

**Ministry of Public Health of Ukraine
National O.O. Bohomolets Medical University**



Medical and General Chemistry Department

ANALYTICAL CHEMISTRY

Part 2 " QUANTITATIVE ANALYSIS"

A Workbook

Galina Zaitseva

Kyiv-2021

There is not a lot that needs to be memorized to do analytical chemistry well. Just about everything you need to know has already been covered in the first semester. The problem is learning to apply this knowledge to real laboratory situations. Our goal is getting you to think for yourself when faced with a laboratory problem, rather than filling in the blanks in a well-controlled laboratory exercise.

The only way you will acquire this skill is through PRACTICE. In lecture there will be assigned homework. Do this faithfully and on time. If you get stuck, ask questions during lab, during lecture, or during the office hours of your instructor. Do not wait until a day or so before an exam to start "learning" the material. In lab, learn to think through the chemistry and mathematics behind each experiment. Do required calculations yourself; don't rely on others to tell you how much to weigh out, or how to do a statistical calculation. Each step along the way is easy to learn and to do. You will only become lost if you let the material pile up on you.

The material in this Survival Guide is meant to give you a few anchor points around which you can add your own accumulated wisdom. *If you don't understand the examples in this brief Guide, the more advanced material in the course will make no sense to you at all.* The examples given will not cover all the things that will face you in the course, but do cover a set of basic methods that you are expected to MASTER. Your book, handouts from your instructor, and lecture notes will provide additional material. The skills required to handle all of this, however, can only come through your own efforts.

Remember, as a human being you are skilled at seeing patterns and solving problems. The lectures will emphasize the Human approach to solving problems. Even dumb (but fast!) computers can plug into a formula. Humans, however, can solve real-world problems containing poorly organized information.

When faced with a complex problem in analytical chemistry:

- 1) Write down everything you are given about the problem. Draw pictures and arrows if necessary to make the situation clear. Include the units with any values given.
- 2) Clearly state what you are solving for.
- 3) Look at what you have written and drawn; think about how the basic operations you have learned can be used to solve this problem. It often helps to work backwards from the solution to the information you have written.
- 4) Identify any simpler sub-tasks that can be done first (converting grams to moles, perhaps) before solving the main body of the problem.
- 5) Look at the number you have generated. Does it make sense? (If you got 1.23×10^{43} M for a concentration, you have probably done something wrong!)

Practical lesson 11

Titrimetric analysis. Method of neutralization. Preparation of solutions for the method of neutralization. Solution of problems and situational tasks. Basic practical skills of the measuring volumetric glassware using.

CONTROL QUESTIONS FOR STUDENTS OUT-OF-CLASS WORK

1. Theoretical questions

The main principles and tasks of quantitative analysis. Areas of application of quantitative analysis.

Classification of methods of quantitative analysis.

The basis of titrimetric methods of analysis. Basic concepts.

Classification of titrimetric analysis methods by type of chemical reaction.

Requirements for titrimetric reactions.

Conditions for titrimetric determinations.

Measuring volumes. Measuring chemical ware. Checking the capacity of measuring chemical ware.

Titrated solutions. Methods of their preparation. Primary and secondary standards. Requirements to the primary standards. Methods for expressing of the concentration of titrated solutions.

Calculations in titrimetric analysis. Expression of measurement results

2. Test items for licensing examination Krok 1 PHARMACY

The correct answer is first

- 1) The molar mass of calcium hydroxide equivalent ($M(\text{Ca}(\text{OH})_2) = 74 \text{ g/mol}$) is:
 - A. 37 g/mol
 - B. 19 g/mol
 - C. 32 g/mol
 - D. 74 g/mol
 - E. 148 g/mol
- 2) To prepare 600 g of 10% solution of potassium hydroxide the following amount of potassium must be taken:
 - A. 60 g
 - B. 0,6 g
 - C. 6 g
 - D. 10 g
 - E. 12 g
- 3) Molar mass equivalent to barium hydroxide ($M(\text{Ba}(\text{OH})_2) = 171 \text{ g/mol}$) is:
 - A. 85,5 g/mol
 - B. 34 g/mol
 - C. 42,8 g/mol
 - D. 57 g/mol
 - E. 232 g/mol
- 4) In order to prepare 1 L of 0,1 M solution of sulfuric acid ($M(\text{H}_2\text{SO}_4) = 98 \text{ g/mole}$) it is necessary to take:

- A. 9,8 g of H₂SO₄
- B. 980 g of NaCl
- C. 0,098 g of NaCl
- D. 49 g of NaCl
- E. 98 g of NaCl

3. Calculations Involving Amounts

We use two units to describe how much of something we need to use: the **gram** and the **mole**. To these we add the prefixes of kilo-(10³), milli-(10⁻³), micro-(10⁻⁶), and nano-(10⁻⁹). If you need to weigh something on the analytical balance, you will need the amount in grams. If you need to do a chemical calculation, the amount will almost always need to be in moles. To convert from one form to the other, just remember that **the Gram Formula Weight (GFW) has units of grams/mole**

Example:

You are told to weigh out 0.40 millimoles of MgSO₄ to use in an EDTA titration. The GFW (found on the label of the reagent bottle) for the solid is 120.37 grams/mole. When solving problems, always write the units down.

$$0.40 \times 10^{-3} \text{ moles} \times \frac{120.37 \text{ grams}}{\text{mole}}$$

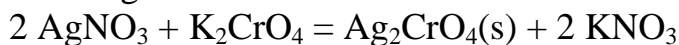
$$= 0.04815 \text{ grams}$$

Remember to check your calculation by cancelling out the units. To test yourself, convert the 0.04815 grams back into moles of magnesium sulfate.

Calculations involving chemical reactions:

First you must have a **balanced** chemical reaction. Precipitation, acid-base, and complex formation reactions can be balanced by inspection. Oxidation-Reduction reactions are best balanced by the half-reaction method. **All calculations are done with moles.** If you are given amounts in grams, convert to moles first. If you are asked for grams, do the calculation with moles, then convert back to grams at the end. The chemical reaction tells you how to convert from moles of one chemical to moles of another.

Example: How many grams of silver chromate can you get by complete precipitation of 0.1273 g of silver nitrate?



$$\begin{array}{ccccccc} 0.1273 \text{ g AgNO}_3 & \text{mole AgNO}_3 & 1 \text{ mole Ag}_2\text{CrO}_4 & 331.73 \text{ g Ag}_2\text{CrO}_4 & & & \\ & 169.87 \text{ g AgNO}_3 & 2 \text{ mole AgNO}_3 & \text{mole Ag}_2\text{CrO}_4 & & & \end{array}$$

$$= 0.1243 \text{ g Ag}_2\text{CrO}_4$$

Working with Concentrations

Concentration is a property of a mixture calculated by dividing one amount by another. Commonly used concentration units include moles/liter, milligrams/liter, milligrams/kilogram, nanograms/gram, and centigrams/gram. When expressed this way, the two amounts are clearly stated. To solve for any concentration, simply figure out Amount A, figure out Amount B, then

$$\text{Concentration} = \frac{\text{Amount A}}{\text{Amount B}}$$

Although current practice is to express all concentrations with the defining units, it is still common to refer to concentrations by name.

Name	Defining Units
Molarity (e.g. 0.1200 M)	moles of solute/liter (solutions), or millimoles/milliliter (solutions)
Percent (e.g. 23.45 %)	(grams of substance/grams of sample) x 100%, or centigrams/gram (seldom used)
Parts per million (e.g 2.34 ppm, 2.34 mg/L)	milligrams/liter (solutions), or micrograms/milliliter (solutions) milligrams/kilogram (solids), or micrograms/gram (solids)
Parts per billion (e.g. 0.45 ppb, 0.45 ug/L)	micrograms/liter (solutions), or nanograms/gram (solids)

Example 1: 25.00 mL of solution are found to contain 3.45×10^{-8} moles of fluoride ion. What is ppb F for this solution?

We need ug F/Liters to get parts per billion. First calculate "Amount A."

$$3.45 \times 10^{-8} \text{ moles F} \times \frac{18.9984 \text{ grams F}}{1 \text{ mole F}} \times \frac{10^6 \text{ micrograms}}{1 \text{ gram}}$$

$$= 0.6554 \text{ ug F}$$

Then divide by "Amount B." $0.6554 \text{ ug F} / 0.02500 \text{ liters} = 26.2 \text{ ug/L}$, or 26.2 ppb.

Example 2: Prepare 200 ml of 6 M ammonia solution from the 15.4 M reagent. This is often called a "dilution problem," but it can be solved from the basic definition of Molarity.

We need 200 ml of 6 M solution. We are told the volume, we need to calculate the amount of ammonia needed.

$$(6 \text{ moles ammonia/liter}) \times 0.20 \text{ liters} = 1.20 \text{ moles of ammonia.}$$

The source of the ammonia will be the 15.4 M solution. Again using the units:

$$1.20 \text{ moles ammonia} \times \frac{1 \text{ liter of reagent}}{15.4 \text{ moles ammonia}} \times \frac{1000 \text{ mL}}{1 \text{ liter}}$$

$$= 77.9 \text{ mL of 15.4 M ammonia reagent needed.}$$

Add 77.9 mL of 15.4 M ammonia reagent to 100 mL of water (for safety), then dilute to 200 mL total volume.

Practical lesson 12

Titrimetric analysis. Method of acid-base titration. Laboratory work "Determination of the working solutions exact concentration". Calculations based on the results of the titration. Test control.

CONTROL QUESTIONS FOR STUDENTS OUT-OF-CLASS WORK

1. Theoretical questions

The main principles of titrimetric methods of analysis. Basic concepts.

Classification of methods of titrimetric analysis based on the type of chemical reaction.

Requirements to the titrimetric reactions. Condition of titrimetric determinations

 Titrated (working) solutions, methods of its preparation. Expression of concentration of titrated solutions. Primary and secondary standards. Requirements to the primary standards.

 Calculations in a titrimetric analysis.

 Reactions which the method of acid-base titration based on and requirement to it.

 Bases of acidimetry and alkalimetry. Methods of preparation of titrated solutions of acids and bases, its standardization.

2 Test items for licensing examination Krok 1 PHARMACY

The correct answer is first

- 1) Choose the indicator and titration method to determine hydrogen carbonate ions in a drug:
 - A. Methyl-orange, acidimetry
 - B. Phenolphthalein, acidimetry
 - C. Methyl-orange, alkalimetry
 - D. Phenolphthalein, alkalimetry
 - E. Murexide, acidimetry
- 2) A medicament comprises sodium bicarbonate and sodium chloride. What method is used for quantitative determination of sodium bicarbonate?
 - A. Acid-base titration
 - B. Precipitation titration
 - C. Redox titration
 - D. Complexometric titration
 - E. Coulometric titration
- 3) Specify the standard substance for the standardization of 0,1 M of hydrochloric acid solution:
 - A. Sodium carbonate
 - B. Ammonium hydroxide
 - C. Oxalic acid
 - D. Sodium chloride
 - E. Zinc sulphate
- 4) What indicator is used for the quantitative determination of sodium carbonate in a preparation by the method of acidbase titration?
 - A. Methyl orange
 - B. Murexide
 - C. Methylene blue
 - D. Diphenylamine
 - E. Ferroin
- 5) Choose a pair of titrants for the qualitative determination of ammonia in a solution by the method of back titration:
 - A. HCl, NaOH
 - B. HCl, H₂SO₄

- C. KOH, NaOH
D. NaOH, KCl
E. H₂SO₄, K₂SO₄
- 6) What method of titrimetric analysis can be applied for the quantitative determination of sulphuric acid by means of the potassium hydroxide solution?
A. Alkalimetry
B. Acidimetry
C. Oxidation-reduction
D. Precipitation
E. Complexation
- 7) Choose a pair of titrants for the qualitative determination of ammonia in a solution by the method of back titration:
A. HCl, NaOH
B. HCl, H₂SO₄
C. KOH, NaOH
D. NaOH, KCl
E. H₂SO₄, K₂SO₄
- 8) What substance can be identified by method of acid-base titration and oxidation-reduction titration?
A. Oxalate acid
B. Sodium sulphate
C. Calcium nitrate
D. Sodium hydroxide
E. Ammonium chloride
- 9) Quantitative determination of pharmaceutical substances can be done by means of acidimetry. Its titrant is the secondary standard solution of hydrochloric acid. According to which compound the precise concentration of hydrochloric acid can be determined?
A. Sodium tetraborate
B. Oxalic acid
C. Potassium dichromate
D. Sodium thiosulfate
E. Magnesium sulphate
- 10) Specify the titration method, in which a standardized titrant solution is gradually added to the solution under study until a titration endpoint is reached:
A. Direct titration
B. Back titration
C. Indirect titration
D. Substitution titration
E. Residue titration
- 11) What method of titrimetric analysis can be applied for the quantitative determination of sulphuric acid by means of the potassium hydroxide solution?
A. Alkalimetry
B. Acidimetry

