO_3^- + 12\ H^+ \rightleftharpoons Br_2 + 6\ H_2O$	1	$E^0 = 1.52$ V
$- 2\ e + 2\ Br^- \rightleftharpoons Br_2$	5	$E^0 = 1.087$ V
$BrO_3^- + 5\ Br^- + 6\ H^+ \rightarrow 3\ Br_2 + 3\ H_2O$		

The solution, which contains bromate(V)- and bromide-ions, behaves as the solution of bromine in the acid medium and is applied for determination of:

- derivatives of aromatic amines and phenols (see laboratory work № 4);
- reducers (As (III), Sb (III), Sn^{2+}, N_2H_4, etc.).

The titrant of the method is the solution of potassium bromate (V) $KBrO_3$, which can be prepared as the solution with the determined titre. The exact concentration is determined iodometrically in this case (see laboratory work №2). The SPhU recommends to prepare the solution of primary standardization because potassium bromate (V) satisfies the requirements to standard substances.

Methyl red, methyl orange, indigosulphoacid, which are irreversibly oxidized to colourless products from the excessive drop of the titrant, are used as indicators in bromatometry.

LABORATORY WORKS

LABORATORY WORK № 1
PREPARATION OF 0.1 mole/dm^3 POTASSIUM BROMATE (V) SOLUTION

$$E(KBrO_3) = M(KBrO_3) \cdot f_{eqv};\ f_{eqv} = 1/6.$$

REAGENTS

Potassium bromate (V), c. p.

PROCEDURE OF CARRYING OUT THE WORK

Weigh 2.8 g of potassium bromate (V) with the help of the technical balance, dissolve in water in a beaker and dilute the solution to the volume of 1 dm^3 with water. Pour into a vessel for storing the solution.

LABORATORY WORK № 2
STANDARDIZATION OF THE POTASSIUM BROMATE (V) SOLUTION

Standardization is carried out by the method of iodometric displacement titration. The reaction proceeds under such conditions:

$+ 6\ e + BrO_3^- + 6\ H^+ \rightleftharpoons Br^- + 3\ H_2O$	1	$E^0 = 1.45$ V
$- 2\ e + 3\ I^- \rightleftharpoons [I_3]^-$	3	$E^0 = 0.545$ V
$BrO_3^- + 9\ I^- + 6\ H^+ \rightarrow Br^- + 3\ [I_3]^- + 3\ H_2O$		

Titrate iodine liberated with the sodium thiosulphate solution:

$+ 2\ e + [I_3]^- \rightleftharpoons 3\ I^-$	1	$E^0 = 0.545$ V
$- 2\ e + 2\ S_2O_3^{2-} \rightleftharpoons S_4O_6^{2-}$	1	$E^0 = 0.09$ V
$2\ S_2O_3^{2-} + [I_3]^- \rightarrow S_4O_6^{2-} + 3\ I^-$		

$$E(KBrO_3) = M(KBrO_3) \cdot f_{eqv};\ f_{eqv} = 1/6.$$

REAGENTS

Potassium bromate (V), 0.1 mole/dm^3 solution;

hydrochloric acid, 8.2% solution;

potassium iodide, 20% solution;

sodium thiosulphate, 0.1 mole/dm^3 solution.

PROCEDURE OF CARRYING OUT THE WORK

Transfer the aliquot of the potassium bromate (V) solution prepared into a flask with a ground stopper by a measuring pipette, add approximately 100 cm^3 of water, 5 cm^3 of hydrochloric acid, 10 cm^3 of the potassium iodide solution, close by the stopper, shake and leave for 5 minutes in the dark place. Titrate iodine liberated with the sodium thiosulphate standard solution until a light yellow colour appears, then add 2 – 3 cm^3 of the starch solution and titrate a dark blue solution to decolouration.

Repeat the titration until the reproducible results are obtained.

Calculate the molar concentration of the equivalent substance of potassium bromate (V) in the solution and the correction coefficient (K).

LABORATORY WORK № 3
DETERMINATION OF THE PERCENTAGE OF ARSENIC (III) OXIDE IN THE MEDICINE

Such equations of reactions 1 and 2 are in the basis of the determination:

1) dissolution of arsenic (III) oxide

$$As_2O_3 + 6\ OH^- \rightleftharpoons 2\ AsO_3^{3-} + 3\ H_2O$$

2) oxidation of arsenic (III) to arsenic (V)

$+ 6\ e + BrO_3^- + 6\ H^+ \rightleftharpoons Br^- + 3\ H_2O$	1	$E^0 = 1.45$ V
$- 2\ e + AsO_3^{3-} + H_2O \rightleftharpoons AsO_4^{3-} + 2\ H^+$	3	$E^0 = 0.56$ V
$BrO_3^- + 3\ AsO_3^{3-} \rightarrow Br^- + 3\ AsO_4^{3-}$		

$$E(As_2O_3) = M(As_2O_3) \cdot f_{eqv};\ f_{eqv} = 1/4.$$

REAGENTS

Potassium bromate (V), 0.1 mole/dm^3 solution;
sodium hydroxide, 10% solution;
sulphuric acid, concentrated, pure for analysis;
potassium bromide, pure for analysis;
methyl red, 0.1% solution in 60% ethanol.

PROCEDURE OF CARRYING OUT THE WORK

Transfer the calculated exact sample of the medicine into a conic flask for titration and dissolve in 2 – 3 cm^3 of the sodium hydroxide solution.

Add sequentially 50 cm^3 of water and 10 cm^3 of the concentrated sulphuric acid to the solution. Heat the solution to the boiling point, add 0.5 g of potassium bromide and titrate with the potassium bromate (V) standard solution. At the end of titration add 2 – 3 drops of methyl red and titrate drop by drop to decolouration of the solution.

Repeat the titration until the reproducible results are obtained.

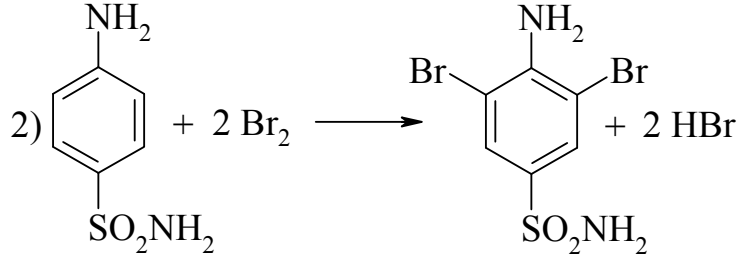
Calculate the percentage of arsenic (III) oxide in the medicine.

LABORATORY WORK № 4
DETERMINATION OF THE PERCENTAGE OF STREPTOCID IN THE MEDICINE

The determination is based on the reactions 1 and 2, which proceed sequentially:

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

Bromine, which is liberated as a result of interaction of bromate(V)-ions with bromide-ions in the acid medium, enters into the reaction of streptocid bromination:



$$E(C_6H_8N_2O_2S) = M(C_6H_8N_2O_2S) \cdot f_{eqv};\ f_{eqv} = 1/4.$$

REAGENTS

Potassium bromate (V), 0.1 mole/dm^3 solution;
sulphuric acid, 2 mole/dm^3 solution;
potassium bromide, 5% solution;
methyl orange, 0.1% solution.

PROCEDURE OF CARRYING OUT THE WORK

Transfer the calculated exact sample of streptocid into a flask for titration and dissolve in 60 cm^3 of 2 mole/dm^3 sulphuric acid solution. Add 15 cm^3 of the potassium bromide solution, 5 drops of the methyl orange solution to the mixture obtained and titrate slowly, while shaking vigorously, with the potassium bromate (V) standard solution to decolouration of the solution pink colour.

Repeat the titration until the reproducible results are obtained.

Calculate the percentage of streptocid.

CHROMATOMETRY

The method is based on using potassium dichromate as a titrant-oxidant for determination of reducers in the acid medium. The reduction of dichromate-ions to Cr^{3+} is proceeded under such conditions:

$$+ 6\ e + Cr_2O_7^{2-} + 14\ H^+ \rightleftharpoons 2\ Cr^{3+} + 7\ H_2O \qquad E^0 = 1.33\ V$$

The standard solution of $K_2Cr_2O_7$ is prepared as the solution of primary standardization. Diphenylamine and other redox-indicators are used as indicators. The method is applied for determination of Fe^{2+}, Sn^{2+}; cations, which form poorly soluble chromates, for example, Ba^{2+}, Pb^{2+}, Ag^+; organic compounds, which are easily oxidized by potassium dichromate to CO_2 and H_2O, for example, methanol.

LABORATORY WORKS

LABORATORY WORK № 1
PREPARATION OF 0.1 mole/dm^3 POTASSIUM DICHROMATE SOLUTION

$$E(K_2Cr_2O_7) = M(K_2Cr_2O_7) \cdot f_{eqv}; f_{eqv} = 1/6.$$

REAGENTS

Potassium dichromate, c. p.

PROCEDURE OF CARRYING OUT THE WORK

Dissolve the calculated exact sample of potassium dichromate recrystallized from hot water and dried at 130 – 150°C to the constant value of weight in water in a measuring flask, dilute the solution to the volume, mix and pour into a vessel for storing.

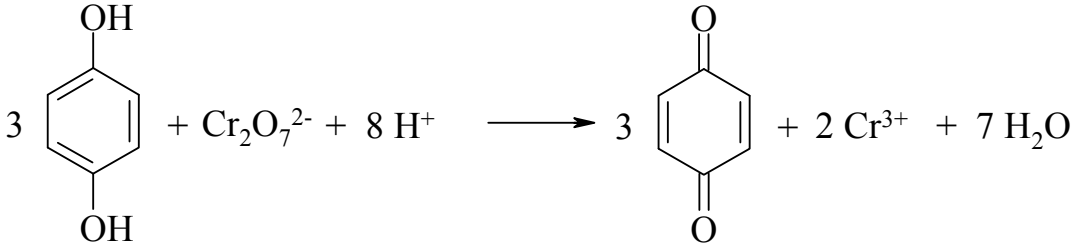
Calculate the molar concentration of the equivalent substance of potassium dichromate in the solution and the correction coefficient (K).