- C. Oxidation-reduction
 - D. Precipitation
 - E. Complexation
- 12) Quantitative determination of pharmaceutical substances can be carried out by method of alkalimetry using 0,1 M sodium hydroxide solution as a titrant. Precise concentration of sodium hydroxide can be determined according to:
- A. Oxalic acid
 - B. Sodium tetraborate
 - C. Potassium dichromate
 - D. Sodium thiosulphate
 - E. Ammonium hydroxide
- 13) A chemist in analytical laboratory needs to standardize solution of sodium hydroxide. What primary standard solution can be applied for this purpose?
- A. Oxalic acid
 - B. Acetate acid
 - C. Chloride acid
 - D. Sodium tetraborate
 - E. Sodium chloride
- 14) Quantitative determination of pharmaceutical substances can be done by means of acidimetry. Its titrant is the secondary standard solution of hydrochloric acid. According to which compound the precise concentration of hydrochloric acid can be determined?
- A. Sodium tetraborate
 - B. Oxalic acid
 - C. Potassium dichromate
 - D. Sodium thiosulfate
 - E. Magnesium sulfate
- 15) Name the pH value, under which occurs the most intense color change of an indicator:
- A. pT value
 - B. pK value
 - C. Color change interval
 - D. Equivalence point
 - E. Titration end point
- 16) Choose the indicator and titration method to determine hydrogen carbonate ions in a drug:
- A. Methyl-orange, acidimetry
 - B. Phenolphthalein, acidimetry
 - C. Methyl-orange, alkalimetry
 - D. Phenolphthalein, alkalimetry
 - E. Murexide, acidimetry

Laboratory work № 2-1
Preparation of the KOH solution

1. Theoretical part.

Solution of KOH is usually prepared by the method of diluting the more concentrated solution, which is prepared by dissolving KOH crystals in water. The density of KOH solution is determined using an aerometer. There is the correlation between density of solution and approximate mass percent or molarity of KOH (see table in an annex in the laboratory journal's end). So, based on law of dilution, it is possible to calculate the volume of KOH solution needed for preparation of the certain volume with the right molar concentration.

2. Procedure:

Pure the concentrated solution of KOH into the cylinder. Then, using the aerometer, measure the density of the solution. Find the value of molar concentration of this solution in the reference table.

By the formula: $c_1(\text{KOH}) \times V_1(\text{sol}) = c_2(\text{KOH}) \times V_2(\text{sol})$

calculate, which volume of KOH concentrated solution is needed to prepare 250 ml of KOH solution with $c(\text{KOH}) = 0,1 \text{ mol/l}$.

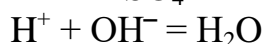
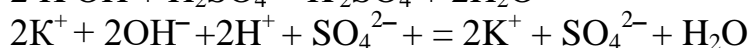
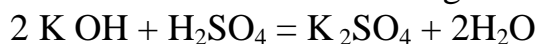
With the graduated cylinder transfer the calculated volume of KOH solution to the 250,0 ml volumetric flask. Then add the distilled water to the calibration mark and thoroughly mix.

Laboratory work № 2-2

Determination the correct molality of equivalent of KOH solution (normality)

1. Theoretical part

The reaction that occur during titration is:



End point break has the interval from 4,0 to 10, that's why we can use indicators, which has the transition interval (pH range) within the titration jump. For example phenolphthalein (transition interval = 8-10), methyl red (transition interval is within 4,2-6,2).

Preliminary Activities

1. Remember that the burettes are only as clean as they were left by the last user. Clean the burette thoroughly. If the stopcock shows brown stains, consult your teacher about cleaning the stopcock before proceeding.
2. Obtain the reagents in the amount you will need.
3. Rinse the burette with about 5 mL of the sodium hydroxide stock solution. Be sure to rinse the tip as well. Drain the burette. If the burette drains properly, fill it with the sodium hydroxide stock solution.
4. Before proceeding with either the standardization or the titration of the analyte, you should do the following to establish the appearance of the end point of the reaction.
5. Place about 25 mL of distilled water in an Erlenmeyer flask and add 4 drops of Phenolphthalein indicator solution. Deliver one drop of sodium hydroxide stock solution and swirl to insure complete mixing. Note the color of the solution.

Analysis of KOH solution.

1. Measure exactly 10.0 mL of the sulphuric acid solution into a 250 mL beaker flask. Add approximately 25 mL of distilled water to the flask
2. Add 4 drops of Phenolphthalein indicator solution.
3. Titrate using the KOH prepared solution. At the end point the color should change from colorless to light pink.
4. Repeat this procedure at least three times.
5. Tabulate the data for the sample analyses.
6. Use this data to calculate the normality of KOH solution in mol/L.

Evaluation

1. Determine the volumes of titrant obtained from a titration and put them in the table below.

2. Calculate the average volume of titrant delivered in the titration

$$V_{av.} = \frac{V_1 + V_2 + V_3}{3} \text{ mL} = \frac{\quad + \quad + \quad}{3} = \quad \text{mL}$$

3. Convert 10.0 mL of sulfuric acid solution $V(\text{H}_2\text{SO}_4)$ and $V_{av.}$ in mL of KOH solution into liters dividing by 1000:

$$1 \text{ L} = 1000 \text{ mL} = 1 \cdot 10^{-3} \text{ mL}$$

$$V(\text{H}_2\text{SO}_4) \text{ mL} \cdot 1 \text{ L} / 1000 \text{ ml} = 10 \cdot 10^{-3} \text{ L}$$

$$V_{av.}(\text{KOH}) \text{ mL} \cdot 1 \text{ L} / 1000 \text{ ml} = V_{av.}(\text{KOH}) \text{ ml} \cdot 10^{-3} \text{ L} = \quad \cdot 10^{-3} \text{ L}$$

4. Calculate the normality of KOH solution using formula:

$$c(\text{KOH}) = \frac{c(\frac{1}{2} \text{H}_2\text{SO}_4) \cdot V(\text{H}_2\text{SO}_4)}{V(\text{KOH})} = \frac{\quad \cdot \quad}{\quad} = \quad =$$

$$= \quad \text{mol/L}$$

Evaluation table

$$c(\text{H}_2\text{SO}_4) = \dots\dots\dots V(\text{H}_2\text{SO}_4) = \dots\dots\dots$$

Nº	V(KOH), ml	V _{av.} KOH, ml	C(KOH), mol/l
1			
2			
3			

Conclusions: normality of KOH solution is _____ mol/L

Practical lesson 13

Quantitative determination of the method of neutralization. Laboratory work "Determination of the hydrochloric acid's content in the drugs". Solution of problems and situational tasks. Test control.

CONTROL QUESTIONS FOR STUDENTS OUT-OF-CLASS WORK

1. Theoretical questions

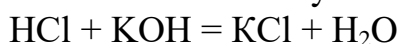
1. Possibilities of acid-basic titration.
2. End-point of titration. Titration curves.
3. Theory of acid-basic indicators. Interval of transition of acid-basic indicator, index of titration (pT). Methods of indicators choosing.
4. Methods of titration (direct titration, back titration, substitutive titration).
5. Ways of implementation of titration (an aliquot part and mass of sample).
6. Calculation based on results of titrimetric analysis

Laboratory work №3

Determination of the HCl contents in the pharmaceutical drug.

1. Theoretical part

Acetic acid is usually titrated by the NaOH or KOH standart solution:



This solution at the equivalent point is neutral (pH= 7). End point break observes at pH 4 – 10. According to the indicator's selection rules we should take an acid-base indicator with the transition pH range being within the limits of the end point break. In this situation phenolphthalein or methyl red corresponds to the conditions.

Procedure:

1. Fill the burette by KOH standard solution.
2. Into three conical flasks with a glass stopper add 20 ml of distilled water and accurately weigh each of them. Write down data in the table 1.
3. Open the flasks and add into each of them 1.5 ml sample solution of hydrochloric acid. Close the flasks by glass stopper and weigh each of them. Write down data in the table 1.
4. Add 2-3 drops of Phenolphthalein solution into this beaker.
5. Add drop by drop of titrant from burette to the acid solution in the beaker until the indicator's color changes light pink color.
6. Repeat titration 2-3 times and determine average significance of volume of standard solution.

7. Write down data in the table.

8. Calculate molarity of the hydrochloric acid (HCl) solution using the next formula:

$$c(\text{HCl}) = \frac{c(\text{KOH}) V(\text{average})(\text{KOH})}{V(\text{HCl})}, \text{ mol/L}$$

2. Results and calculations.

Calculate the mass of solution contains HCl :

$$m(\text{solution of HCl}) = m(\text{flask with H}_2\text{O} + \text{HCl}) - m(\text{flask with H}_2\text{O}).$$

$$m_1(\text{solution of HCl}) =$$

$$m_2(\text{solution of HCl}) =$$

$$m_3(\text{solution of HCl}) =$$

Calculate the mass of HCl :

$$m(\text{HCl}) = c(\text{KOH}) \cdot \frac{V(\text{KOH})}{1000} \cdot M(\text{HCl})$$

3.

$$m_1(\text{HCl}) =$$

$$m_2(\text{HCl}) =$$

$$m_3(\text{HCl}) =$$

Mass percent of HCl in the solution analyzed:

$$\omega(\text{HCl}) = \frac{m(\text{HCl})}{m(\text{p - ny})} \cdot 100\%$$

4.

$$\omega_1(\text{HCl}) =$$

$$\omega_2(\text{HCl}) =$$

$$\omega_3(\text{HCl}) =$$

Calculate average value of $\omega(\text{HCl})$:

$$\omega_{\text{серед.}}(\text{HCl}) = \frac{\omega_1(\text{HCl}) + \omega_2(\text{HCl}) + \omega_3(\text{HCl})}{3} =$$

5.

Evaluation table

N	m(flask with H ₂ O)	m(flask with H ₂ O + HCl)	m(solution of HCl)	V(KOH)	m(HCl)	$\omega(\text{HCl})$	$\omega_{\text{av}}(\text{HCl})$
1							
2							
3							

Practical lesson 14

Calculations based on the results of the titration of separate portions and the titration of aliquots. Solution of problems. Laboratory work “Determination of the acetic acid’s content in the vinegar”. Situational tasks.

CONTROL QUESTIONS FOR STUDENTS OUT-OF-CLASS WORK

1. Theoretical questions

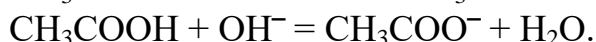
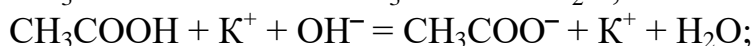
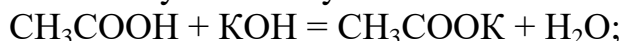
1. Direct and back titration, cases of their application.
8. Determination of hydrolysed salts by the acid-base titration method.
9. Determination of acids (bases) mixtures by the acid-base titration method.

Laboratory work №4

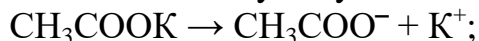
“Determination of the acetic acid’s content in the vinegar”

Theoretical part

Acetic acid is usually titrated by the NaOH or KOH standart solution:



At the equivalent point the solution will contain the CH_3COOK reaction product. This is the salt, which is formed by the cation from the strong base and the anion from the weak acid. This salt hydrolyzes according to the next equation:



This solution in the equivalent point will have the alkaline reaction ($\text{pH} > 7$). End point break remains also in the alkaline range. According to the indicator’s selection rules we should take an acid-base indicator with the transition pH range being within the limits of the end point break. In this situation phenolphthalein corresponds to the conditions.

The calculation shows us, that it is impossible to perform the titration of the acetic acid with its mass fraction of approximately 9% without an extra dilution. First of all we should dilute the solution of acetic acid. We dilute initial CH_3COOH solution so there will be no more than 25 ml and no less than 10 ml of KOH titrant spend for the titration of 10 ml diluted CH_3COOH solution (for example: 20 ml). In the quantitative analysis volumetric flasks and certain pipets are used.

One of the optional versions to perform such calculation

1. We determinate, what mass of CH_3COOH can react, if for the titration there were used approximately 20 ml of KOH solution;

$$c(\text{KOH}) = 0,1 \text{ mol/l}; \quad m(\text{CH}_3\text{COOH}) = c(\text{KOH}) \cdot V(\text{KOH}) \cdot M(\text{CH}_3\text{COOH});$$

$$m(\text{CH}_3\text{COOH}) = 0,1 \text{ mol/l} \cdot 20 \cdot 10^{-3} \text{ l} \cdot 60,052 \text{ g/mol} = 0,1201 \text{ g};$$

2. With the help of one of the known methods we determinate, which volumetric flask and pipet should be used to dilute 9% CH_3COOH solution the way 10ml of this

diluted solution will contain $\approx 0,12\text{g}$ of CH_3COOH . The solution density is $1\text{g}/\text{cm}^3$, so 1g of this solution takes up the space as 1ml does.

The optimal variant of the dilution is to:

dilute 10ml of acetum with the distilled water in the 100ml volumetric flask or 20ml of acetum with the distilled water in the 200ml volumetric flask;
for each titration pipet 10ml of the prepared solution.

1. Procedure:

Using the pipet transfer to the 200ml volumetric flask 20ml of acetum ($m(\text{sol}) = 20\text{g}$), add distilled water to the line on flask and mix.

Using the 10ml pipet, that was washed out beforehand with the distilled water and prepared in the volumetric flask CH_3COOH solution, transfer to the beaker flask 10ml of the diluted solution; then add 2-3 drops of the phenolphthalein and; titrate with the KOH process solution until the faint pink colour appears. Repeat titration for 3 times. For calculations use the average volume of KOH solution of three titrations.

2. Results and calculations.

Write down the numerical value of the titrants concentration $c(\text{KOH})$ and the results of the titration:

$c(\text{KOH}) =$ _____ mol/l

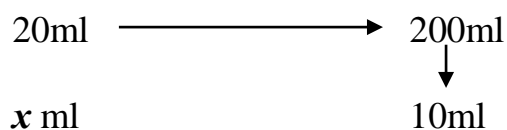
$v_1(\text{KOH}) =$	$V_{\text{average}}(\text{KOH}) =$
$v_2(\text{KOH}) =$	
$v_3(\text{KOH}) =$	

By the value of the $V_{\text{average}}(\text{KOH})$ calculate the mass of CH_3COOH in the probe, that has been titrated:

$$m(\text{CH}_3\text{COOH}) = c(\text{KOH}) \times v_{\text{average}}(\text{KOH}) \times M(\text{CH}_3\text{COOH}).$$

$m(\text{CH}_3\text{COOH}) =$ _____.

Then make the dilution schema of the acetum analyte solution:



By this dilution schema calculate how many ml of this acetum solution as a result of dilution were transferred into the aliquot probe for the titration:

$$x = \frac{20 \times 10}{200} = 1\text{ml}.$$

So, in the titration probe there is only 1ml of the acetum solution, which density is $1\text{g}/\text{ml}$. That's why the acetum analyte mass $m(\text{sol}) = 1\text{g}$.

By the findings (the $m(\text{CH}_3\text{COOH})$ and $m(\text{sol}) = 1\text{g}$) calculate the mass fraction of CH_3COOH in the acetum.

$$\omega(\text{CH}_3\text{COOH}) = \frac{m(\text{CH}_3\text{COOH})}{m(\text{p} - \text{ny})} \cdot 100\% = \text{_____} \cdot 100\% =$$

Practical lesson 15

Calculation of the optimal sample analyte for titration based on separate portions or aliquots. Practical skills. Test control based on test Krok 1, topic "Method of acid-base titration".

CONTROL QUESTIONS FOR STUDENTS OUT-OF-CLASS WORK

1. Theoretical questions

- 1) Classification of titrimetric methods of analysis.
- 2) Requirements to the reactions in the titrimetric methods of analysis.
- 3) Titrants (standard solutions), methods of their preparation.
- 4) Methods of expression of concentration of titrants: molarity, molarity of equivalent, titer.
- 5) Methods (direct, reverse, substitution) and methods (separate sample and pipet) of titration.
- 6) Point of equivalence, end point of titration. Methods of end point determination.
- 7) Measuring of volumes. Calibration of the measured tableware.
- 8) Calculations are in titrimetric methods.
- 9) Formulas for a calculation.
- 10) Errors are in a quantitative analysis.
- 11) Statistical treatment of results of analysis.
- 12) Influence of nature of solvent is on acid-basic properties of analytes. Classification of non-aqueous solvents.
- 13) Titrants of method of acid-basic titration. Preparation and standardization of solutions of acids and bases. Primary and secondary standards of acidimetry and alkalimetry.
- 14) pH-indicators, interval of transition of indicator. .
- 15) Principle of construction of curves of titration.
- 16) Character of curves of titration of different acids and bases (strong, weak, polybasic). A choice of indicator based on the curves of titration.
- 17) Indicatory errors.
- 18) Application of method of acid-basic titration.

Practical lesson 16

Methods of Redox titration. The method of permanganometry. Determination of KMnO_4 molarity. Problem solving and situational tasks. Test control.

CONTROL QUESTIONS FOR STUDENTS OUT-OF-CLASS WORK

1. The content of the methods of oxidation-reduction titration, their classification.
2. Requirements to redox reactions, which are in the basis of the methods of oxidation-reduction titration.
3. Methods of indication of the end-point of titration in the methods of oxidation-reduction titration. External, internal, mixed indicators.

4. The ways of oxidation-reduction titration (direct, back, substitution). Give the examples and explain them.
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 potassium permanganate solution.
7. What standard substances are used for standardization of potassium permanganate solution? The content 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 permanganometry for creating the acid medium of the solution?

These questions are taken from the Test items for licensing examination Krok 1 PHARMACY

The correct answer is first

- 1) Specify the titration method, in which a standardized titrant solution is gradually added to the solution under study until a titration endpoint is reached:
 - A. Direct titration
 - B. Back titration
 - C. Indirect titration
 - D. Substitution titration
 - E. Residue titration
- 2) Specify the standard solutions that are used in permanganometry to quantify the oxidants by the residual titration method:
 - A. Potassium permanganate, iron (II) sulfate
 - B. Potassium dichromate, sodium thiosulfate
 - C. Potassium bromate, sodium thiosulfate
 - D. Potassium iodate, sodium thiosulfate
 - E. Cerium (IV) sulfate, iron (II) sulfate
- 3) Permanganometric titration of hydrogen peroxide is carried out in the following medium:
 - A. Sulfate
 - B. Alkaline
 - C. Nitrate
 - D. Hydrochloric
 - E. Alcohol
- 4) Which indicatorless method enables quantitative determination of iron (II) content?
 - A. Permanganometry
 - B. Chelatometry

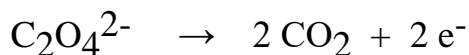
- C. Argentometry
D. Iodometry
E. Nitritometry
- 5) Choose a pair of substances that can be used for standardization of 0,1 M solution of KMnO_4 :
- A. $\text{Na}_2\text{C}_2\text{O}_4$, $\text{H}_2\text{C}_2\text{O}_4$
B. K_2CO_3 , CH_3COOH
C. CH_3COOK , $\text{H}_2\text{C}_2\text{O}_4$
D. KHC_2O_4 , HCOOH
E. $\text{Na}_2\text{C}_2\text{O}_4$, CH_3COOH
- 6) Permanganatometry enables determination of H_2O_2 in high-acidity medium. What acid can be used for production of such medium?
- A. H_2SO_4
B. HCl
C. HNO_3
D. CH_3COOH
E. H_3PO_4
- 7) Potassium permanganate reacting with hydrogen peroxide in acidic medium acts as:
- A. Oxidant
B. Reductant
C. Disproportionation agent
D. Oxidant and reductant
E. Does not act either as an oxidant, or as a reductant
- 8) 0,1 M solution of potassium permanganate is used as a titrant in permanganatometry. The solution is prepared like the secondary standard solution and standardized according to:
- A. Ammonia oxide
B. Potassium dichromate
C. Sodium chloride
D. Sodium carbonate
E. Calcium oxide
- 9) Quantitative content of iron (II) can be determined by non-indicator method of:
- A. Permanganatometry
B. Chelatometry
C. Argentometry
D. Iodometry
E. Nitritometry
- 10) Permanganatometric determination of H_2O_2 can be done in a very acid medium. What acid allows to produce medium for permanganatometric determination?
- A. H_2SO_4
B. HCl
C. HNO_3

- D. CH₃COOH
E. H₃PO₄
- 11) Specify the standard solutions that are used in permanganatometry to quantify the oxidants by means of back titration:
- A. Potassium permanganate, iron (II) sulfate
B. Potassium dichromate, sodium thiosulfate
C. Potassium bromate, sodium thiosulfate
D. Potassium iodate, sodium thiosulfate
E. Cerium (IV) sulfate, iron (II) sulfate
- 12) What substance can be identified by method of acid-base titration and oxidation-reduction titration?
- A. Oxalate acid
B. Sodium sulphate
C. Calcium nitrate
D. Sodium hydroxide
E. Ammonium chloride

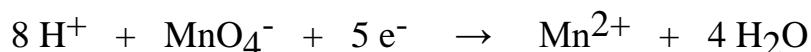
Laboratory work № 4
Standartization of the KMnO₄ solution

The technique of titration has been used previously in acid-base reactions to detect the amount of acid using a known base (or the reverse). It can also be used in situations in which the reaction involves oxidation and reduction.

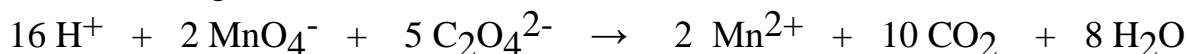
Oxidation is defined as the loss of electrons (on right of arrow) or increase in oxidation state (each C changes from +3 to +4) as shown below by the half-reaction involving oxalate ion.



Reduction is shown by the permanganate ion as it gains electrons and Mn decreases in oxidation state from +7 to +2.



Oxidation and reduction must occur together and are often designated as **redox** standartes to emphasize this; the number of electrons lost by one substance must equal the number of electrons gained by the other substance. If we combine the two half-reactions above, we would end with a **balanced net ionic equation** if we have a total of 10 electrons exchanged.



Because the materials we weigh and measure occur as compounds, it is often useful to have the **balanced molecular equation** (sometimes called the balanced total equation).



Potassium permanganate is reduced because it contains the permanganate ion; we can also say that it behaves as an oxidizing agent because it causes something else to

become oxidized (the oxalate). Sodium oxalate is oxidized because it has the oxalate ion and we could also specify it as the reducing agent because it causes the permanganate to become reduced. It can also be seen from both the net ionic equation or molecular equation that acid is required for this reaction to occur; i.e., H^+ or H_2SO_4 show up in the balanced equations. We also know from the previous experience that a temperature higher than room temperature makes a reaction more rapid.

Preliminary Activities

1. Remember that the burettes are only as clean as the last user left them.
2. Clean the burette thoroughly.
3. If the stopcock shows brown stains, consult your teacher about cleaning the stopcock before proceeding.
4. Obtain the reagents in the amount you will need.
5. Rinse twice with about 10-mL of your $KMnO_4$ solution (discard the rinsings in the container in the hood)
6. Fill the burette with the $KMnO_4$ solution, making sure that the tip contains no air bubbles.
7. Before proceeding with either the standardization or the titration of the hydrogen peroxide, you should do the following to establish the appearance of the end point of the reaction:
 - a) Place 5 mL of 4 M sulfuric acid using a graduated cylinder in an Erlenmeyer flask and add about 50 mL of distilled water.
 - b) Deliver one drop of the stock solution of $KMnO_4$ to the solution and swirl to insure complete mixing.
 - c) Note the color of the solution: _____.

Standardization of $KMnO_4$ solution

A **standard solution of $H_2C_2O_4$ 0.050 M** is on the reagent table. Record this concentration of this solution on your REPORT FORM (7)

1. Pipet **10.00 mL of the standard $H_2C_2O_4$** solution into each of three 125 (or 250) mL Erlenmeyer flasks. Record this volume on the REPORT FORM
2. SLOWLY and CAREFULLY add 5ml of H_2SO_4 solution ($\omega(H_2SO_4) = 10\%$) to each flask with vigorous stirring.
3. Heat the solution in one flask to 50-60° C. (DO NOT BOIL! Because $H_2C_2O_4$ starts to partially dissociate:



4. Record on your REPORT FORM the buret reading at the beginning of the standardization process to the nearest 0.01 mL. Because the $KMnO_4$ is opaque, the buret is read at the *top* of the meniscus.
5. Begin titrating this hot solution by adding the $KMnO_4$ solution from the buret very slowly at first. (NOTE: If the solution is added too rapidly, brown MnO_2 forms, the solution looks muddy, and the titration is ruined.)