LABORATORY WORK № 2
DETERMINATION OF THE PERCENTAGE OF HYDROQUINONE IN CHINHYDRONE

Such equations of the reactions are in the basis of the determination:

$-2\ e + C_6H_4(OH)_2 \rightleftharpoons C_6H_4O_2 + 2\ H^+$	3	$E^0 = 0.6994$ V
$+6\ e + Cr_2O_7^{2-} + 14\ H^+ \rightleftharpoons 2\ Cr^{3+} + 7\ H_2O$	1	$E^0 = 1.33$ V

$$3\ C_6H_4(OH)_2 + Cr_2O_7^{2-} + 8\ H^+ \rightleftharpoons 3\ C_6H_4O_2 + 2\ Cr^{3+} + 7\ H_2O$$



$$E(K_2Cr_2O_7) = M(K_2Cr_2O_7) \cdot f_{eqv}; f_{eqv} = 1/6;$$
$$E(C_6H_4(OH)_2) = M(C_6H_4(OH)_2) \cdot f_{eqv}; f_{eqv} = 1/2.$$

REAGENTS

Potassium dichromate, 0.1 mole/dm^3 solution;
hydrochloric acid, 4 mole/dm^3 solution;
diphenylamine, 1% solution in H_2SO_4 concentrated.

PROCEDURE OF CARRYING OUT THE WORK

Transfer the calculated exact sample of chinhydrone into a conic flask for titration and dissolve in 20 – 30 cm^3 of hot water. Then add 15 – 20 cm^3 of hydrochloric acid, 3 drops of the diphenylamine solution and titrate the hot solution (40 – 60°C) with the potassium dichromate standard solution until the colour changes from dark-green to violet. Close to the point of equivalence the titrant solution is added slowly, with the speed not more than 1 drop for 10 sec.

Repeat the titration until the reproducible results are obtained.

Calculate the percentage of hydroquinone in chinhydrone.

LABORATORY WORK № 3
DETERMINATION OF THE PERCENTAGE OF Fe^{2+}-IONS IN IRON (II) SULPHATE

Such equation of the reaction is in the basis of the determination:

$-\,e + Fe^{2+} \rightleftharpoons Fe^{3+}$	6	$E^0 = 0.771$ V
$+\,6\,e + Cr_2O_7^{2-} + 14\,H^+ \rightleftharpoons 2\,Cr^{3+} + 7\,H_2O$	1	$E^0 = 1.33$ V
$6\,Fe^{2+} + Cr_2O_7^{2-} + 14\,H^+ \rightarrow 6\,Fe^{3+} + 2\,Cr^{3+} + 7\,H_2O$		

$$E(K_2Cr_2O_7) = M(K_2Cr_2O_7) \cdot f_{eqv}; f_{eqv} = 1/6;$$
$$E(Fe^{2+}) = M(Fe^{2+}) \cdot f_{eqv}; f_{eqv} = 1.$$

REAGENTS

Potassium dichromate, 0.1 mole/dm^3 solution;
sulphuric acid, 2 mole/dm^3 solution;
phosphoric acid, concentrated;
sodium (barium) diphenylaminesulphonate, 0.05% solution.

PROCEDURE OF CARRYING OUT THE WORK

Transfer the calculated exact sample of iron (II) sulphate in a measuring flask and dissolve in 30 cm^3 of distilled water, then add 30 cm^3 of the sulphuric acid solution and 20 cm^3 of the concentrated phosphoric acid*.

Shake the content of the flask carefully, cool to the room temperature and dilute the solution to the volume with water. Take the aliquot of the solution into a flask for titration by a measuring pipette, add some drops of the sodium diphenylaminesulphonate solution and titrate with $K_2Cr_2O_7$ standard solution from green to the violet colour.

Repeat the titration until the reproducible results are obtained.

Calculate the percentage of Fe^{2+}-ions in iron (II) sulphate.

* Phosphoric acid is added for fixing of the Fe^{3+}-ions formed with the purpose of their masking:

$$Fe^{3+} + 2\ PO_4^{3-} \rightleftharpoons [Fe(PO_4)_2]^{3-}$$

IODOMETRY

The iodometric method of analysis is based on using the oxidation-reduction properties of the system $[I_3]^-/3\ I^-$.

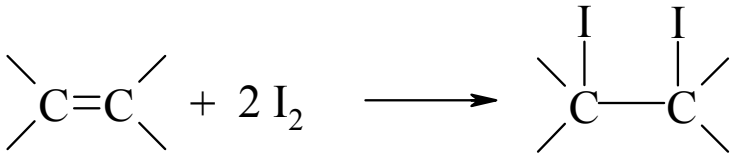
Relatively low value of the systems standard potential $[I_3]^-/3\ I^-$ (E^0 = 0.545 V) shows that there is a number of reducers ($E^0 < 0.545$ V), which are able to be oxidized by free iodine, and a number of oxidants ($E^0 > 0.545$ V), which are able to be reduced by iodide-ions.

These properties of the redox pair $[I_3]^-/3\ I^-$ are used in titrimetric analysis for determination of reducers, which are oxidized by the iodine solution, and for determination of oxidants, which are reduced by iodide-ions.

Oxidation-reduction processes, which proceed in iodometric determinations, can be presented by the following semi-reaction:

$$[I_3]^- + 2\ e \rightleftharpoons 3\ I^-$$

Besides, iodine is able to enter into addition reactions used in analytical chemistry for determination of double bonds in unsaturated organic compounds:



The unsaturation degree of organic compounds are determined by the iodine number, that is the quantity of iodine in percents, which is added to the substance.

Iodine can also enter into displacement reactions of hydrogen atoms in aromatic and heterocyclic compounds (phenols, diphenols, aromatic amines, etc.) that are used for quantitative determination of these substances.

Titrants of the method

In iodometry two titrants are used:

- the solution of sodium thiosulphate (in determination of oxidants);
- the solution of iodine in potassium iodide (in determination of reducers).

The solution of sodium thiosulphate (0.05 – 0.1 mole/dm^3)

Sodium thiosulphate is not a standard substance because it leaves crystalline water easily, and its aqueous solutions are unstable and change their concentration under the influence of such factors as:

- sodium thiosulphate reacts with carbon (IV) oxide presented in water:

$$S_2O_3^{2-} + CO_2 + H_2O \rightarrow HSO_3^- + S\downarrow + HCO_3^- \qquad (1)$$

- sodium thiosulphate is oxidized by oxygen of the air:

$$2\ S_2O_3^{2-} + O_2 \rightarrow 2\ SO_4^{2-} + 2\ S\downarrow \qquad (2)$$

- the titrant is decomposed by thiobacteria; this process accelerates light, but it is inhibited in the presence of an antiseptic – mercury (II) iodide.

Owing to the first reaction the molar concentration of the solution prepared increases, and it decreases due to the second and third reactions.

Therefore, the secondary standard solution is prepared from sodium thiosulphate. Its standardization is started in 1 – 2 days after preparation and the solution concentration is checked periodically.

It is possible to standardize the prepared solution of sodium thiosulphate:

- against standard substances – against potassium iodate, potassium bromate, potassium ferricyanide (III), potassium dichromate;
- by titration with standard solutions of iodine, potassium permanganate, etc.

It is necessary to store the prepared solution of the titrant in vessels of a dark glass, in a dark place, without the access of oxygen.

The solution of iodine (0.05 – 0.1 mole/dm^3)

It is possible to prepare the solution of iodine both with the prepared (the primary standard solution) and with the determined (the secondary standard solution) titre.

The standard solution of iodine with the prepared titre is obtained from the exact sample of a chemically pure iodine obtained by sublimation.

Iodine is a volatile compound, its vapours are poisonous, cause corrosion of metals, and, therefore, it is necessary to carry out all operations with it under draught. It is necessary to bring iodine in a weighed room and weigh it with the help of the analytical balance only in closed vessels. The concentration of iodine can change owing to volatility of iodine, therefore, the secondary standard solution is prepared from it more often.

Because of a poor solubility of iodine in water its sample is dissolved in the concentrated solution of potassium iodide, with which iodine forms a soluble complex ions of a red-brown colour:

$$I_2 + I^- \rightleftharpoons [I_3]^-$$

Formation of the complex $[I_3]^-$ increases solubility of iodine in water and decreases its volatility. It is possible to standardize the solution prepared:

- against standard substances – against barium thiosulphate, arsenic (III) oxide, hydrazine sulphate;
- by titration with standard solutions of sodium thiosulphate.

The solution prepared is stored in vessel of a dark glass with a ground stopper in a dark place.

Direct, back and displacement titration are possible in iodometry.

Direct titration. Strong reducers (SO_3^{2-}, $S_2O_3^{2-}$, SO_2, ascorbic acid, etc.), which are able to reduce iodine to iodide-ions, are determined by the method of direct iodometric titration. Iodine and its concentration in solutions are also determined by this method, the standard solution of sodium thiosulphate is used as a titrant.

Back titration. Reducers, which react with iodine slowly (S^{2-}, glucose, antipyrine, etc.) are determined by the method of back titration in iodometry. The excess of the iodine standard solution is added to the substance to be analysed and the rest of iodine is titrated with the standard solution of sodium thiosulphate after the time when the reaction has taken place.

Displacement titration. When determining strong oxidants they are replaced in the acid medium with the equivalent quantity of iodine (liberated in interaction with potassium iodide), the last is titrated with the standard solution of sodium thiosulphate. Schematically determination of oxidants by the iodometric method can be presented in the following way:

The 1st stage – an oxidant + excess of KI + $H^+ \rightarrow [I_3]^-$ (the excess of potassium iodide is required for dissolving iodine liberated and decreasing its volatility);

The 2nd stage – $[I_3]^- + 2\ S_2O_3^{2-} \rightarrow 3\ I^- + S_4O_6^{2-}$.

The method is used for determination of oxidants, for example, $KMnO_4$, $KClO_3$, active chlorine in bleach powder, H_2O_2, salts of iron(III)-, copper(II)-ions, etc.

The end-point of titration in iodometry is determined:

- without an indicator: the solution of iodine in potassium iodide has an intensive colour, therefore, when titrating with the iodine solution its excessive drop colours the solution being titrated in a light yellow colour;
- without an indicator (in the presence of organic solvents): to determine the moment of equivalence in iodometry organic solvents that are immiscible with water – benzene, chloroform, CCl_4, etc., are used. Iodine is soluble better in them than in water, and colour them in a red-violet

colour, and it allows to reveal its smaller quantity than with starch and to carry out determination in the strong acid medium;

– with an indicator: 0.5% solution of starch. In the presence of starch, which forms a compound of the intensive blue colour with iodine, the end-point of titration is determined very distinctly. When titrating reducers with the iodine solution starch is added immediately, before the beginning titration, and the colourless solution is titrated until a blue colour appears. If the iodine solution is titrated with the solution of sodium thiosulphate, starch is added after the main mass of iodine is titrated and the brown colour of the solution changes to the light yellow one. In this moment the indicator is added into the solution and it is continued to titrate till decolouration of the blue colour of the solution. In this case addition of starch before the beginning titration leads to obtaining the results with conservative values.