- After a few mL of KMnO_4 solution have been added, the rate of addition can be increased. (NOTE: The reaction between KMnO_4 and $\text{H}_2\text{C}_2\text{O}_4$ is catalyzed by the ion Mn^{2+} which is produced.)
- When you think you have reached the endpoint, read the buret to the nearest 0.01 mL. (NOTE: As the end point is approached the KMnO_4 is so intensely colored that it serves as its own indicator. The endpoint is the point at which a faint pink coloration persists throughout the stirred solution for at least thirty seconds.)
- Add one more drop of KMnO_4 . An intense pink coloration tells you that you have exceeded the amount of KMnO_4 needed to oxidize the amount of $\text{H}_2\text{C}_2\text{O}_4$
- Calculate the volume of the KMnO_4 solution used.
- Repeat Steps 1-9 on the other $\text{H}_2\text{C}_2\text{O}_4$ samples. You should have at least two values for volume of that agree within ± 2 in the third significant digit.
- Calculate the molarity of solution using Equation 3 and the average molarity of the solution. Record these values on the REPORT FORM

Partial decomposition of the permanganate to MnO_2 may occur if it remains in the buret for a long time. Clean the buret with a dilute sodium bisulfite solution.

Evaluation

- Calculate the average volume of titrant delivered in the titration

$$V_{av.} = \frac{V_1 + V_2 + V_3}{3} \text{ mL} = \frac{\quad + \quad + \quad}{3} = \quad \text{mL}$$

- Convert 10.0 mL of the sample $V(\text{H}_2\text{C}_2\text{O}_4)$ and $V_{av.}$ in mL of KMnO_4 solution to liters by dividing by 1000:

$$1 \text{ L} = 1000 \text{ mL} = 1 \cdot 10^{-3} \text{ mL}$$

$$V(\text{H}_2\text{O}_2) \text{ mL} \cdot 1 \text{ L} / 1000 \text{ ml} = 10 \cdot 10^{-3} \text{ L}$$

$$V_{av}(\text{KMnO}_4) \text{ mL} \cdot 1 \text{ L} / 1000 \text{ ml} = V_{av}(\text{KMnO}_4) \text{ ml} \cdot 10^{-3} \text{ L} = \quad \cdot 10^{-3} \text{ L}$$

- Calculate the molarity of equivalent of KMnO_4 using formula:

$$c\left(\frac{1}{2} \text{H}_2\text{C}_2\text{O}_4\right) \cdot V(\text{H}_2\text{C}_2\text{O}_4) = c\left(\frac{1}{5} \text{KMnO}_4\right) \cdot V_{av.}(\text{KMnO}_4)$$

$$c\left(\frac{1}{5} \text{KMnO}_4\right) = \frac{c\left(\frac{1}{2} \text{H}_2\text{C}_2\text{O}_4\right) \cdot V(\text{H}_2\text{C}_2\text{O}_4)}{V_{av.}(\text{KMnO}_4)}$$

$$c_{\frac{1}{5} \text{KMnO}_4} = \frac{\quad}{\quad} = \quad \text{mol/l.}$$

Evaluation table.

$$c(\text{H}_2\text{C}_2\text{O}_4) = \dots \text{mol/l.}$$

$$V(\text{H}_2\text{C}_2\text{O}_4) \dots \text{ml}$$

№	V(KMnO ₄), ml			V(KMnO ₄), ml	c _{1/5} KMnO ₄ mol/l
	initial	final	used	average	

1				}	
2					
3					

Practical lesson 17

The method of permanganatometry. Determination of H₂O₂ content in the sample. Bromo- and bromatometry. Nitritometry. Test control.

CONTROL QUESTIONS FOR STUDENTS OUT-OF-CLASS WORK

- 1) Application of permanganatometry in analysis of medicines.
- 2) What method should be used for the determination of H₂O₂ content?
- 3) What standard solution and indicator are used for titrimetric determination of H₂O₂ content? How can the equivalence point be fixed?
- 4) Write the formulas are used for calculation of normality (molarity of equivalent $c^{(1/z)}$) and mass of the H₂O₂ according to titrimetric data.
- 5) What laboratory glassware should be used and how it should be prepared?
- 6) The content of bromatometric determinations of organic and inorganic compounds.
- 7) The titrant of bromatometry, its preparation and properties. Determination of the end-point of titration in bromatometry. Application of bromatometric method in analysis.
- 8) The content of the nitritometric method of analysis. Factors, which influence on completeness and speed of the diazotization reaction.
- 9) Preparation of the titrant in nitritometry and its standardization. Determination of the end-point of titration in nitritometry. Application of external, internal and mixed indicators.
- 10) Application of nitritometry in analysis.

These questions are taken from the Test items for licensing examination Krok 1 PHARMACY

The correct answer is first

- 1) Specify the titration method, in which a standardized titrant solution is gradually added to the solution under study until a titration endpoint is reached:
 - A. Direct titration
 - B. Back titration
 - C. Indirect titration
 - D. Substitution titration
 - E. Residue titration

- 2) Permanganometric titration of hydrogen peroxide is carried out in the following medium:
- A. Sulfate
 - B. Alkaline
 - C. Nitrate
 - D. Hydrochloric
 - E. Alcohol
- 3) Which indicatorless method enables quantitative determination of iron (II) content?
- A. Permanganometry
 - B. Chelatometry
 - C. Argentometry
 - D. Iodometry
 - E. Nitritometry
- 4) Potassium permanganate reacting with hydrogen peroxide in acidic medium acts as:
- A. Oxidant
 - B. Reductant
 - C. Disproportionation agent
 - D. Oxidant and reductant
 - E. Does not act either as an oxidant, or as a reductant
- 5) Permanganometric determination of H_2O_2 can be done in a very acid medium. What acid allows to produce medium for permanganometric determination?
- A. H_2SO_4
 - B. HCl
 - C. HNO_3
 - D. CH_3COOH
 - E. H_3PO_4
- 6) It is required to determine amount of sodium salicylate in a solution. What titrimetric method can be applied for the quantitative determination of aromatic compounds?
- A. Bromometry
 - B. Mercurimetry
 - C. Cerimetry
 - D. Argentometry
 - E. Chelatometry
- 7) Nitritometric determination of compounds containing primary aromatic amino group can be carried out under the following conditions:
- A. With observation of all the mentioned conditions
 - B. At a temperature up to 10°C
 - C. With adding of the crystalline KBr (catalyst)
 - D. Chloric acid excess
 - E. Slow titration

- 8) Sulfanilamide drugs contain primary aromatic amides in their structure. Specify the method of quantitative determination of these compounds:
- A. Nitritometry
 - B. Iodometry
 - C. Dichromatometry
 - D. Permanganatometry
 - E. Cerimetry
- 9) What titrant is used in bromatometry?
- A. KBrO_3
 - B. KBr
 - C. Br_2
 - D. $\text{KBrO}_4 + \text{KCl}$
 - E. KBrO_4
- 10) Dispensing chemist conducts quantitative determination of pharmaceutical substance with restorative properties through direct bromate titration. What solution is the titrant?
- A. Potassium bromate
 - B. Iodine solution in potassium iodide
 - C. Sodium thiosulfate
 - D. Potassium iodide
 - E. Chloride acid
- 11) Both external and internal indicators are used in the following titrimetric method of analysis
- A. Nitritometry
 - B. Alkalimetry
 - C. Chelatometry
 - D. Permanganatometry
 - E. Argentometry
- 12) Nitritometric determination of compounds containing primary aromatic amino group can be carried out under the following conditions:
- A. With observation of all the mentioned conditions
 - B. At a temperature up to 10°C
 - C. With adding of the crystalline KBr (catalyst)
 - D. Chloric acid excess
 - E. Slow titration
- 13) Specify the relevant indicators for fixation of the titration endpoint when using nitritometric method:
- A. Tropaeolin 00 + methylene blue
 - B. Methylene blue
 - C. Methylene orange
 - D. Starch solution
 - E. Diphenylamine
- 14) Choose an appropriate indicator for fixation of titration end point in method of bromatometry:

- A. Methyl red
 - B. Phenolphthalein
 - C. Starch
 - D. Methyl blue
 - E. Tropeolin 00
- 15) Sulfanilamide drugs contain primary aromatic amides in their structure. Specify the method of quantitative determination of these compounds:
- A. Nitritometry
 - B. Iodometry
 - C. Dichromatometry
 - D. Permanganatometry
 - E. Cerimetry
- 16) Direct titration CANNOT be applied for quantitative determination of calcium chloride by means of permanganatometry, because:
- A. The investigated substance does not interact with the titrant
 - B. The reaction runs very quickly
 - C. It is impossible to select the indicator to determine titration end point
 - D. Side reactions are possible
 - E. The reaction runs slowly

Laboratory work N 5

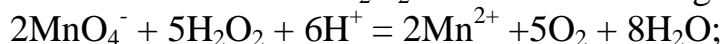
Determination of the hydrogen peroxide mass percent in the sample

Purpose: To use a volumetric titration method to determine content of H₂O₂ in the sample based on redox reaction.

Background:

The most common use of titration is for measuring unknown concentrations. This is done by titration a known volume of the unknown solution with a solution of known concentration (where the two react in a predictable manner) and finding the volume of titrant needed to reach the equivalence point using some method appropriate to the particular reaction. Then, the volume and concentration of titrant can be used to calculate the moles of titrant added, which, when used with the reaction stoichiometry, gives the number of moles of substance being titrated. Finally, this quantity, along with the volume of substance being titrated, gives the unknown concentration.

The content of H₂O₂ is determined using KMnO₄ as titrant in acidic solution:



No indicator is needed – excess reagent produces a pink solution.

Reagents and Equipment

H ₂ O ₂ sample solution	Burette
KMnO ₄ standard solution	5 mL pipett
10 mL pipette	
Distilled water	250 mL beaker flask

Analysis of the H₂O₂ in the sample.

1. Transfer 10ml of H₂O₂ sample using a pipet into the 500ml volumetric flask.

2. Add water to the 500-mL line and mix.
3. Pipet 10ml of the H₂O₂ prepared solution and transfer to a Erlenmeyer flask;
4. Add 5 mL of 4 M sulfuric acid using a graduated cylinder in an Erlenmeyer flask;
5. Titrate with potassium permanganate till a very faint pink solution appears. In this case, no heating of the solution is required.

REPEAT ABOVE PROCEDURE (Steps 3-5 above) TWICE MORE. If the volumes of KMnO₄ you use in these titrations have a percent deviation larger than 2%, repeat the titration. Note that each titration is performed on the same volume of hydrogen peroxide solution. Therefore, if the concentration of the hydrogen peroxide solution is uniform and the pipette has been used properly, the volume of potassium permanganate required should be the same in each titration.

Evaluation

4. Determine the **volumes of titrant delivered in a titration** and enter them in the table below.

5. Calculate the average volume of titrant delivered in the titration

$$V_{av.} = \frac{V_1 + V_2 + V_3}{3} \text{ mL} = \frac{\quad + \quad + \quad}{3} = \quad \text{mL}$$

6. Convert 10.0 mL of the sample V(H₂O₂) and V_{av.} in mL of KMnO₄ solution to liters by dividing by 1000:

$$1 \text{ L} = 1000 \text{ mL} = 1 \cdot 10^{-3} \text{ mL}$$

$$V(\text{H}_2\text{O}_2) \text{ mL} \cdot 1 \text{ L} / 1000 \text{ ml} = 10 \cdot 10^{-3} \text{ L}$$

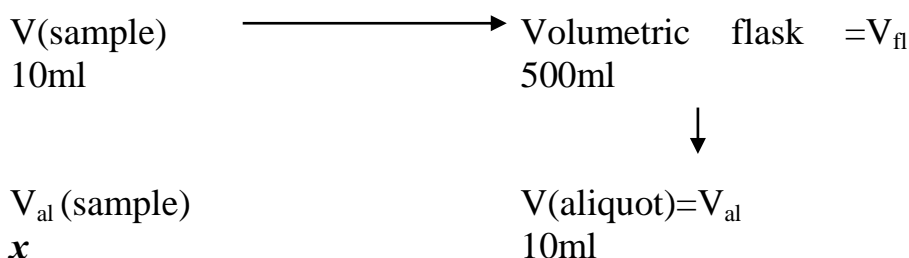
$$V_{av.}(\text{KMnO}_4) \text{ mL} \cdot 1 \text{ L} / 1000 \text{ ml} = V_{av.}(\text{KMnO}_4) \text{ mL} \cdot 10^{-3} \text{ L} = \quad \cdot 10^{-3} \text{ L}$$

7. Calculate the mass of H₂O₂ in the aliquot using formula:

$$m_{al}(\text{H}_2\text{O}_2) = C\left(\frac{1}{2} \text{KMnO}_4\right) \cdot V(\text{KMnO}_4) \cdot M\left(\frac{1}{2} \text{H}_2\text{O}_2\right) = \frac{\quad \cdot \quad \cdot \quad}{2} =$$

$$= \quad \text{g}$$

8. Make a schema of dilution and calculate the volume of the sample in aliquot V_{al} (sample)



$$x = \frac{10 \cdot 10}{500} = 0,2 \text{ ml}.$$

9. Calculate the mass of the sample in aliquot (m_{al}(sample)). For a first approximation we should take the density of the initial solution as 1g/ml, so m_{al}(sample) = 0,2g.