Conditions of iodometric determinations

When creating the necessary conditions of titration properties of titrants, indicator and substances to be analysed are taken into account, therefore, conditions of direct titration; conditions of back titration; conditions of displacement titration are distinguished.

Conditions of direct titration

1. Titration is carried out in cold because iodine is a volatile substance, and when heating the sensitivity of starch as an indicator decreases.

2. The medium of the solution to be titrated should be acid or neutral because in the alkaline medium the reaction of iodine disproportionation occurs:

$$I_2 + 2\ OH^- \rightleftharpoons IO^- + I^- + H_2O$$

Conditions of back titration

1. Titration is carried out in cold.

2. The medium of the solution to be titrated should be close to neutral because in the alkaline medium the reaction of iodine disproportionation occurs:

$$I_2 + 2\ OH^- \rightleftharpoons IO^- + I^- + H_2O\ ,$$

that causes a side reaction of:

$$S_2O_3^{2-} + 2\ OH^- + 4\ IO^- \rightleftharpoons 2\ SO_4^{2-} + H_2O + 4\ I^-\ ;$$

in the acid medium the proceeding of the side reaction is possible:

$$4\ I^- + O_2 + 4\ H^+ \rightarrow 2\ I_2 + 2\ H_2O\ ,$$

as well as decomposition of the titrant $Na_2S_2O_3$ is possible:

$$S_2O_3^{2-} + 2\ H^+ \rightleftharpoons SO_2\uparrow + S\downarrow + H_2O\ .$$

If during the proceeding of the reaction hydrogen-ions are formed, they are bound by adding sodium hydrocarbonate to the solution:

$$H^+ + HCO_3^- \rightleftharpoons H_2CO_3 \rightarrow H_2O + CO_2\uparrow\ .$$

Conditions of displacement titration (in determination of oxidants):

1. Titration is carried out in cold.

2. The medium of the solution to be titrated should be acid or neutral because in the alkaline medium the reaction of iodine disproportionation occurs.

3. The excess of potassium iodide is added to the solution, iodine liberated forms the complex with it:

$$I_2 + I^- \rightleftharpoons [I_3]^-\ \ (K_н = 7.68 \cdot 10^2),$$

that increases solubility of iodine in water and decreases its volatility.

4. After having added potassium iodide the reaction mixture is kept in a dark place to prevent the side reaction:

$$4\ I^- + O_2 + 4\ H^+ \rightarrow 2\ I_2 + 2\ H_2O$$

5. Iodine liberated is titrated in completing the reaction in 10 – 15 minutes after the solution of potassium iodide is added to the oxidant because the reaction between them proceeds slowly.

LABORATORY WORKS

LABORATORY WORK № 1
PREPARATION OF 0.1 mole/dm^3 SODIUM THIOSULPHATE SOLUTION

$$E(Na_2S_2O_3 \cdot 5H_2O) = M(Na_2S_2O_3 \cdot 5H_2O) \cdot f_{eqv}; f_{eqv} = 1.$$

REAGENTS

Sodium thiosulphate, c. p.;
sodium carbonate anhydrous, c. p.;
mercury (II) iodide, c. p.

PROCEDURE OF CARRYING OUT THE WORK

Weigh the calculated sample of sodium thiosulphate with the help of the technical balance, transfer into a beaker, dissolve in fresh boiled cooled water, add 0.1 g of anhydrous sodium carbonate*, 10 mg of mercury (II) iodide** and dilute the solution to the volume of 1 dm^3, mix and pour the solution prepared into a vessel for storing.

* Na_2CO_3 is added for binding CO_2 of the air, it prevents decomposition of sodium thiosulphate by carbon (IV) oxide:

$$Na_2S_2O_3 + H_2CO_3 \rightleftharpoons NaHSO_3 + NaHCO_3 + S\downarrow.$$

** HgI_2 is added to prevent decomposition of the sodium thiosulphate solution by thiobacteria.

LABORATORY WORK № 2

STANDARDIZATION OF THE SODIUM THIOSULPHATE SOLUTION AGAINST POTASSIUM DICHROMATE

Such equations of the reactions are in the basis of the determination:

$+ 6\ e + Cr_2O_7^{2-} + 14\ H^+ \rightleftharpoons 2\ Cr^{3+} + 7\ H_2O$	1	$E^0 = 1.33$ V
$- 2\ e + 3\ I^- \rightleftharpoons [I_3]^-$	3	$E^0 = 0.545$ V
$Cr_2O_7^{2-} + 14\ H^+ + 9\ I^- \rightarrow 2\ Cr^{3+} + 7\ H_2O + 3\ [I_3]^-$		

$+ 2\ e + [I_3]^- \rightleftharpoons 3\ I^-$	1	$E^0 = 0.545$ V
$- 2\ e + 2\ S_2O_3^{2-} \rightleftharpoons S_4O_6^{2-}$	1	$E^0 = 0.09$ V
$2\ S_2O_3^{2-} + [I_3]^- \rightarrow S_4O_6^{2-} + 3\ I^-$		

$$E(K_2Cr_2O_7) = M(K_2Cr_2O_7) \cdot f_{eqv}; f_{eqv} = 1/6.$$

REAGENTS

Potassium dichromate, c. p.;
potassium iodide, c. p.;
sulphuric acid, 1 mole/dm^3 solution;
starch, 0.5% solution.

PROCEDURE OF CARRYING OUT THE WORK

Transfer the calculated exact sample of potassium dichromate into a measuring flask, dissolve in distilled water, dilute the solution to the volume with water, mix carefully. Take the aliquot of the solution prepared by a measuring pipette, transfer into the flask with a ground stopper, add 2 g of potassium iodide, 10 – 15 cm^3 of the sulphuric acid solution, mix and leave for 10 – 15 minutes in a dark place. Then wash the stopper over a flask by distilled water, add approximately 200 cm^3 of distilled water and titrate with the solution of sodium thiosulphate until a light yellow colour appears; then add 2 cm^3 of the starch solution and continue to titrate till the solution changes the blue colour to light green from one drop of the sodium thiosulphate solution.

Repeat the titration until the reproducible results are obtained.

Calculate the molar concentration of the equivalent substance of sodium thiosulphate in the solution and the correction coefficient (K).

LABORATORY WORK № 3
PREPARATION OF 0.1 mole/dm^3 IODINE SOLUTION

$$E(I_2) = M(I_2) \cdot f_{eqv}; f_{eqv} = 1/2.$$

REAGENTS

Iodine, p.;
potassium iodide, c. p.

PROCEDURE OF CARRYING OUT THE WORK

Weigh 36 g of potassium iodide with the help of the technical balance, transfer into a beaker and dissolve in 50 cm^3 of distilled water, then weigh (with the help of the same balance) the calculated sample of iodine in a weighing bottle and dissolve it in the potassium iodide solution, transfer into a beaker, dilute the solution to the volume of 1 dm^3 and pour it into a vessel of a dark glass for storing.

LABORATORY WORK № 4
STANDARDIZATION OF 0.1 mole/dm^3 IODINE SOLUTION BY THE SODIUM THIOSULPHATE STANDARD SOLUTION

Such equation of the reaction is in the basis of the determination:

$+ 2\ e + [I_3]^- \rightleftharpoons 3\ I^-$	1	$E^0 = 0.545$ V
$- 2\ e + 2\ S_2O_3^{2-} \rightleftharpoons S_4O_6^{2-}$	1	$E^0 = 0.09$ V
$2\ S_2O_3^{2-} + [I_3]^- \rightarrow S_4O_6^{2-} + 3\ I^-$		

REAGENTS

Sodium thiosulphate, 0.1 mole/dm^3 solution;
starch, 0.5% solution.

PROCEDURE OF CARRYING OUT THE WORK

Fill the first burette with the iodine solution prepared, the second one with the sodium thiosulphate standard solution.

Measure the exact volume of the sodium thiosulphate solution (20.00; 21.00; 22.00 cm^3) into a flask for titration, add 2 cm^3 of the starch solution and titrate with the iodine solution until the solution becomes of a blue colour from one drop of the titrant. Recalculate the volumes of the iodine solution used for titration for 20.00 cm^3 of the sodium thiosulphate solution.

Repeat the titration until the reproducible results are obtained.

Calculate the molar concentration of the equivalent substance of iodine in the solution and the correction coefficient (K).

Determination of reducers by the iodometric method

LABORATORY WORK № 5

DETERMINATION OF THE PERCENTAGE OF SODIUM ARSENITE IN THE MEDICINE

Such equation of the reaction is in the basis of the determination:

$-2\ e + AsO_2^- + 4\ OH^- \rightleftharpoons AsO_4^{3-} + 2\ H_2O$	1	$E^0 = -0.71$ V
$+2\ e + [I_3]^- \rightleftharpoons 3\ I^-$	1	$E^0 = 0.545$ V
$AsO_2^- + [I_3]^- + 4\ OH^- \rightarrow AsO_4^{3-} + 3\ I^- + 2\ H_2O$		

$$E(NaAsO_2) = M(NaAsO_2) \cdot f_{eqv}; f_{eqv} = 1/2.$$

REAGENTS

Iodine, 0.1 mole/dm^3 solution;
sodium hydrocarbonate, the saturated solution;
starch, 0.5% solution.

PROCEDURE OF CARRYING OUT THE WORK

Transfer the calculated exact sample of sodium arsenite into a conic flask for titration, dissolve in the volume of water suitable for titration, add

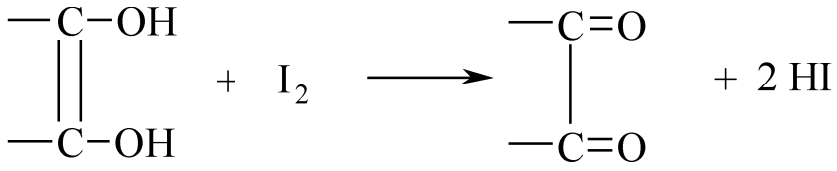
10 cm^3 of the saturated sodium hydrocarbonate solution, 2 cm^3 of the starch solution and titrate with the iodine standard solution until the solution becomes of a blue colour.

Repeat the titration until the reproducible results are obtained.

Calculate the percentage of sodium arsenite.

LABORATORY WORK № 6
DETERMINATION OF THE PERCENTAGE OF ASCORBIC ACID IN THE MEDICINE

Such equation of the oxidation reaction of ascorbic acid endiol group is in the basis of the determination:



$$E(C_6H_8O_6) = M(C_6H_8O_6) \cdot f_{eqv}; f_{eqv} = 1/2.$$

REAGENTS

Iodine, 0.1 mole/dm^3 solution;

starch, 0.5% solution.