10. Using the following formula, calculate the mass percent of H₂O₂ in the sample:

$$\omega(\text{H}_2\text{O}_2) = \frac{m_{al}(\text{H}_2\text{O}_2)}{m_{al}(\text{sample})} \times 100\% =$$

Evaluation table.Molarity of KMnO_4 solution _____ mol/LVolume of the H_2O_2 sample _____ mL **KMnO_4 titration of H_2O_2 sample**

KMnO_4 volume	KMnO_4 volume	average	$m(\text{H}_2\text{O}_2)$	$\omega(\text{H}_2\text{O}_2)$
--	--	----------------	---	--

Trial 1 _____ mL

Trial 2 _____ mL _____ mL _____ g _____ %

Trial 3 _____ mL

ConclusionsMass percent of H_2O_2 in analyzed sample is _____**Practical lesson 18**

Iodometric methods of oxidants determination. Determination of titrant (solution of the sodium thiosulfate) molarity and mass percent of "activ" chlorine in chloramine.

CONTROL QUESTIONS FOR STUDENTS OUT-OF-CLASS WORK

1. The content of the iodometric method of analysis, its potentialities.
2. The titrants of the iodometric method, their preparation and standardization.
3. The ways of iodometric titration. Iodometric determination of strong oxidants.
4. 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.
5. The conditions of iodometric determinations. Give the examples of the necessary reaction equations.
6. The content of the method of iodochlorimetry. The reactions, which are in the basis of determinations, potentialities of the method.
7. The advantages of iodochlorimetry in comparison with the iodometric method of analysis. Determination of the equivalence point in iodochlorimetry. Preparation and standardization of the titrant in iodochlorimetry. Standard substances and standard solutions.
8. Determination of reducers by the iodochlorimetric method, examples of determinations.
9. Determination of oxidants by the iodochlorimetric method, examples of determinations.

*These questions are taken from the Test items for licensing examination Krok 1
PHARMACY*

The correct answer is first

- 1) The mass percentage of ascorbic acid can be determined by the cerimetric analysis in the presence of the following redox indicator:
 - A. Ferroin
 - B. Methylene red
 - C. Eosin
 - D. Fluorescein
 - E. Methylene orange
 - E. Chelatometry
- 2) Content of potassium dichromate in a solution was determined by iodometric method. Name the titrant of iodometric method for oxidant determination:
 - A. Sodium thiosulfate
 - B. Sodium hydroxide
 - C. Potassium iodide
 - D. Potassium permanganate
 - E. Potassium bromate
- 3) Quantitative determination of iodide can be done by method of:
 - A. Oxidation-reduction titration
 - B. Acid-base titration
 - C. Chelatometry
 - D. Spectrophotometry
 - E. Precipitating titration
- 4) What substance can be identified by method of acid-base titration and oxidation-reduction titration?
 - A. Oxalate acid
 - B. Sodium sulphate
 - C. Calcium nitrate
 - D. Sodium hydroxide
 - E. Ammonium chloride
- 5) Specify the standardized solutions used for direct and back titration of reducing agents in the iodometric method:
 - A. I_2 , $Na_2S_2O_3$
 - B. $K_2Cr_2O_7$, $Na_2S_2O_3$
 - C. I_2 , KI
 - D. $KMnO_4$, KI
 - E. $K_2Cr_2O_7$, I_2
- 6) When determining oxidizing agents by means of iodometry in the presence of starch the following phenomenon can be observed at the titration end point:
 - A. Blue coloring disappears
 - B. Red coloring appears
 - C. Green coloring of precipitate appears

- D. Green coloring of solution disappears
E. White precipitate occurs
- 7) Specify the standard solution (titrant) for the iodometric determination of oxidants:
- A. $\text{Na}_2\text{S}_2\text{O}_3$
 - B. KMnO_4
 - C. I_2
 - D. $\text{K}_2\text{Cr}_2\text{O}_7$
 - E. KBrO_3
- 8) Specify the standard solution for the iodometric determination of reducing agents (direct titration):
- A. I_2
 - B. KMnO_4
 - C. $\text{Na}_2\text{S}_2\text{O}_3$
 - D. $\text{K}_2\text{Cr}_2\text{O}_7$
 - E. KI
- 9) Iodometric determination of formaldehyde in formaline can be done by the back titration. Iodine surplus is titrated with the standard solution of:
- A. Sodium thiosulphate
 - B. Sodium nitrate
 - C. Sodium sulphate
 - D. Sodium carbonate
 - E. Sodium phosphate
- 10) Specify the standard solution (titrant) for the iodometric determination of oxidants:
- A. $\text{Na}_2\text{S}_2\text{O}_3$
 - B. KMnO_4
 - C. I_2
 - D. $\text{K}_2\text{Cr}_2\text{O}_7$
 - E. KBrO_3
- 11) Concentration of potassium dichromate in a solution was determined by means of iodometry. Name a titrant of iodometric method for determination of strong oxidizer:
- A. Sodium thiosulfate
 - B. Sodium hydroxide
 - C. Potassium iodide
 - D. Potassium permanganate
 - E. Potassium bromate
- 12) When determining oxidizing agents by means of iodometry in the presence of starch the following phenomenon can be observed at the titration end point:
- A. Blue coloring disappears
 - B. Red coloring appears
 - C. Green coloring of precipitate appears
 - D. Green coloring of solution disappears

E. White precipitate occurs

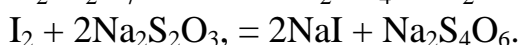
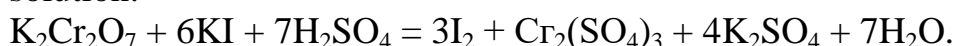
Laboratory work №6

Determining the correct normality of standart sodium thiosulfate solution.

1. Theoretical part

Primary standart for determination of the molarity of standart sodium thiosulfate solution is the chemically pure $K_2Cr_2O_7$. A primary standard is a soluble solid compound that is very pure, with a consistent formula that does not change on exposure to the atmosphere, and has a relatively high molar mass, completely and without any side reactions interacts with the standart solution.

The next chemical reactions take place during standartization of $Na_2S_2O_3$ solution:



Equivalence factor of $K_2Cr_2O_7$ is $1/6$ and of $Na_2S_2O_3$ is 1 .

An indicator of the iodometric method is the starch solution forms dark-blue colour surface complex with the I_2 molecules. More than that, between starch and iodine can occur the side redox reaction, which depends on of I_2 concentration. So, to prevent this side reaction, starch should be added to the solution titrated only near the end of titration, when the content of molecular iodine is still insignificant and solution has a pale yellow colour.

2. Procedure

1. Fill the buret with $Na_2S_2O_3$ standart solution.
2. Using a pipet transfer into the beaker flask 10ml of $K_2Cr_2O_7$ solution.
3. With a beaker add ≈ 10 ml of H_2SO_4 solution and ≈ 10 ml of KI solution.
4. Titrate with the $Na_2S_2O_3$ solution:
 - At first you should perform the titration without indicator until the pale yellow color appears.
 - Then add 1-2 drops of starch solution (blue colour appears) and continue titration until the blue colour is completely disappeared.
5. Repeat titration for 3 times.
6. For the calculations use the average value of $Na_2S_2O_3$ solution volume.

3. Results and calculations

$$c(1/6K_2Cr_2O_7) = \dots\dots\dots \text{mol/l}; V(K_2Cr_2O_7) = 10\text{ml} = 0,011$$

$$V_1(Na_2S_2O_3) = \dots\dots\dots$$

$$V_2(Na_2S_2O_3) = \dots\dots\dots$$

$$V_3(Na_2S_2O_3) = \dots\dots\dots$$

$$V_{\text{aver.}}(Na_2S_2O_3) =$$

$$c(Na_2S_2O_3) = \frac{\dots\dots\dots}{\dots\dots\dots}$$

$$C(Na_2S_2O_3) = \dots\dots\dots \text{mol/l.}$$

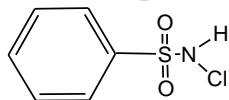
Laboratory work №7

Determining the «active» chlorine mass fraction in the chloramine B

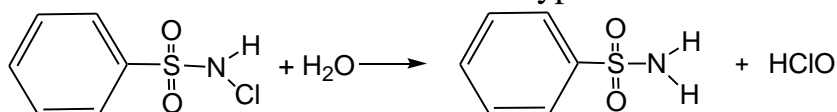
1. Theoretical part

Chloramines are widely used as disinfectants within medical and sanitary-hygienic practice. There are several different chloramines – chloramine B, chloramine T, etc. Actually, chloramines are the chloramides of benzenesulphonic acid and its derivatives or of the derivatives of benzoic acid.

Chloramine B in state of crystalloid is the hydrate of monochloramide sodium salt of benzenesulphonic acid:



In water solution this compound remains in a form of molecules, which in a very small amount react with water and form hypochlorous acid:



Just due to hypochlorous acid, which is formed because of interaction between chloramine and water, disinfecting abilities of chloramine reveals. Quantitative characteristic of chloramine B quality is the mass fraction of «active» chlorine in chloramine B. For quantitative determination of «active» chlorine we should add an excess quantity of KI and H₂SO₄ to the chloramine solution. As a result, free iodine is being liberated.



The quantity of free iodine is equivalent to the quantity of «active» chlorine, which contents in chloramine probe B.

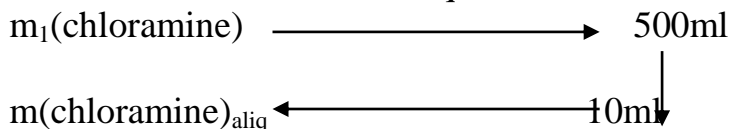
Procedure

1. Measure using a pharmaceutical balance 4,0g of chloramine B, pour into a weighing cup.
2. Using the analytical balance determine the correct mass of a weighing cup and a batch of chloramine B.
3. Transfer 4,0g chloramine B through the conical funnel to the 500ml volumetric flask, then weight the empty weighing cup using the analytical balance.
4. Calculate the chloramine B mass by the difference between the container mass with the chloramine B and after that, when the chloramine powder was poured into the volumetric flask.
5. Add water to the 500-mL line and mix.
6. Using a pipet transfer 10ml of the prepared solution to a beaker flask, add using the graduated cylinder \approx 8 – 10ml of KI and the same quantity of H₂SO₄ solution.
7. Close the flask with a clock glass for 3-5 minutes to finish the reaction.
8. Fill a buret with the standart Na₂S₂O₃ solution.
9. Titrate with the sodium thiosulfate standart solution until the yellow colour appears.
10. Add 1-2ml of starch solution and without diluting from a buret continue titrating until the blue colour disappears.

11. Repeat the titration for 3 times.

Evaluation

1. Chloramine's sample mass $m(\text{chloramine}) = \dots\dots\dots \text{g}$.
2. Make a dilution schema, which allow to calculate the mass the of chloramine's samhle were transferred to the aliquote in result of dilution:



$$m(\text{chloramine})_{\text{aliqu}} = \frac{m_1(\text{chloramine}) \cdot 10}{500} =$$

3. Calculate the mass of the «active» chlorine in an aliquote has been titrated:

$$4. m(\text{Cl}_2)_{\text{aliqu}} = c(\text{Na}_2\text{S}_2\text{O}_3) \cdot V(\text{Na}_2\text{S}_2\text{O}_3) \cdot M\left(\frac{1}{2} \text{Cl}_2\right) =$$

5. Calculate the “active” chlorine mass percent of the “active” chlorine in the chloramine B by the formula:

$$\omega(\text{Cl}_{\text{act}}) = \frac{m(\text{Cl}_2)_{\text{aliqu}}}{m(\text{chloramine})_{\text{aliqu}}} \cdot 100\% = \dots\dots\dots \cdot 100\% = \dots\dots\dots \%$$

Evaluation table.