PROCEDURE OF CARRYING OUT THE WORK

Transfer the calculated exact sample of ascorbic acid into a conic flask, dissolve in the volume of water suitable for titration, add 2 cm^3 of the starch solution and titrate with the iodine standard solution until a blue colour of the solution appears.

Repeat the titration until the reproducible results are obtained.

Calculate the percentage of ascorbic acid.

LABORATORY WORK № 7

DETERMINATION OF THE PERCENTAGE OF FORMALDEHYDE IN FORMALIN (BACK TITRATION)

The oxidation reactions of formaldehyde by the excess of iodine in the alkaline medium are in the basis of the determination*:

* Formaldehyde is oxidized by NaIO formed in the reaction of interaction of iodine with sodium hydroxide.

$$I_2 + NaOH \rightarrow NaIO + NaI + H_2O$$

$$H-\overset{\overset{O}{\|}}{C}-H + NaIO \longrightarrow HCOOH + NaI + H_2O$$

When acidifying the solution by sulphuric acid from the excess of NaIO free iodine is liberated:

$$NaIO + NaI + H_2SO_4 \rightarrow I_2 + Na_2SO_4 + H_2O \ ,$$

which is titrated by the sodium thiosulphate standard solution:

$+ 2\ e + [I_3]^- \rightleftharpoons 3\ I^-$	1	$E^0 = 0.545$ V
$- 2\ e + 2\ S_2O_3^{2-} \rightleftharpoons S_4O_6^{2-}$	1	$E^0 = 0.09$ V
$2\ S_2O_3^{2-} + [I_3]^- \rightarrow S_4O_6^{2-} + 3\ I^-$		

$$E(CH_2O) = M(CH_2O) \cdot f_{eqv}; f_{eqv} = 1/2.$$

REAGENTS

Iodine, 0.1 mole/dm^3 solution;
sodium thiosulphate, 0.1 mole/dm^3 solution;
sodium hydroxide, 2 mole/dm^3 solution;
sulphuric acid, 0.5 mole/dm^3 solution;
starch, 0.5% solution.

PROCEDURE OF CARRYING OUT THE WORK

Weigh the calculated exact sample of formalin with the help of the analytical balance in a weighing bottle, transfer quantitatively into a measur-

ing flask, dilute the solution to the volume with distilled water and mix thoroughly.

Take the aliquot of the solution prepared by a measuring pipette, transfer into the flask with a ground stopper, add 20.00 cm^3 of the iodine standard solution from the burette, 10 cm^3 of the sodium hydroxide solution, mix thoroughly and leave for 10 minutes in a dark place. Then wash the stopper over a flask with distilled water, add 10 cm^3 of the sulphuric acid solution and titrate iodine liberated with the sodium thiosulphate standard solution until a light yellow colour of the solution appears; then add 1 cm^3 of the starch solution and continue to titrate till decolouration of the solution.

Calculate the percentage of formaldehyde.

Determination of oxidants by the iodometric method

LABORATORY WORK № 8
DETERMINATION OF THE PERCENTAGE OF IODINE IN THE MEDICINE

Such equation of the reaction is in the basis of the determination:

$+ 2\ e + [I_3]^- \rightleftharpoons 3\ I^-$	1	$E^0 = 0.545$ V
$- 2\ e + 2\ S_2O_3^{2-} \rightleftharpoons S_4O_6^{2-}$	1	$E^0 = 0.09$ V
$2\ S_2O_3^{2-} + [I_3]^- \rightarrow S_4O_6^{2-} + 3\ I^-$		

$$E(I_2) = M(I_2) \cdot f_{eqv}; f_{eqv} = 1/2.$$

REAGENTS

Sodium thiosulphate, 0.1 mole/dm^3 solution;
potassium iodide, c. p.;
starch, 0.5% solution.

PROCEDURE OF CARRYING OUT THE WORK

Pour 20.00 cm^3 of the potassium iodide solution into a flask with a ground stopper and weigh with the help of the analytical balance, transfer

the iodine triturated in the mortar into the flask and weigh it again. Mix thoroughly the solution obtained, add 20 cm^3 of distilled water and titrate with the sodium thiosulphate standard solution until a light yellow colour appears; then add 2 cm^3 of the starch solution and continue to titrate till decolouration of the solution.

Repeat the titration until the reproducible results are obtained.

Calculate the percentage of iodine.

LABORATORY WORK № 9
DETERMINATION OF THE PERCENTAGE OF COPPER (II) SULPHATE IN THE MEDICINE

Such equations of the reactions are in the basis of the determination:

$+ 1\ e + Cu^{2+} \rightleftharpoons Cu^{+}$	1	$E^0 = 0.167$ V
$- 2\ e + 3\ I^- \rightleftharpoons [I_3]^-$	1	$E^0 = 0.545$ V
$2\ Cu^{2+} + 3\ I^- \rightarrow 2\ Cu^{+} + [I_3]^-$		

$Cu^{+} + I^- \rightleftharpoons CuI\downarrow$ $\qquad K_S^0(CuI) = 1.1 \cdot 10^{-12}$

$2\ CuSO_4 + 4\ KI \rightarrow 2\ CuI\downarrow + 2\ K_2SO_4 + I_2$

$+ 2\ e + [I_3]^- \rightleftharpoons 3\ I^-$	1	$E^0 = 0.545$ V
$- 2\ e + 2\ S_2O_3^{2-} \rightleftharpoons S_4O_6^{2-}$	1	$E^0 = 0.09$ V
$2\ S_2O_3^{2-} + [I_3]^- \rightarrow S_4O_6^{2-} + 3\ I^-$		

$$E(CuSO_4 \cdot 5H_2O) = M(CuSO_4 \cdot 5H_2O) \cdot f_{eqv}; f_{eqv} = 1.$$

As it follows from the given values of the standard redox potentials of semi-reactions $E^0Cu^{2+}/Cu^{+} = 0.167$ V < $E^0[I_3]^-/3\ I^- = 0.545$ V, the first system should show properties of a reducer, that is the sum reaction should proceed in the opposite direction. But formation of a slightly soluble compound CuI↓ ($K_S^0(CuI) = 1.1 \cdot 10^{-12}$) shifts the direction of the reaction from left to right, $[Cu^+] = \sqrt{K_S^0} = 10^{-6}$ mole/dm^3, and the concentration of

Cu^{2+}-ions reaches rather great values, i. e. $[Cu^{2+}] >> [Cu^{+}]$. The equilibrium potential of the system Cu^{2+}/Cu^{+}, which equals $E = E^{0}_{Cu^{2+}/Cu^{+}} + 0{,}059\, lg \frac{[Cu^{2+}]}{[Cu^{+}]}$, increases to 0.886 V and the reaction of copper(II)-ions with iodide-ions proceeds from left to right practically up to the end.

REAGENTS

Sodium thiosulphate, 0.1 mole/dm^3 solution;
sulphuric acid, 1 mole/dm^3 solution;
potassium iodide, c. p.;
starch, 0.5% solution.

PROCEDURE OF CARRYING OUT THE WORK

Transfer the calculated exact sample of copper (II) sulphate into a measuring flask, dissolve in distilled water, dilute the solution to the volume with water and mix carefully. Take the aliquot of the solution prepared by a measuring pipette, transfer into a flask for titration, add 4 – 5 cm^3 of the sulphuric acid solution, 3 g of potassium iodide. Titrate iodine liberated with the sodium thiosulphate standard solution (in the presence of copper (I) iodide precipitate) until a light yellow colour of the solution appears; then add 2 cm^3 of the starch solution and titrate till decolouration of the solution.

Repeat the titration until the reproducible results are obtained.

Calculate the percentage of copper (II) sulphate.

LABORATORY WORK № 10

DETERMINATION OF THE PERCENTAGE OF POTASSIUM PERMANGANATE

Such equations of the reactions are in the basis of the determination:

$+ 5\ e + MnO_4^- + 8\ H^+ \rightleftharpoons Mn^{2+} + 4\ H_2O$	2	$E^0 = 1.51$ V
$- 2\ e + 3\ I^- \rightleftharpoons [I_3]^-$	5	$E^0 = 0.545$ V
$2\ MnO_4^- + 16\ H^+ + 15\ I^- \rightarrow 2\ Mn^{2+} + 5\ [I_3]^- + 8\ H_2O$		

$+ 2\ e + [I_3]^- \rightleftharpoons 3\ I^-$	1	$E^0 = 0.545$ V
$- 2\ e + 2\ S_2O_3^{2-} \rightleftharpoons S_4O_6^{2-}$	1	$E^0 = 0.09$ V
$2\ S_2O_3^{2-} + [I_3]^- \rightarrow S_4O_6^{2-} + 3\ I^-$		

$$E(KMnO_4) = M(KMnO_4) \cdot f_{eqv}; f_{eqv} = 1/5.$$

REAGENTS

Sodium thiosulphate, 0.1 mole/dm^3 solution;
sulphuric acid, 0.1 mole/dm^3 solution;
potassium iodide, 20% solution;
starch, 0.5% solution.

PROCEDURE OF CARRYING OUT THE WORK

Transfer the calculated exact sample of potassium permanganate into a measuring flask, dissolve in water, dilute the solution to the volume with water and mix carefully. Take the aliquot of the solution prepared by a measuring pipette, transfer into the bottle with a ground stopper, add 10 cm^3 of the potassium iodide solution into it, add 5 cm^3 of the sulphuric acid solution, close the bottle by a stopper wetted with the potassium iodide solution and leave for 10 minutes in a dark place. In 10 minutes wash the stopper over the flask with distilled water, add 100 cm^3 of water into the bottle and titrate iodine liberated with the sodium thiosulphate standard solution until a light yellow colour appears. Add 2 cm^3 of the starch solution and continue to titrate till decolouration of the solution.

Repeat the titration until the reproducible results are obtained.

Calculate the percentage of potassium permanganate in the medicine.

IODOCHLORIMETRY

The method is based on oxidation properties of iodine monochloride, which enters into redox reactions and is reduced either to I^- or to I_2 according to the equations (1) and (2):

$$1) + 2\ e + ICl \rightleftharpoons I^- + Cl^- \qquad E^0 = 0.795\ V$$
$$2) + 2\ e + 2\ ICl \rightleftharpoons I_2 + 2\ Cl^- \qquad E^0 = 1.19\ V$$

Reduction to I^--ions (1) takes place if ΔE of the system does not exceed ≈ 0.4 V; reduction to I_2 (2) occurs if ΔE of the system is within the range of +0.4 ÷ 0.6 V.

The equilibrium redox potential of the system depends on the hydrochloric acid concentration. Iodochlorimetric determinations are similar to iodometric ones, but they have some advantages:

- solutions of iodine monochloride are more stable than solutions of iodine;
- in oxidation reactions the redox potential of the semi-reaction $E^0ICl/I^- + Cl^- = 0.795\ V > E^0[I_3]^-/3\ I^- = 0.545\ V$, it extends potentialities of the iodochlorimetric method;
- in titration by the displacement method the reaction proceeds irreversibly unlike the similar determinations in iodometry.

It is possible to determine cyanides, ferricyanides (II), thiourea, sulphanylamides, barbiturates, aromatic amines derivatives, phenols, etc., by the iodochlorimetric method.

As a titrant in iodochlorimetry 0.1 mole/dm^3 solution of iodine monochloride prepared as the secondary standard solution is used. As a rule, it is obtained by oxidation of iodide-ions by iodate-ions in the medium of the concentrated hydrochloric acid:

$-2\ e + I^- + Cl^- \rightleftharpoons ICl$	2
$+4\ e + IO_3^- + 6\ H^+ + Cl^- \rightleftharpoons ICl + 3\ H_2O$	1
$2\ I^- + IO_3^- + 6\ H^+ + 3\ Cl^- \rightleftharpoons 3\ ICl + 3\ H_2O$	

The solution of iodine monochloride is stable in the acid medium of hydrochloric acid (not less than 100 cm^3 of the concentrated HCl per 1000

cm^3 of the solution prepared). To standardize the iodine monochloride solution prepared is possible against standard substances: arsenic (III) oxide As_2O_3, potassium ferricyanide (II) $K_4[Fe(CN)_6]$, hydrazine sulphate $N_2H_4 \cdot H_2SO_4$; by standard solutions of potassium iodide, sodium thiosulphate, etc.

Direct, back and displacement titration is possible in iodochlorimetry.

Sn^{2+}, SCN^-, SO_3^{2-}-ions, ascorbic acid in the presence of the indicator – the starch solution or organic solvents are determined by *direct* iodochlorimetric titration. The blue colour appears or the organic solvent layer becomes violet when the iodine monochloride excess appears in the solution, for example:

$$SO_3^{2-} + ICl + H_2O \rightarrow SO_4^{2-} + Cl^- + I^- + 2\ H^+$$

$$ICl + I^- \rightarrow I_2 + Cl^-$$

Back titration is used for determination of Hg^{2+}, Fe^{2+}-ions, Hg_2Cl_2 etc. The ICl solution excess is added to the solution being titrated, then free iodine is liberated quantitatively with the help of the KI solution from the rest of ICl, iodine is titrated with the standard solution of $Na_2S_2O_3$. For example:

$$Hg_2Cl_2 + 2\ ICl + 2\ H^+ \rightarrow 2\ HgCl_2 + 2\ HI$$

$$KI + ICl \rightarrow KCl + I_2$$

$$I_2 + 2\ Na_2S_2O_3 \rightarrow 2\ NaI + Na_2S_4O_6$$

Displacement titration is based on forming the equivalent quantity of I_2 in the interaction of the iodine monochloride solution with reducers, I_2 is titrated with the standard solution of $Na_2S_2O_3$.

The end-point of titration is determined:

- by the end-point method without an indicator – free iodine formed as a result of the reaction colours the solution into a light yellow colour, or the layer of the organic solvent is coloured;
- with an indicator – the starch solution;
- by the electrochemical methods: potentiometry, amperometry, etc.

LABORATORY WORKS

LABORATORY WORK № 1
PREPARATION OF 0.1 mole/dm^3 IODINE MONOCHLORIDE SOLUTION

Preparation of the iodine monochloride solution is accompanied by the following equation of the reaction:

$$2\ KI + KIO_3 + 6\ HCl \rightarrow 3\ ICl + 3\ KCl + 3\ H_2O$$

$$E(ICl) = M(ICl) \cdot f_{eqv};\ f_{eqv} = 1/2.$$

REAGENTS

Potassium iodide, c. p.;
potassium iodate, c. p.;
potassium iodide, 1% solution;
potassium iodate, 1% solution;
concentrated hydrochloric acid, c. p.;
chloroform, c. p.

PROCEDURE OF CARRYING OUT THE WORK

Weigh samples of 5.53 g of potassium iodide and 3.55 g of potassium iodate with the help of the technical balance, transfer into a flask with a ground stopper, add 50 cm^3 of distilled water, 40 cm^3 of the concentrated hydrochloric acid and shake till dissolution of iodine formed as a result of the reaction. Then add 10 cm^3 of chloroform, transfer into a separating funnel and shake it again. If the chloroform layer while shaking is coloured in a red-violet colour, add 1% solution of potassium iodate (with shaking thoroughly) to the solution drop by drop till decolouration of the chloroform layer (oxidation of the KI excess). If the chloroform layer is colourless, add 1% solution of potassium iodide to the solution drop by drop until a light pink colour of the chloroform layer appears, and then add 1% solution of potassium iodate till its decolouration (reduction of the

KIO_3 excess), leave the solution till its layering, after that pour the water layer and dilute the solution to the volume of 1 dm^3 with water. The solution should have a lemon colour.

LABORATORY WORK № 2
STANDARDIZATION OF 0.1 mole/dm^3 IODINE MONOCHLORIDE SOLUTION BY THE SODIUM THIOSULPHATE STANDARD SOLUTION

Such equations of the reactions are in the basis of the determination:

1) + 2 e + 2 ICl $\rightleftharpoons$ I_2 + 2 Cl^-	1	E^0 = 1.19 V
– 2 e + 2 I^- $\rightleftharpoons$ I_2	1	E^0 = 0.545 V
ICl + I^- $\rightarrow$ I_2 + Cl^-		

2) ICl + 2 I^- $\rightarrow$ $[I_3]^-$ + Cl^-

3) + 2 e + $[I_3]^-$ $\rightleftharpoons$ 3 I^-	1	E^0 = 0.545 V
– 2 e + 2 $S_2O_3^{2-}$ $\rightleftharpoons$ $S_4O_6^{2-}$	1	E^0 = 0.09 V
2 $S_2O_3^{2-}$ + $[I_3]^-$ $\rightarrow$ $S_4O_6^{2-}$ + 3 I^-		

REAGENTS

Sodium thiosulphate, 0.1 mole/dm^3 solution;
potassium iodide, c. p.;
starch, 0.5% solution.

PROCEDURE OF CARRYING OUT THE WORK

Take the aliquot of the iodine monochloride solution prepared by a measuring pipette, transfer it into the flask with a ground stopper, add 1 g of potassium iodide and leave for 15 minutes in the place protected from light. Then wash the stopper over the flask with distilled water and titrate iodine liberated with the sodium thiosulphate standard solution until a light yellow colour of the solution appears, then add 2 cm^3 of the starch solution and continue to titrate till decolouration of the solution.

Repeat the titration until the reproducible results are obtained.

Calculate the molar concentration of the equivalent substance of iodine monochloride in the solution and the correction coefficient (K).

LABORATORY WORK № 3
DETERMINATION OF THE PERCENTAGE OF SODIUM SULPHITE IN THE MEDICINE

Such equations of the reactions are in the basis of the determination:

1) + 2 e + ICl $\rightleftharpoons$ I^- + Cl^-	1	E^0 = 0.795 V
– 2 e + SO_3^{2-} + H_2O $\rightleftharpoons$ SO_4^{2-} + $2H^+$	1	E^0 = 0.938 V
SO_3^{2-} + H_2O + ICl $\rightarrow$ SO_4^{2-} + 2 H^+ + Cl^- + I^-		

2) + 2 e + ICl $\rightleftharpoons$ I^- + Cl^-	1	E^0 = 0.795 V
– 2 e + 3 I^- $\rightleftharpoons$ $[I_3]^-$	1	E^0 = 0.545 V
ICl + 2 I^- $\rightarrow$ $[I_3]^-$ + Cl^-		

$$E(Na_2SO_3) = M(Na_2SO_3) \cdot f_{eqv}; f_{eqv} = 1/2.$$

REAGENTS

Iodine monochloride, 0.1 mole/dm^3 solution;

chloroform, c. p.

PROCEDURE OF CARRYING OUT THE WORK

Transfer the calculated exact sample of sodium sulphite into a conic flask, dissolve in the volume of water suitable for titration, add 5 cm^3 of chloroform and titrate with the iodine monochloride standard solution while mixing of the mixture being titrated thoroughly until of a red-violet colour of the chloroform layer appears.

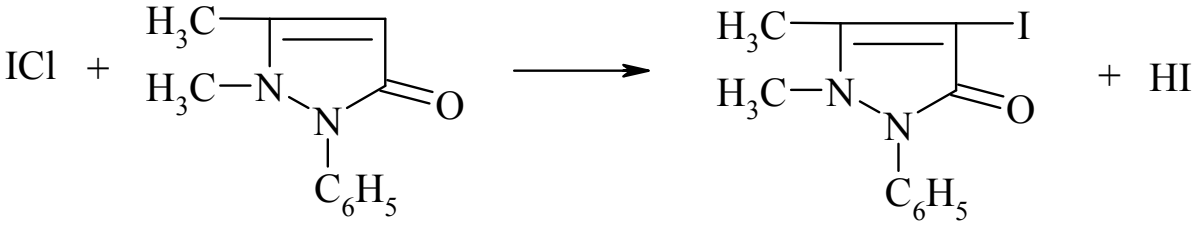
Repeat the titration until the reproducible results are obtained.

Calculate the percentage of sodium sulphite.

LABORATORY WORK № 4

DETERMINATION OF THE PERCENTAGE OF ANTIPYRINE IN THE MEDICINE

Such equations of the reactions are in the basis of the determination:



$+ 2\ e + ICl \rightleftharpoons I^- + Cl^-$	1	$E^0 = 0.795$ V
$- 2\ e + 3\ I^- \rightleftharpoons [I_3]^-$	1	$E^0 = 0.545$ V
$ICl + 2\ I^- \rightarrow [I_3]^- + Cl^-$		

$$E(C_{11}H_{12}N_2O) = M(C_{11}H_{12}N_2O) \cdot f_{eqv}; f_{eqv} = 1/2.$$

REAGENTS

Iodine monochloride, 0.1 mole/dm^3 solution;

potassium iodide, 1% solution;

starch, 0.5% solution.