$c(\text{Na}_2\text{S}_2\text{O}_3) = \dots\dots\dots \text{mol/l}$
 $v_1(\text{Na}_2\text{S}_2\text{O}_3) = \dots\dots\dots$
 $v_2(\text{Na}_2\text{S}_2\text{O}_3) = \dots\dots\dots V_{\text{aver}}(\text{Na}_2\text{S}_2\text{O}_3) = \dots\dots\dots$
 $v_3(\text{Na}_2\text{S}_2\text{O}_3) = \dots\dots\dots$

Conclusions

Mass percent of “active” chlorine in analyzed sample is _____

Practical lesson 19

Iodimetric methods of reductants determination. Determination of titrant (solution of the iodine) molarity and mass percent of a ascorbic acid in an sample. Writing control work and test.

CONTROL QUESTIONS FOR STUDENTS OUT-OF-CLASS WORK

1. The content of the iodimetric method of analysis, its potentialities.
2. The titrants of the iodometric method, their preparation and standardization.
3. The ways of iodometric titration. Iodimetric determination of reductants.
4. Determination of the end-point of titration in iodometry. Application of the starch solution as an indicator when determining reducers.
5. The content of the cerimetric method of analysis, the reactions, which are in the basis of determinations.

6. The titrant of the cerimetric method, its preparation and standardization. Standard substances and standard solutions.
7. Determination of the end-point of titration in cerimetry.
8. Potentialities, advantages and disadvantages of the cerimetric method of analysis in comparison with other redox methods.

These questions are taken from the Test items for licensing examination Krok 1 PHARMACY

The correct answer is first

- 1) The mass percentage of ascorbic acid can be determined by the cerimetric analysis in the presence of the following redox indicator:
 - A. Ferroin
 - B. Methylene red
 - C. Eosin
 - D. Fluorescein
 - E. Methylene orange
- 2) Quantitative determination of iodide can be done by method of:
 - A. Oxidation-reduction titration
 - B. Acid-base titration
 - C. Chelatometry
 - D. Spectrophotometry
 - E. Precipitating titration
- 3) Specify the standardized solutions used for direct and back titration of reducing agents in the iodometric method:
 - A. I_2 , $Na_2S_2O_3$
 - B. $K_2Cr_2O_7$, $Na_2S_2O_3$
 - C. I_2 , KI
 - D. $KMnO_4$, KI
 - E. $K_2Cr_2O_7$, I_2
- 4) When determining reducing agents by means of iodometry in the presence of starch the following phenomenon can be observed at the titration end point:
 - A. Blue coloring appears
 - B. Red coloring appears
 - C. Green coloring of precipitate appears
 - D. Green coloring of solution disappears
 - E. White precipitate occurs
- 5) Specify the standard solution (titrant) for the iodometric determination of reductants:
 - A. I_2
 - B. $KMnO_4$
 - C. $Na_2S_2O_3$
 - D. $K_2Cr_2O_7$
 - E. $KBrO_3$

- 6) Specify the standard solution for the iodometric determination of reducing agents (direct titration):
- A. I_2
 - B. $KMnO_4$
 - C. $Na_2S_2O_3$
 - D. $K_2Cr_2O_7$
 - E. KI
- 7) Name the type of reaction that takes place during detection of ascorbic acid in a preparation by iodometric method:
- A. Oxidation-reduction
 - B. Acylation
 - C. Neutralization
 - D. Precipitation
 - E. Complexing
- 8) Iodometric determination of formaldehyde in formaline can be done by the back titration. Iodine surplus is titrated with the standard solution of:
- A. Sodium thiosulphate
 - B. Sodium nitrate
 - C. Sodium sulphate
 - D. Sodium carbonate
 - E. Sodium phosphate
- 9) Iodimetry involves use of standard solutions of iodine and $Na_2S_2O_3$. What substance is used to standardize the sodium thiosulfate solution?
- A. $K_2Cr_2O_7$
 - B. NaCl
 - C. $Na_2B_4O_7$
 - D. K_2CO_3
 - E. As_2O_3
- 10) Name a standard solution of iodometric determination of reducing agents (direct titration)?
- A. Solution of I_2
 - B. Solution of $KMnO_4$
 - C. Solution of $Na_2S_2O_3$
 - D. Solution of $K_2Cr_2O_7$
 - E. Solution of KI

What standard solution can be used to standardize the solution of I₂?

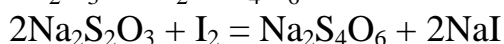
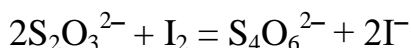
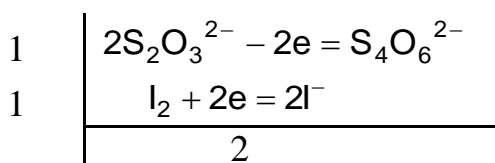
- A. Sodium thiosulfate solution**
- B. Potassium iodide solution**
- C. Potassium dichromate solution**
- D. Potassium permanganate solution**
- E. Sodium nitrite solution**

Laboratory work № 8

Standartization of I₂ solution with the titrated Na₂S₂O₃ solution.

1. Theoretical part

The correct concentration of the standart I₂ solution is determined by the titrated Na₂S₂O₃ solution. According to the following equation free iodine quantitatively reacts with sodium thiosulfate solution without any side reaction:



The indicator for this titration is a solution of starch, which from the excessive drop of I₂ paints the analyte in pale blue colour (in case of a significant I₂ excess – blue colour).

2. Procedure

Using a pipet transfer into a beaker flask 10 ml of titrated Na₂S₂O₃ solution, which has the known normality.

Add 1-2ml of a starch solution and titrate with the standart I₂ solution until the stable light pale blue colour appears.

Repeat the titration for 3 times.

For calculations use the average volume value of the I₂ solution.

3. Results and calculations

C(Na₂S₂O₃) =; V(Na₂S₂O₃) = 10ml = 0,01

V₁(I₂)=.....;

V₂(I₂)=.....;

V₃(I₂)=.....

$$V_{\text{aver.}}(\text{I}_2) = \frac{V_1(\text{I}_2) + V_2(\text{I}_2) + V_3(\text{I}_2)}{3} = \underline{\hspace{2cm}}$$

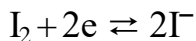
$$c(\frac{1}{2}\text{I}_2) = \frac{c(\text{Na}_2\text{S}_2\text{O}_3) \cdot V(\text{Na}_2\text{S}_2\text{O}_3)}{V_{\text{aver.}}(\text{I}_2)} =$$

Laboratory work № 9

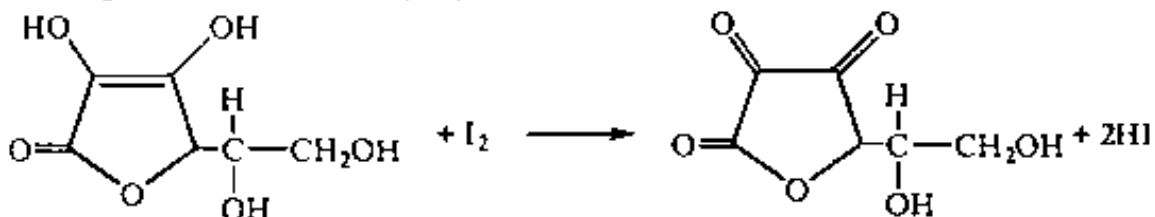
Determining the mass fraction of the ascorbic acid in the compound

1. Theoretical part

The main equation of the method:



This is a reversible reaction. Depending on the conditions it can go in direct and indirect way. Equivalence factor for free $I_2 = \frac{1}{2}$. Free I_2 is the middle power oxidizing agent: the normal redox potential is +0,54B. Reducing agents are easily acidified by the free iodine. An example can be the acidifying of the ascorbic acid with iodine:



Ascorbic acid - $C_6H_8O_6$; $M(C_6H_8O_6) = 88,065$ g/mol.

This reaction is used for the iodometric determination of the ascorbic acid.

2. Procedure

Using the pharmaceutical balance measure 0,1g of a compound, which contains ascorbic acid, and pure it into a clean container. On the analytical balance with the readability 0,0001 g determine the mass of the container filled with a compound batch. Pure the ascorbic acid compound into the beaker flask to perform the quantitative determination and weight the empty container on the analytical balance. Calculate the correct batch mass of ascorbic acid compound as the difference between the container mass with a batch and the mass of the empty container.

Dissolve the batch of the ascorbic acid compound, add 1-2ml of the starch solution and titrate with the standart iodine solution until it gets a stable pale blue colour.

3. Results and calculations

$c(I_2) = \dots$ $V(I_2) =$
m(container with batch) =g.
m(container without batch) =g.
m(ascorbic acid compound) =g.

Practical lesson 20

Chelatometry. Determination of the correct molarity of the EDTA solution. Determination of the general water hardness. Problem solving and situational tasks. Writing control work and test.

CONTROL QUESTIONS FOR STUDENTS OUT-OF-CLASS WORK

1. The concept of complexones, their characteristic and properties.
2. What methods of complexometric titration do you know? Their content and possibilities.
3. Metallochromic indicators. The mechanism of their action.

4. Using the literature, give the characteristics of complexometric determination features:
- 1) Co^{2+} , Ni^{2+} ;
 - 2) Pb^{2+} in the precipitate of PbSO_4 ;
 - 3) Mg^{2+} in the precipitate of $\text{Mg}_2\text{P}_2\text{O}_7$;
 - 4) Ca^{2+} and Fe^{3+} .
5. What is the content and what are the possibilities of the mercurimetric method of analysis?
6. The characteristic of indicators used in mercurimetry.

These questions are taken from the Test items for licensing examination Krok 1 PHARMACY

The correct answer is first

- 1) You are given 0,05 M solution of versene. What is standard substance for standardization of this solution?
 - A. Metallic zinc
 - B. Sodium tetraborate
 - C. Sodium hydroxide
 - D. Oxalic acid
 - E. Potassium dichromate
- 2) Quantitative determination of calcium chloride is carried out by method of direct chelatometric titration. Choose an indicator for fixation of the titration endpoint:
 - A. Eriochrome black T
 - B. Phenolphthalein
 - C. Methyl red
 - D. Eosin
 - E. Starch
- 3) Solution of Trilon B is the titrant in chelatometry. It makes complex compounds with metal cations irrespective of their valency with the following proportion:
 - A. 1:1
 - B. 1:3
 - C. 1:2
 - D. 2:1
 - E. 3:1
- 4) Specify the titration method, in which a standardized titrant solution is gradually added to the solution under study until a titration endpoint is reached:
 - A. Direct titration
 - B. Back titration
 - C. Indirect titration
 - D. Substitution titration
 - E. Residue titration
- 5) A solution containing calcium and magnesium cations is titrated with Trilon B solution. Complexometric titration of these cations requires the following medium:

- A. Ammonium buffer solution
 - B. Formate buffer solution
 - C. Neutral medium
 - D. Acidic solution
 - E. Acetate buffer solution
- 6) Quantitative analysis of zinc salts is performed by method of trilonometry. What indicator is used for this purpose?
- A. Eriochrome black T
 - B. Phenolphthalein
 - C. Methyl black
 - D. Potassium dichromate
 - E. Thymol blue
- 7) Concentration of magnesium sulfate in a drug can be determined by complexometric titration. Choose an indicator to detect the end point of titration:
- A. Chromogen black
 - B. Phenolphthalein
 - C. Methyl orange
 - D. Eosin
 - E. –
- 8) Quantitative analysis of magnesium salts is performed by method of trilonometry. What indicator is used for this purpose?
- A. Eriochrome black-T
 - B. Phenolphthalein
 - C. Methyl black
 - D. Potassium dichromate
 - E. Thymol blue
- 9) In titration analysis aimed at determining the substances by means of mercurimetry the following substance can be used as the indicator:
- A. Diphenylcarbazide
 - B. Potassium chromate
 - C. Eriochrome black T
 - D. Starch
 - E. Tropeolin OO
- 10) What indicator is used to fix the endpoint of mercurimetric titration?
- A. Thiocyanate complexes of iron (III)
 - B. Fluorescein
 - C. Eosin
 - D. Murexide
 - E. Potassium chromate
- 11) Determination of chlorides in potable water can be done by means of mercurimetry. The following solution is used as a titrant:
- A. $\text{Hg}(\text{NO}_3)_2$
 - B. $\text{Hg}_2(\text{NO}_3)_2$

- C. HgCl_2
- D. HgSO_4
- E. Hg_2Cl_2

12) Which of the ligands is bidentate?