PROCEDURE OF CARRYING OUT THE WORK

Dissolve the calculated exact sample of antipyrine in distilled water in a conic flask for titration, add 1 drop of the potassium iodide solution, 2 cm^3 of the starch solution and titrate with the iodine monochloride standard solution until the colour changes from dark blue to light violet.

Repeat the titration until the reproducible results are obtained.

Calculate the percentage of antipyrine.

LABORATORY WORK № 5

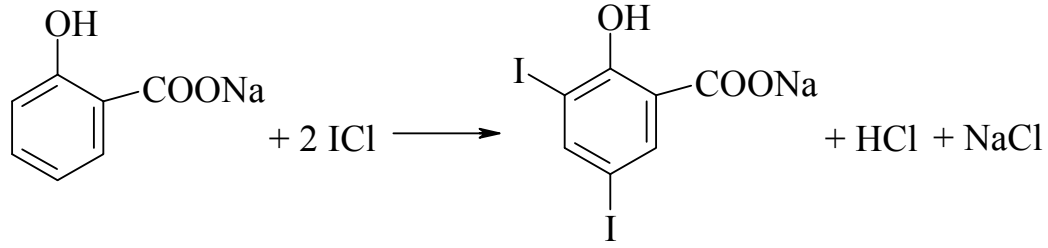
DETERMINATION OF THE PERCENTAGE OF POTASSIUM IODIDE (DISPLACEMENT METHOD)

Such equations of the reactions are in the basis of the determination:

1) + 2 e + ICl ⇌ I^- + Cl^-	1	E^0 = 0.795 V
– 2 e + 3 I^- ⇌ $[I_3]^-$	1	E^0 = 0.545 V

ICl + 2 I^- → $[I_3]^-$ + Cl^-

2)



3) + 2 e + $[I_3]^-$ ⇌ 3 I^-	1	E^0 = 0.545 V
– 2 e + 2 $S_2O_3^{2-}$ ⇌ $S_4O_6^{2-}$	1	E^0 = 0.09 V

2 $S_2O_3^{2-}$ + $[I_3]^-$ → $S_4O_6^{2-}$ + 3 I^-

REAGENTS

Iodine monochloride, 0.1 mole/dm^3 solution;
sodium thiosulphate, 0.1 mole/dm^3 solution;
sodium salicylate, 1% solution.

PROCEDURE OF CARRYING OUT THE WORK

Transfer the calculated exact sample of potassium iodide into a flask with a ground stopper, dissolve in 10 – 15 cm^3 of distilled water, add the excess (20.00 – 30.00 cm^3) of the iodine monochloride standard solution and shake. Add 100 cm^3 of distilled water, 10 cm^3 of the sodium salicylate solution, leave for 5 – 10 minutes in a dark place, wash the stopper over the flask with distilled water and titrate iodine liberated with the sodium thiosulphate standard solution until a light yellow colour of the solution appears, then add 2 cm^3 of the starch solution and continue to titrate till decolouration.

Repeat the titration until the reproducible results are obtained.

Calculate the percentage of potassium iodide.

CERIMETRY

The cerimetric method of analysis is based on oxidation-reduction properties of redox-pair Ce^{4+}/Ce^{3+}. It is possible to present processes occurring in cerimetric determination by the semi-reaction:

$$+ e + Ce^{4+} \rightleftharpoons Ce^{3+}$$

Semi-reactions standard redox-potentials of the cerium complex salts system used in analysis depend on anions contained in them:

$$E^0_{[Ce(SO_4)_3]^{2-}/Ce^{3+}} = 1.45 \text{ V},$$

$$E^0_{[Ce(NO_3)_6]^{2-}/Ce^{3+}} = 1.60 \text{ V},$$

$$E^0_{[CeCl_6]^{2-}/Ce^{3+}} = 1.40 \text{ V}.$$

A high value of E^0 of the Ce^{4+}/Ce^{3+} system allows to determine quantitatively substances, which potentials are below than cerium (IV) has. By this method it is possible to determine Fe (II)-, As (III)-, Sb (III)-, NO_2^-, oxalate-ions, H_2O_2, formaldehyde and other reducers, as well as many compounds, which cannot be determined by other redox-methods. Cerimetric determinations are similar to permanganatometric ones, but when compared with other redox-methods they have a number of advantages:

- titrants are stable in cold and heating;
- when titrating with Ce (IV) salts, as a rule, the by-products that reduce accuracy and extend the process of titration are not formed;
- titration can be carried out in the HCl medium (unlike permanganatometry).

0.1 mole/dm^3 and 0.01 mole/dm^3 solutions of cerium (IV) sulphate $Ce(SO_4)_2 \cdot 4H_2O$ or cerium (IV) ammonium sulphate $[Ce(SO_4)_2 \cdot 2(NH_4)_2SO_4] \cdot 2H_2O$ are used as titrants in the cerimetric method. These salts do not satisfy the standard substances requirements, therefore, secondary standard solutions are prepared from them.

The solutions of titrants are standardized against standard substances – sodium or ammonium oxalate:

$$\begin{array}{l|l} + e + Ce^{4+} \rightleftharpoons Ce^{3+} & 2 \\ - 2\,e + H_2C_2O_4 \rightleftharpoons 2\,CO_2\uparrow + 2\,H^+ & 1 \\ \hline H_2C_2O_4 + 2\,Ce^{4+} \rightarrow 2\,CO_2\uparrow + 2\,Ce^{3+} + 2\,H^+ & \end{array}$$

or by the iodometric method by $Na_2S_2O_3$ standard solution (see laboratory work № 2).

Direct, back and displacement titration is possible in cerimetry.

The end-point of titration is determined:

- by the method without an indicator (Ce^{3+}-ions are colourless, Ce^{4+}-ions have yellow colour);
- by redox-indicators – diphenylamine, ferroin; by irreversible indicators – methyl orange, methyl red;
- by electrochemical methods – potentiometric, amperometric.

LABORATORY WORKS

LABORATORY WORK № 1
PREPARATION OF 0.1 mole/dm^3 CERIUM (IV) SULPHATE SOLUTION

$$E(Ce(SO_4)_2 \cdot 4H_2O) = M(Ce(SO_4)_2 \cdot 4H_2O) \cdot f_{eqv};\ f_{eqv} = 1.$$

REAGENTS

Cerium (IV) sulphate, c. p.;
sulphuric acid, concentrated.

PROCEDURE OF CARRYING OUT THE WORK

Transfer the calculated sample of cerium (IV) sulphate into a beaker, dissolve in 500 cm^3 of distilled water containing 20 cm^3 of the concentrated sulphuric acid; if it is necessary, heat, cool and dilute the solution to the volume of 1 dm^3. Mix the solution carefully and pour into a vessel for storage.

LABORATORY WORK № 2

STANDARDIZATION OF 0.1 mole/dm^3 CERIUM (IV) SULPHATE SOLUTION BY THE SODIUM THIOSULPHATE STANDARD SOLUTION

The cerium (IV) sulphate solution is standardized by iodometric displacement titration. The following equations of the reactions are in the basis of the determination:

$+ e + Ce^{4+} \rightleftharpoons Ce^{3+}$	2	$E^0 = 1.44$ V
$- 2 e + 3 I^- \rightleftharpoons [I_3]^-$	1	$E^0 = 0.545$ V
$2 Ce^{4+} + 3 I^- \rightarrow 2 Ce^{3+} + [I_3]^-$		

$+ 2 e + [I_3]^- \rightleftharpoons 3 I^-$	1	$E^0 = 0.545$ V
$- 2 e + 2 S_2O_3^{2-} \rightleftharpoons S_4O_6^{2-}$	1	$E^0 = 0.09$ V
$2 S_2O_3^{2-} + [I_3]^- \rightarrow S_4O_6^{2-} + 3 I^-$		

$$E(Ce(SO_4)_2 \cdot 4H_2O) = M(Ce(SO_4)_2 \cdot 4H_2O) \cdot f_{eqv}; f_{eqv} = 1.$$

REAGENTS

Sodium thiosulphate, 0.1 mole/dm^3 solution;
sulphuric acid, 0.3 mole/dm^3 solution;
potassium iodide, 20% solution;
starch, 1% solution.

PROCEDURE OF CARRYING OUT THE WORK

Measure 25.00 cm^3 of the cerium (IV) sulphate solution into a conic flask with a ground stopper, add 20 cm^3 of the sulphuric acid solution, 20 cm^3 of distilled water, 10 cm^3 of the potassium iodide solution, close by the stopper and leave for 10 – 15 minutes in a dark place. Wash the stopper over the flask with water, titrate iodine liberated with the sodium thiosulphate standard solution until a light yellow colour appears, then add 2 cm^3 of the starch solution and continue to titrate until a blue colour of the solution disappears.

Repeat the titration until the reproducible results are obtained.

Calculate the molar concentration of the equivalent substance of cerium (IV) sulphate in the solution and the correction coefficient (K).

LABORATORY WORK № 3
DETERMINATION OF THE PERCENTAGE OF IRON (II) SULPHATE IN THE MEDICINE

Such equation of the reaction is in the basis of the determination:

$-e + Fe^{2+} \rightleftharpoons Fe^{3+}$	1	$E^0 = 0.77$ V
$+e + Ce^{4+} \rightleftharpoons Ce^{3+}$	1	$E^0 = 1.44$ V
$Ce^{4+} + Fe^{2+} \rightarrow Ce^{3+} + Fe^{3+}$		

$$E(FeSO_4) = M(FeSO_4) \cdot f_{eqv}; f_{eqv} = 1.$$

REAGENTS

Cerium (IV) sulphate, 0.1 mole/dm^3 solution;

sulphuric acid, 1 mole/dm^3 solution;

ferroin, 0.025 mole/dm^3 solution.

PROCEDURE OF CARRYING OUT THE WORK

Transfer the calculated exact sample of iron (II) sulphate into a conic flask, dissolve in 20 cm^3 of the sulphuric acid solution, add one drop of the ferroin solution and titrate with the cerium (IV) sulphate standard solution until the solution changes its colour from red to blue.

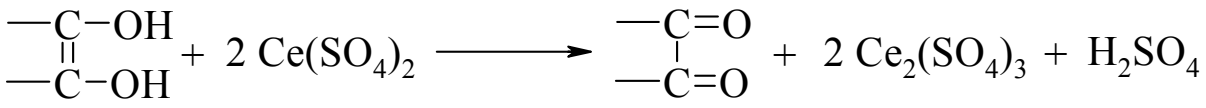
Repeat the titration until the reproducible results are obtained.