- A. Ethylenediamine
- B. Thiocyanate ion
- C. Cyanide ion
- D. Pyridine
- E. Hydroxide ion

13) Name the mercurimetry titrant:

- A. 0,1 M solution of $\text{Hg}_2(\text{NO}_3)_2$
- B. 0,1 M solution of NaNO_2
- C. 0,1 M solution of AgNO_3
- D. 0,1 M solution of KSCN
- E. 0,1 M solution of NH_4SCN

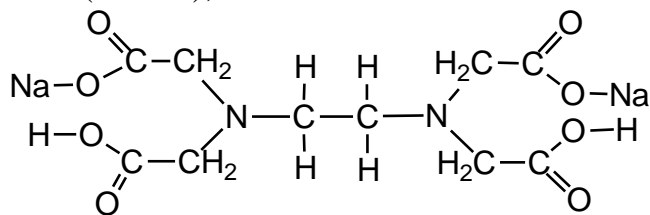
14) During mercurimetric titration of halogenide ions in the presence of diphenylcarbazone, at the titration end point the precipitate is produced. This precipitate will be colored:

- A. Blue
- B. Red
- C. Yellow
- D. Green
- E. Brown

Laboratory work 10

Standardization of EDTA Solution

The most common complexone is the disodium salt of ethylenediaminetetraacetic acid (EDTA), which has the next formula:



This compound is also named as “EDTA” or “complexone III”. Schematically the molecule of EDTA is marked as $\text{Na}_2\text{H}_2\text{L}$.

EDTA titration can be used for direct determination of many metal cations. It reacts directly with Mg, Ca, Zn, Cd, Pb, Cu, Ni, Co, Fe, Bi, Th, Zr and others. With the help of back titration this list can be made much longer, as back titration can be used in the cases when the complex is created too slowly (as it happens in the case of Al and Cr), when it is not possible to choose good end point indicator, or when metal could precipitate as hydroxide at pH required for a direct titration.

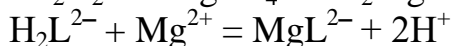
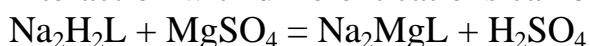
Using back titration it is also possible to determine some anions - for example SO_4^{2-} can be determined by BaSO_4 precipitation with the use of BaCl_2 and titration of excess barium left in the solution.

Method is not selective - EDTA reacts with almost everything - but careful selection of solution pH allows in some cases to determine one metal in the presence of others. Cations with higher charges (like Bi^{3+} , Fe^{3+}) have much larger stability constants, so they can be titrated at low pH, in the presence of divalent cations (like Ca^{2+} , Mg^{2+}) which will not interfere in this conditions.

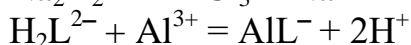
EDTA solution is not only stable - it can be stored for months - but it can be also prepared without a need of standardization. First, EDTA can be obtained in the form pure enough. Second, after thorough drying its crystalline form has pretty well defined amount of water of crystallization.

Crystalline EDTA - in the form of either disodium EDTA dihydrate or anhydrous disodium EDTA salt.

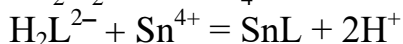
Together with the metal ions EDTA forms soluble complexes. The important characteristic of EDTA interaction with ions of different metals is that **1 mol of EDTA always reacts with 1 mol of metal.** That's why the equivalence factor of EDTA depends on the cation charge. If we mark the EDTA formula as $\text{Na}_2\text{H}_2\text{L}$, then the equation of its interaction with different cations can be written as:



Equivalence factor of EDTA = 1/2



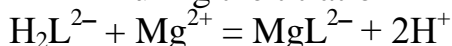
Equivalence factor of EDTA = 1/3



Equivalence factor of EDTA = 1/4

The end of titration is defined with the metal-indicators - agents, which with the metal cations form the coloured complexes. Its colour differs from the colour of a free indicator. One of this metal-indicators is black eriochrome T. Most of the trilonometric determinations with this indicator are performed in a weakly alkaline solution (pH \approx 10 – 12). In a solution, which does **not** contain free magnesium or calcium ions, this indicator has blue-black colour. In a solution, which contains free magnesium or calcium ions, this indicator has dirty red colour.

During the titration EDTA firstly reacts with the free Mg^{2+} ions:



Comparably not stable indicator complex with Mg^{2+} ions remains unchanged and at the same time the colour of the solution remains dirty-red.

After all the free Mg^{2+} ions react with the EDTA, the next drop of EDTA solution takes the Mg^{2+} ions from this dirty-red complex with the indicator. This way the free blue coloured indicator is being created. So in the equivalence point the colour of the solution changes from dirty red to blue.

EDTA can be standardized against many reagents, be it metallic magnesium, calcium carbonate, metallic bismuth and so on. For best results it is good to standardize EDTA solution against the same cation and using the same method as will be later used

during sample analysis. Note, that EDTA solution can be prepared without a need for standardization, as EDTA itself can be obtained in form pure enough.

Procedure

1. Clean your burette and fill it with the EDTA (disodium dihydrogen ethyldiaminetetraacetate dihydrate) solution (approx. concentration 0.05M).
2. Transfer exactly 10.00 mL of the Mg^{2+} standard solution into a 250 mL conical flask.
3. Add about 10 mL of the ammonium buffer pH=10.
4. Add 5 drops of the Eriochrome Black T indicator.
5. Titrate against the EDTA solution till the end point is approached (at the end point the color should change from red to blue).
6. Record the volume to two significant figures after the decimal point.
7. Repeat till you get concordant values.
8. Calculate the molarity of equivalent of EDTA - Na_2H_2L .

Evaluation

11. Calculate the average volume of titrant delivered in the titration

$$V_{av.} = \frac{V_1 + V_2 + V_3}{3} \text{ mL} = \frac{\quad + \quad + \quad}{3} = \quad \text{mL}$$

12. Convert 10.0 mL of the sample $V(MgSO_4)$ and $V_{av.}$ in mL of Na_2H_2L solution to liters by dividing by 1000:

$$1 \text{ L} = 1000 \text{ mL} = 1 \cdot 10^{-3} \text{ mL}$$

$$V(MgSO_4) \text{ mL} \cdot 1 \text{ L} / 1000 \text{ ml} = 10 \cdot 10^{-3} \text{ L}$$

$$V_{av}(Na_2H_2L) \text{ mL} \cdot 1 \text{ L} / 1000 \text{ ml} = V_{av}(Na_2H_2L) \text{ mL} \cdot 10^{-3} \text{ L} = \quad \cdot 10^{-3} \text{ L}$$

13. Calculate the molarity of equivalent of Na_2H_2L using formula:

$$c(\frac{1}{2} Na_2H_2L) = \frac{c(\frac{1}{2} MgSO_4) \cdot v(MgSO_4)}{v(Na_2H_2L)_{aver.}}$$

$$c(\frac{1}{2} Na_2H_2L) = \frac{\quad}{\quad} = \quad \text{mol/l}$$

Evaluation table.

$$C(\frac{1}{2} MgSO_4) = \dots\dots\dots \text{mol/l}; \quad V(MgSO_4) = \dots\dots\dots \text{l}$$

No	$V(Na_2H_2L)$, ml	$V(Na_2H_2L)_{aver.}$ ml
1		}
2		
3		

Laboratory work 11

DETERMINATION OF THE GENERAL WATER HARDNESS.

Purpose: This experiment is designed to demonstrate a method of determination of the hardness of water samples. It also serves as an example of the method of using complex ion formation to do quantitative analysis.

Introduction

The total concentration of alkaline earth metal ions, such as calcium and magnesium, in water determine the hardness of water. The term "hard water" comes from the fact that these metal ions precipitate soap molecules from water making it "hard" to get things clean. The calcium in hard water precipitates as calcium carbonate (lime scale), if the water is boiled.

The hardness of water is usually determined by measuring the total amount of calcium and magnesium present, since the concentrations of these ions far exceed those of other alkaline earth metals. Table gives a classification of the hardness of water:

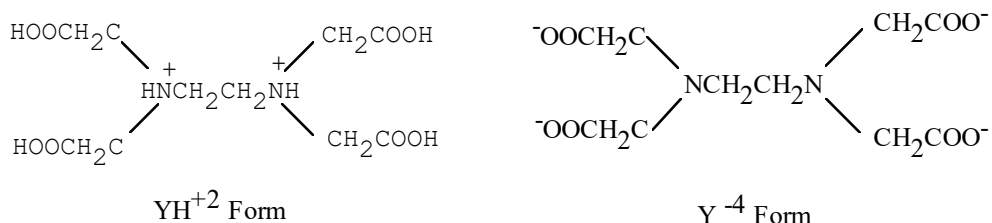
soft	medium	hard	very hard
<1.3 mmol/L	1.3 - 2.5 mmol/L	2.5 - 3.8 mmol/L	>3.8 mmol/L

According to the Ukrainian standart water hardness is expressed in mg-eq/l (mmol/l). In other countries the water hardness is expressed in the conditional grades, for example:

- ✦ German degree corresponds to 10mg of Ca²⁺ in 1 l of water;
- ✦ Franch degree corresponds to 10mg of CaCO₃ in 1 l of water;
- ✦ English degree corresponds to 10mg of CaCO₃ in 0,7 l of water(1 gran of CaCO₃ in English gallon of water) ;
- ✦ American degree corresponds to 1mg of CaCO₃ in 1 l of water (1 gran of CaCO₃ in 1 American gallon of water).

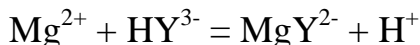
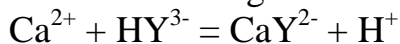
According to the sanitary standards of food production we can use the soft and moderately hard water (hardness under 8 mmol/l).

There are several methods used for measuring hardness. We will titrate using ethylenediamine-N,N,N',N' tetraacetic acid (EDTA)



Background

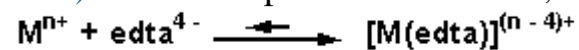
EDTA is a chelating agent that can donate electrons (Lewis base) thereby forming a complex with metal ions (Lewis acid). The EDTA will complex first with the Ca²⁺ and then with the Mg²⁺ :



The following conditions of the complex formation are decisive:

- 1) The complexes [M(Y)]⁽ⁿ⁻⁴⁾⁺ are very stable; the equilibrium is ~100% to the side of the complexes.

- 2) The complexes are labile; the equilibria are established instantaneously.

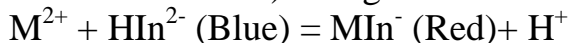


- 3) The stoichiometry of the complexes is definite, Mⁿ⁺ / Y⁴⁻ = 1/1, because edta⁴⁻ occupies all the coordination sites of the metal.

4) There are indicators to detect the equivalence point. They are dyes which form a complex with the metal cation and are displaced by edta^{4-} at the equivalence point. The color of the complex “M-indicator” differs from that of the free indicator (analogy to the acid/base indicators, where the color change at the equivalence point is due to the deprotonation of the “H-indicator”).

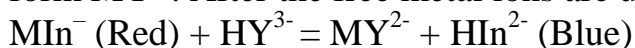
Endpoint Detection:

The indicator (Eriochrome Black T - H_3In Form ; H_2In^- (red) ; the HIn^{2-} (blue), abbreviated HIn^{2-}) changes color when it binds to a metal ion:



When the indicator is added to a sample solution, it will react with a small amount of metal ion to form MIn^- (Solution has a red color).

During the titration, EDTA is added to the solution and reacts with the free metal ions to form MY^{2-} . After the free metal ions are used up, the EDTA will react with MIn^- :



Initially the color turns to purple (a mixture of MIn^- and HIn^{2-}), then blue. The end point of the titration is measured when the solution turns completely to blue (HIn^{2-} only).

Reagents and Equipment

Drinking water sample

EDTA standard solution

Buffer solution at a pH of 10

Eriochrome Black T indicator solution

Distilled water

Burette

5 mL pipette

10 mL pipette

250 mL beaker flask

Experiment

Time: about 45 min.

7. Fill the burette by EDTA standard solution.

8. Measure exactly 10.0 mL of the water sample into a 250 mL beaker flask.

9. Add 10.0 mL of the buffer solution. The remainder of the titration must be completed within 15 minutes of time when the buffer is added.