Calculate the percentage of iron (II) sulphate.

LABORATORY WORK № 4

DETERMINATION OF THE PERCENTAGE OF ASCORBIC ACID IN THE MEDICINE

The oxidation reaction of ascorbic acid endiol group by cerium (IV) sulphate is in the basis of the determination:



$$E(C_6H_8O_6) = M(C_6H_8O_6) \cdot f_{eqv}; f_{eqv} = 1/2.$$

REAGENTS

Cerium (IV) sulphate, 0.1 mole/dm^3 solution;
sulphuric acid, 1 mole/dm^3 solution;
ferroin, 0.025 mole/dm^3 solution.

PROCEDURE OF CARRYING OUT THE WORK

Transfer the calculated exact sample of ascorbic acid into a flask for titration, add 20 cm^3 of sulphuric acid, one drop of the ferroin solution and titrate with the cerium (IV) sulphate standard solution until a blue colour of the solution appears.

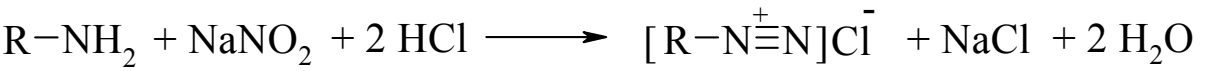
Repeat the titration until the reproducible results are obtained.

Calculate the percentage of ascorbic acid.

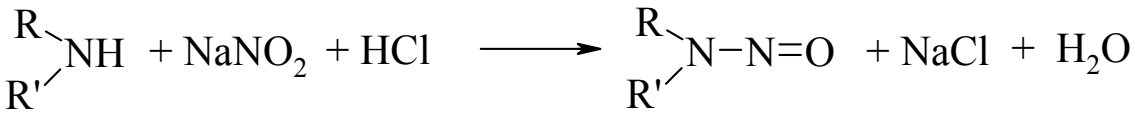
NITRITOMETRY

The method is based on oxidation-reduction and diazotization properties of nitrous acid.

The majority of nitritometric determinations are based on diazotization reactions of primary aromatic amines:



and nitrosification reactions of secondary amines:



Besides, nitrites of alkaline metals reveal oxidation or reduction properties depending on conditions.

Thus, H_2O_2, $KMnO_4$, active chlorine in bleach powder, cerium (IV) and other oxidants oxidize nitrite-ions to nitrate-ions:

$$-2\ e + HNO_2 + H_2O \rightleftharpoons NO_3^- + 3\ H^+ \qquad E_0 = 0.94\ V$$

Reducers, for example, sulphamic acid, reduce NO_2^- to N_2 (N_2O):

$$+6\ e + 2\ HNO_2 + 6\ H^+ \rightleftharpoons N_2\uparrow + 4\ H_2O \qquad E_0 = 1.44\ V$$

The titrant of the method is 0.1 mole/dm^3 solution of $NaNO_2$, it is prepared as the secondary standard solution. The exact concentration of sodium nitrite is determined against sulphanilic acid (see laboratory work № 2), *p*-aminobenzoic acid, hydrazine sulphate, potassium permanganate (back titration):

$$1)\ 5\ NaNO_2 + 2\ KMnO_4 + 3\ H_2SO_4 \rightarrow$$
$$\rightarrow 5\ NaNO_3 + 2\ MnSO_4 + K_2SO_4 + 3\ H_2O$$
$$2)\ \text{excess}\ 2\ KMnO_4 + 10\ KI + H_2SO_4 \rightarrow$$
$$\rightarrow 2\ MnSO_4 + 5\ I_2 + 6\ K_2SO_4 + 8\ H_2O$$
$$3)\ I_2 + 2\ Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2\ NaI$$

Internal and external indicators are used in the method. Diphenylamine, dyes, for example, tropeoline-00, safranile, both individually and in the mixture with methylene blue are used as internal redox indicators. Methylene blue performs the role of background, which allows to see changing of the indicator colour more clearly.

Iodine-starch paper is used as an external indicator. Having reached the point of equivalence, when there is no free oxidant in the solution yet, the colour of iodine-starch paper is not changed. After the point of equiva-

lence, when the excess quantity of the titrant is appeared in the solution, nitrite-ions oxidize iodide-ions to free iodine:

$$\begin{array}{l|l} -2\,e + 3\,I^- \rightleftharpoons [I_3]^- & 1 \\ +e + NO_2^- + 2\,H^+ \rightleftharpoons NO\uparrow + H_2O & 2 \\ \hline 2\,NO_2^- + 4\,H^+ + 3\,I^- \rightleftharpoons 2\,NO\uparrow + [I_3]^- + 2\,H_2O & \end{array}$$

Iodine liberated interacts with starch, iodine-starch paper is coloured in a dark blue colour.

The nitritometric method of the analysis is widely used for determination of many medicines containing aromatic aminogroup: novocaine, sulphanylamides, *p*-aminobenzoic acid and its derivatives, etc.

Conditions of nitritometric determinations of aromatic amines derivatives are:

- titration is carried out at low temperature (0° – 10°C) in the presence of the double excess of hydrochloric acid with the purpose of increasing the stability of diazo-compounds in many cases;
- the catalyst – crystalline KBr is added to accelerate the diazotization reaction proceeding, titration is carried out slowly, with shaking thoroughly, close to the point of equivalence – with the speed of one drop per minute;
- the preference is given to internal indicators, and it decreases the indicator error significantly when determining the point of equivalence.

LABORATORY WORKS

LABORATORY WORK № 1
PREPARATION OF 0.1 mole/dm^3 SODIUM NITRITE SOLUTION

$$E(NaNO_2) = M(NaNO_2) \cdot f_{eqv};\ f_{eqv} = 1.$$

REAGENTS

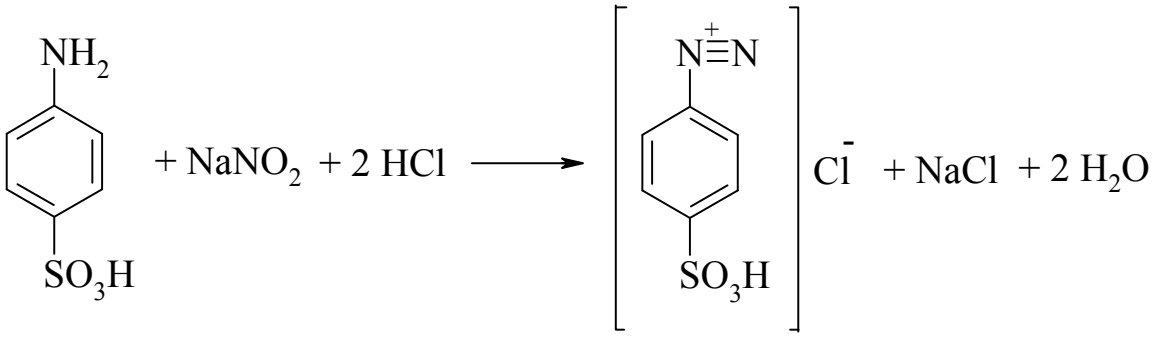
Sodium nitrite, pure for analysis.

PROCEDURE OF CARRYING OUT THE WORK

Weigh the calculated exact sample of sodium nitrite with the help of the technical balance, transfer into a beaker with the capacity of 1 dm^3, dissolve in a small quantity of water and dilute the solution to the volume. Pour into a vessel for storing the solution.

LABORATORY WORK № 2
STANDARDIZATION OF 0.1 mole/dm^3 SODIUM NITRITE SOLUTION AGAINST SULPHANILIC ACID

Such equation of the reaction is in the basis of the determination:



$$E(C_6H_7NO_3S) = M(C_6H_7NO_3S) \cdot f_{eqv};\ f_{eqv} = 1.$$

REAGENTS

Sulphanilic acid, recrystallized twice;
sodium hydrocarbonate, pure for analysis;
potassium bromide, pure for analysis;
hydrochloric acid, 8% solution;
tropeoline-00, 0.1% solution;
methylene blue, 0.5%, solution.

PROCEDURE OF CARRYING OUT THE WORK

Transfer the calculated exact sample of sulphanilic acid into the thick-walled glass, add 0.1 g of sodium hydrocarbonate, 70 cm^3 of 8% hydrochloric acid solution, 1 g of potassium bromide, 4 drops of the tropeoline-00 solution and 2 drops of the methylene blue solution. Titrate with the solution of sodium nitrite with constant mixing. At first add the titrant with

the speed of 2 cm^3 per minute, and at the end of titration – add 0.05 cm^3 per minute. Continue the titration until the solution colour changes from red-violet into dark blue.

Repeat the titration until the reproducible results are obtained.

Calculate the molar concentration of the equivalent substance of sodium nitrite in the solution and the correction coefficient (K).

LABORATORY WORK № 3
DETERMINATION OF THE PERCENTAGE OF SULPHAMIC ACID IN THE MEDICINE

Determination is based on sulphamic acid oxidation by sodium nitrite in the acid medium:

$$\begin{array}{l|l} -6\,e + 2\,NH_2SO_2OH + 2\,H_2O \rightleftharpoons 2\,SO_4^{2-} + N_2\uparrow + 10\,H^+ & 1 \\ +6\,e + 2\,HNO_2 + 6\,H^+ \rightleftharpoons N_2\uparrow + 4\,H_2O & 1 \end{array}$$

$$NH_2SO_2OH + HNO_2 \rightarrow SO_4^{2-} + 2\,H^+ + N_2\uparrow + H_2O$$

$$E(NH_2SO_2OH) = M(NH_2SO_2OH) \cdot f_{eqv};\ f_{eqv} = 1.$$

REAGENTS

Sodium nitrite, 0.1 mole/dm^3 solution;
sulphuric acid, 10% solution;
iodine-starch paper.

PROCEDURE OF CARRYING OUT THE WORK

Dissolve the calculated exact sample of sulphamic acid in 20 cm^3 of water in a conic flask for titration, add 10 cm^3 of the H_2SO_4 solution and titrate slowly with the sodium nitrite standard solution with the external indicator – iodine-starch paper.

Titrate until the drop of the reaction mixture taken in one minute after addition of the next portion of the titrant colours the indicator paper immediately in dark blue.

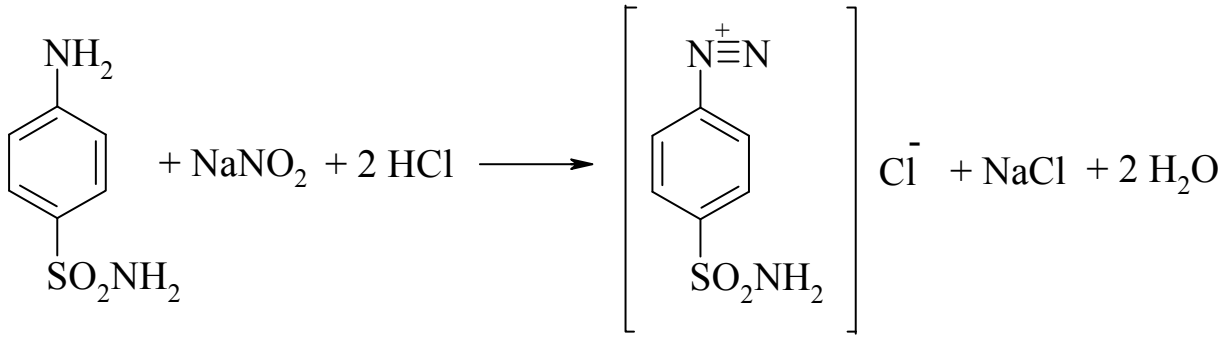
Repeat the titration until the reproducible results are obtained.

Calculate the percentage of sulphamic acid.

LABORATORY WORK № 4

DETERMINATION OF THE PERCENTAGE OF STREPTOCID IN THE MEDICINE

Determination is based on the streptocid diazotization reaction:



$$E(C_6H_8N_2O_2S) = M(C_6H_8N_2O_2S) \cdot f_{eqv}; f_{eqv} = 1.$$

REAGENTS

Sodium nitrite, 0.1 mole/dm^3 solution;
hydrochloric acid, 8% solution;
potassium bromide, pure for analysis;
tropeoline-00, 0.1% solution;
methylene blue, 0.5%, solution.

PROCEDURE OF CARRYING OUT THE WORK

Transfer the calculated exact sample of streptocid into a conic flask for titration and dissolve in 20 cm^3 of the diluted hydrochloric acid, add 60 cm^3 of water, 1 g of potassium bromide, 4 drops of the tropeoline-00 solution and 1 – 2 drops of the methylene blue solution. Titrate with the solution of sodium nitrite at room temperature when mixing vigorously. Add the titrant at the end of titration with the speed of one drop per minute.

Repeat the titration until the reproducible results are obtained.

Calculate the percentage of streptocid in the medicine.

CONTROL QUESTIONS FOR IN-CLASS AND OUT-OF-CLASS WORK OF STUDENTS

1. The essence of oxidation-reduction titration methods, their classification.
2. Requirements to redox reactions, which are in basis of the oxidation-reduction titration methods.
3. Methods of indication of the end-point of titration in oxidation-reduction titration methods. External, internal, mixed indicators.
4. Methods of oxidation-reduction titration (direct, back, substitution, indirect). Explain each giving examples.
5. The conjugate (induced) oxidation-reduction reactions.
6. Is it possible to prepare the primary standard solution from «chemically pure» potassium permanganate? Preparation and storage conditions of the potassium permanganate solution.
7. What standard substances are used for standardization of the potassium permanganate solution? The essence and standardization conditions of the potassium permanganate solution against sodium oxalate.
8. Oxidation properties of permanganate-ions depending on the medium pH. The conditions of permanganatometric determinations. Determination of the end-point of titration.
9. Why is sulphuric acid used in permanganatometry for creating the acid medium of the solution?
10. Application of permanganatometry in analysis of medicines.
11. The essence of bromatometric determinations of organic and inorganic compounds.
12. A titrant in bromatometry, its preparation and properties.
13. Determination of the end-point of titration in bromatometry.
14. Application of the bromatometric method in analysis.
15. Characteristics of the chromatometric method: the essence of the method, preparation of a titrant, conditions of titration and determination of the end-point of titration, application in analysis.
16. The essence of the iodometric method of analysis, its potentialities.

17. Titrants of the iodometric method, their preparation and standardization.
18. Methods of iodometric titration. Iodometric determination of strong oxidants.
19. Determination of the end-point of titration in iodometry. Application of the starch solution as an indicator when determining reducers, as well as when titrating strong oxidants.
20. The conditions of iodometric determinations. Give the examples of the necessary reaction equations.
21. The essence of the iodochlorimetric method. Reactions, which are in the basis of its determination, potentialities of the method.
22. The advantages of iodochlorimetry in comparison with the iodometric method of analysis. Determination of the moment of equivalence in iodochlorimetry. Preparation and standardization of a titrant in iodochlorimetry. Standard substances and standard solutions.
23. Determination of reducers by the iodochlorimetric method, the examples of determinations.
24. Determination of oxidants by the iodochlorimetric method, the examples of determinations.
25. The essence of the cerimetric method of analysis, reactions, which are in the basis of the determinations.
26. The titrant of the cerimetric method, its preparation and standardization. Standard substances and standard solutions.
27. Determination of the end-point of titration in cerimetry.
28. Potentialities, advantages and disadvantages of the cerimetric method of analysis in comparison with other redox methods.
29. Oxidation-reduction and diazotization properties of nitrous acid and sodium nitrite.
30. The essence of the nitritometric method of titration. Factors influencing on completeness and speed of a diazotization reaction.
31. Preparation of a titrant in nitritometry and its standardization.
32. Determination of the end-point of titration in nitritometry. Application of external, internal and mixed indicators.

33. Application of nitritometry in analysis.
34. What is the molar concentration of the $KMnO_4$ solution, its titre and the titre by $FeSO_4$ if 20.15 cm^3 of the potassium permanganate solution for titration of 0.3038 g of iron (II) sulphate was used?
    Answer: $c(KMnO_4)$ = 0.09993 mole/dm^3, $T(KMnO_4)$ = 0.003137 g/cm^3; $T(KMnO_4/FeSO_4)$ = 0.01519 g/cm^3.
35. What sample of the medicine with the percentage of streptocid of 69.00% should be taken if while titrating streptocid in the acid medium in the presence of potassium bromide 21.05 cm^3 of 0.0987 mole/dm^3 potassium bromate (V) solution was used? Specify the indicator of this determination.
    Answer: m = 0.1274 g.
36. Calculate the molar concentration and the titre of $KMnO_4$ solution if 22.15 cm^3 of the $KMnO_4$ solution is used for titration of 20.00 cm^3 of the sodium oxalate solution obtained by dissolving its sample with the mass of 0.3407 g in a measuring flask with the capacity of 100.00 cm^3.
    Answer: $c(KMnO_4)$ = 0.04590 mole/dm^3, $T(KMnO_4)$ = 0.001451 g/cm^3.
37. Calculate the mass of the potassium dichromate sample for preparation of 500 cm^3 0.1 mole/dm^3 potassium dichromate solution.
    Answer: m = 2.45 g (the exact sample).
38. Determine the percentage of novocaine if 21.50 cm^3 of 0.1021 mole/dm^3 sodium nitrite solution was used for titration of its sample with the mass of 0.6062 g.
    Answer: ω = 96.78%.
39. Calculate the mass of the iodine sample, which is necessary for preparation of 2 dm^3 of 0.01 mole/dm^3 iodine solution.
    Answer: m = 2.5 g.
40. Calculate the mass of $K_2Cr_2O_7$ sample, which is necessary for standardization of 0.1 mole/dm^3 $Na_2S_2O_3$ solution (the pippeting method: $V_{m.f.}$ = 100.00 cm^3, $V_{p.}$ = 10.00 cm^3) if 25.00 cm^3 of the $Na_2S_2O_3$ solution is used for titration of iodine liberated.
    Answer: m = 1.0 g (the exact sample).

41. Calculate the molar concentration, its titre and the titre by iodine of the $Na_2S_2O_3$ solution if 20.05 cm^3 of $Na_2S_2O_3$ solution was used for titration of iodine liberated when adding of the KI excess to the $K_2Cr_2O_7$ sample with the mass of 0.1020 g.
Answer: $c(Na_2S_2O_3)$ = 0.1038 mole/dm^3, $T(Na_2S_2O_3)$ = 0.01641 g/cm^3; $T(Na_2S_2O_3/I_2)$ = 0.01269 g/cm^3.
42. Determine the quantity of chlorine in 1 dm^3 of water, if 20.10 cm^3 of 0.1010 mole/dm^3 $Na_2S_2O_3$ solution was used for titration of iodine liberated when adding of the KI excess to the 50.00 cm^3 of water.
Answer: m = 3.140 g.
43. Determine the percentage of ascorbic acid if 19.45 cm^3 of 0.1008 mole/dm^3 iodine solution was used for titration of the sample with the mass of 0.3975 g.
Answer: ω = 86.89%.
44. Calculate the molar concentration of the iodine monochloride solution and the correction coefficient K if 20.45 cm^3 of $Na_2S_2O_3$ solution (c = 0.1004 mole/dm^3) was used for titration of 20.00 cm^3 of this solution.
Answer: c(ICl) = 0.1027 mole/dm^3, K = 1.027.
45. Determine the percentage of butadione in the medicine if 18.65 cm^3 of 0.1005 mole/dm^3 iodine monochloride solution was used for titration of the sample with the mass of 0.2895 g.
Answer: ω = 99.83%.
46. Calculate the mass of the ammonium cerium (IV) sulphate sample for preparation of 1 dm^3 of 0.1 mole/dm^3 solution.
Answer: m = 63.3 g.
47. Calculate the molar concentration of the cerium (IV) sulphate solution, its titre and the titre by As_2O_3 if 21.05 cm^3 of this solution was used for titration of the As_2O_3 sample with the mass of 0.2015 g?
Answer: $c(Ce(SO_4)_2)$ = 0.1021 mole/dm^3, $T(Ce(SO_4)_2)$ = 0.03883 g/cm^3; $T(Ce(SO_4)_2/As_2O_3)$ = 0.0989 g/cm^3.

CONTENTS

Навчальний посібник, підготовлений на кафедрі аналітичної хімії НФаУ, відповідає сучасному рівню розвитку теорії та практики аналізу речовин, їх сумішей, у тому числі лікарських препаратів. Цю частину навчального посібника присвячено кількісному аналізу речовин. Представлено теоретичні основи, лабораторні роботи, теоретичні та контрольні питання для студентів, ситуаційні завдання, приклади рішення типових вправ.

Для іноземних студентів фармацевтичних вищих навчальних закладів та фармацевтичних факультетів медичних вищих навчальних закладів III – IV рівнів акредитації.

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АНАЛІТИЧНА ХІМІЯ

ЧАСТИНА II

КІЛЬКІСНИЙ АНАЛІЗ

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