10. Add 5 drops of Eriochrome Black T indicator solution.

11. Titrate using the EDTA titrant. At the end point the color should change from red to blue.

12. Repeat this procedure at least three times.

13. Tabulate the data for the sample analyses.

14. Use this data to calculate the hardness of your water sample in mmol/L.

Evaluation

5. Determine the volumes of titrant obtained from a titration and put them in the table below.

6. Calculate the average volume of titrant delivered in the titration

$$V_{av.} = \frac{V_1 + V_2 + V_3}{3} \text{ mL} = \frac{\quad + \quad + \quad}{3} = \quad \text{mL}$$

7. Convert 10.0 mL of the water sample $V(\text{H}_2\text{O})$ and $V_{av.}$ in mL of EDTA solution into liters dividing by 1000:

$$1 \text{ L} = 1000 \text{ mL} = 1 \cdot 10^{-3} \text{ mL}$$

$$V(\text{H}_2\text{O}) \text{ mL} \cdot 1 \text{ L} / 1000 \text{ mL} = 10 \cdot 10^{-3} \text{ L}$$

$$V_{av.}(\text{EDTA}) \text{ mL} \cdot 1 \text{ L} / 1000 \text{ mL} = V_{av.}(\text{EDTA}) \text{ mL} \cdot 10^{-3} \text{ L} = \quad \cdot 10^{-3} \text{ L}$$

8. Calculate the total hardness of water using formula:

$$\text{Hardness} = \frac{C(\text{EDTA}) \text{ mol/L} \cdot V_{av.}(\text{EDTA}), \text{L}}{V(\text{H}_2\text{O}), \text{L}} \cdot 10^3, \text{ mmol/L} = \frac{\quad \cdot \quad}{\quad} \cdot 10^3 = \quad =$$

$$= \quad \text{mmol/L}$$

Evaluation table.

Molarity of EDTA solution \quad mol/L

Volume of the water sample \quad mL

<i>EDTA titration of water sample</i>		
EDTA volume	EDTA average volume	Hardness
Trial 1 \quad mL	\quad mL	\quad mmol/L
Trial 2 \quad mL		
Trial 3 \quad mL		

Conclusions

The total hardness of the analyzed sample of drinking water is

Can this water be used for drinking?

Practical lesson 21

Precipitation titration. Problem solving and situational tasks. Determination the mass concentration of the zinc ions in solution by Hexacianoferratometry Writing control work and test.

CONTROL QUESTIONS FOR STUDENTS OUT-OF-CLASS WORK

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 the basis of the method;
 - the titrants of the methods, their 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 titrants solutions.
6. Give the chemical explanation of the mechanism of the indicator action and the conditions of carrying out the analysis by the Volgard method.
7. Specify and substantiate possible mistakes when determining chloride- and iodide-ions by the back Volgard method. Which practical arrangements are used for their prevention?
8. Give the characteristic of the mercurimetric method specifying the titrant, indicators of the method, conditions of titration.

These questions are taken from the Test items for licensing examination Krok 1 PHARMACY

The correct answer is first

Sodium and potassium chlorides in preparations can be detected by means of:

- A. Argentometry, More's method
 - B. Oxidation-reduction titration
 - C. Alkalimetry
 - D. Acidimetry
 - E. Chelatometry
- 1) What standard solution (titrant) is used in Folgard's method of direct titration?
 - A. Ammonium thiocyanate
 - B. Sodium chloride
 - C. Silver nitrate
 - D. Potassium chromate
 - E. Potassium dichromate
 - 2) Determination of sodium and potassium chlorides in pharmaceuticals can be done by means of:
 - A. Argentometry, Mohr method
 - B. Reduction-oxidation titration
 - C. Alkalimetry

- D. Acidimetry
E. Chelatometry
- 3) Thiocyanatometry is based upon using of secondary standard solution of potassium thiocyanate that should be standardized according to the following standard solution of:
- Silver nitrate
 - Hydrochloric acid
 - Sulfuric acid
 - Iron (II) sulfate
 - Copper (II) nitrate
- 4) What is the primary standard for standardization of $\text{Hg}_2(\text{NO}_3)_2$ solution?
- Sodium chloride
 - Sodium bromide
 - Sosium sulphate
 - Sodium hydroxide
 - Sodium dichromate
- 5) Specify the titration method, in which a standardized titrant solution is gradually added to the solution under study until a titration endpoint is reached:
- Direct titration
 - Back titration
 - Indirect titration
 - Substitution titration
 - Residue titration
- 6) Mass fraction of Fe^{2+} ions in Mohr's salt can be determined by gravimetric sedimentation method using:
- NH_4OH
 - Na_2S
 - K_3PO_4
 - BaCl_2
 - ZnCl_2
- 7) What working solutions (titrants) are used in the method of precipitation titration - Folgard method?
- AgNO_3 and NH_4SCN
 - H_2SO_4 and NaOH
 - $\text{Na}_2\text{S}_2\text{O}_3$ and $\text{K}(\text{I}_3)$
 - KMnO_4 and KBrO_3
 - HClO_4 and KOH
- 8) The Volhard method is used to define sodium chloride mass concentration. Name titrant of this method.
- Ammonium thiocyanate
 - Mercury (I) nitrate
 - Sodium tetraborate
 - Mercury (II) nitrate
 - Sodium hydroxide

- 9) Mass fraction of Fe^{2+} ions in Mohr's salt can be determined by gravimetric sedimentation method using:
- A. NH_4OH
 - B. Na_2S
 - C. K_3PO_4
 - D. BaCl_2
 - E. ZnCl_2
- 10) The Volhard method is used to determine sodium chloride mass concentration. Name the titrant of this method:
- A. Ammonium thiocyanate
 - B. Mercury (I) nitrate
 - C. Sodium tetraborate
 - D. Mercury (II) nitrate
 - E. Sodium hydroxide
- 11) Fajans titration with fluorescein is performed within the following pH range of a medium:
- A. 7-10
 - B. 1-3
 - C. 3-5
 - D. 5-7
 - E. 10-13
- 12) Determination of silver salts by ammonium thiocyanate titration is performed in the presence of the following indicator:
- A. $(\text{NH}_4)\text{Fe}(\text{SO}_4)_2$
 - B. FeSO_4
 - C. FeCl_2
 - D. $(\text{NH}_4)_2\text{SO}_4$
 - E. NH_4SCN
- 13) The Mohr method is used to determine sodium chloride mass concentration in isotonic solution. Titration is carried out with the following indicator present:
- A. Potassium chromate
 - B. Fluorescein
 - C. Ammonium iron (III) sulfate
 - D. Diphenylcarbazone
 - E. Ferroin
- 14) What analytical effect is observed when titration end point in the Volhard method is registered?
- A. Red coloration of solution
 - B. Red precipitate
 - C. Yellow coloration of solution
 - D. Brown precipitate
 - E. Yellow precipitate
- 15) What kind of standard solution (titrant) is used according to Volhard's direct titration method?

- A. Ammonium thiocyanate
 - B. Sodium chloride
 - C. Silver nitrate
 - D. Potassium chromate
 - E. Potassium dichromate
- 16) The Mohr method is used to determine mass concentration of sodium chloride in an isotonic solution. Titration is carried out with the following indicator:
- A. Potassium chromate
 - B. Fluorescein
 - C. Ammonium iron (III) sulfate
 - D. Diphenylcarbazone
 - E. Ferroin
- 17) Thiocyanatometric titration method requires secondary standard solution of potassium thiocyanate. This solution is standardized with standard solution of:
- A. Silver nitrate
 - B. Hydrochloric acid
 - C. Sulfuric acid
 - D. Iron (II) sulfate
 - E. Copper (II) nitrate
- 18) Thiocyanatometric titration method requires secondary standard solution of potassium thiocyanate that is standardized with standard solution of:
- A. Silver nitrate
 - B. Hydrochloric acid
 - C. Sulfuric acid
 - D. Iron (II) sulfate
 - E. Copper (II) nitrate
- 19) Specify the precipitating agent to be used in gravimetric determination of calcium salts:
- A. $(\text{NH}_4)_2\text{C}_2\text{O}_4$
 - B. $\text{K}_2\text{C}_2\text{O}_4$
 - C. $\text{Na}_2\text{C}_2\text{O}_4$
 - D. Na_2CO_3
 - E. K_2CO_3
- 20) In order to determine mass fraction of calcium in a pharmaceutical preparation, gravimetric method was applied. Ammonium oxalate solution was used as a precipitating agent. What is the gravimetric form in this case?
- A. Calcium chloride
 - B. Anhydrous calcium oxalate
 - C. Monohydrated calcium oxalate
 - D. Calcium carbonate
 - E. Calcium hydroxide

- 21) During gravimetric determination of mass fraction of sulfate ions in the magnesium sulfate preparation precipitation is performed by means of barium chloride solution. Precipitated barium sulfate should be rinsed with:
- Diluted solution of sulfate acid
 - Distilled water
 - Solution of barium chloride
 - Solution of sodium sulfate
 - Solution of hydrochloride acid
- 22) To determine mass concentration of calcium in a medical preparation the gravimetric precipitation method was applied. Solution of ammonium oxalate was used as a precipitator. The gravimetric form in this case is:
- Calcium oxide
 - Anhydrous calcium oxalate
 - Monohydrated calcium oxalate
 - Calcium carbonate
 - Calcium hydroxide

To determine mass fraction of sodium chloride in a drug, the Fajans method should be applied. Titration is to be performed in the presence of the following indicator solution:

- Fluorescein*
- Methyl red*
- Potassium chromate*
- Ammonium iron (III) sulfate*
- Phenolphthalein*

Laboratory work № 12

DETERMINATION OF THE MASS CONCENTRATION OF ZINC IONS IN SOLUTION BY THE HEXACYANOFERRATOMETRY

1. Theoretical part.

Hexacyanoferratometry - this is a precipitation titration in which $K_4[Fe(CN)_6]$ is the titrant.

- Titrant: secondary standard solution $K_4[Fe(CN)_6]$
- Standardization: primary standard is solution of $KMnO_4$ in medium of sulfuric acid according to the reaction:



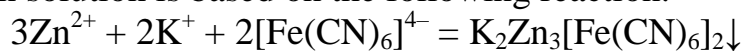
Indicator for standardization - Methyl violet (changes color from yellow-green to red-brown).

Indicators of the hexacyanoferratometry:

- diphenylamine at the presence of a small amount of potassium hexacyanoferrate (III) for definition Zn^{2+} , Mn^{2+}
- 3,3-dimethylnaftizin for definition Cu^{2+} , Zn^{2+} , Cd^{2+} , Pb^{2+} , Fe^{2+} , Ni^{2+} etc.
- alizarin red S for definition Zn^{2+} , Pb^{2+} , Th(IV)
- diphenylcarbazone for definition Cd^{2+}

Application: metal cations (direct titration), phosphate ions (displacement titration).

The hexacyanoferrate titrimetry for determination of the mass concentration of zinc ions in solution is based on the following reaction:



In result of reaction the precipitate $\text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$ is formed.

For determination of the end point of titration the redox indicator diphenylamine is used. Conditions of it using:

1. Before titration to the flask contains solution of analyte add 1 drop of 3% $\text{K}_3[\text{Fe}(\text{CN})_6]$ solution. That leads to becoming of blue-violet color of solution due to interaction between $\text{K}_3[\text{Fe}(\text{CN})_6]$ with oxidizing form of the diphenylamine.

2. At the end point of titration the concentration of $\text{K}_4[\text{Fe}(\text{CN})_6]$ increases that causes of redox potential reducing and, in result, diphenylamine becomes colorless (reducing form).

The titration carry out slowly and carefully stirring to prevent adsorption of the zinc ions on the surface of precipitate before the end point of titration riches. If the titration carry out quickly the solution becomes colorless before the real end point and results of titration will understated.

2. Procedure

1. Clean your burette and fill it with the $\text{K}_4[\text{Fe}(\text{CN})_6]$ solution
2. Transfer 10 ml (using pipet) of solution contains zinc ions into a 150 or 250ml volumetric conical flask, add the distilled water to the line 40 ml and mix.
3. Add 10.00 mL (using measuring beaker) of sulfuric acid solution.
4. Add 1 drop of indicator diphenylamine.
5. Add 1 drop of 3% $\text{K}_3[\text{Fe}(\text{CN})_6]$ solution. Check the colour changes to blue-violet.
6. Titrate against the $\text{K}_4[\text{Fe}(\text{CN})_6]$ solution very slowly (drop by drop) and carefully stir it till the end point is riches.
7. Near to the end point carefully stir the mixture in the flask not less than 10 c. Remember at the end point the blue-violet color changes to light green. Explain why.
8. Record the volume to two significant figures after the decimal point.
9. **Repeat at least 5 times** till you get concordant values (the results of three titrations will differ no more then by 0,05ml).

3. Results and calculations

Evaluation

14. Calculate the average volume of titrant delivered in the titration

$$V_{av.} = \frac{V_1 + V_2 + V_3 + V_4 + V_5}{5} \text{ mL} = \frac{\quad\quad\quad}{5} =$$

= mL

15. Convert 10.0 mL of the sample $V(\text{Zn}^{2+})$ and $V_{av.}$ in mL of $\text{K}_4[\text{Fe}(\text{CN})_6]$ solution to liters by dividing by 1000:

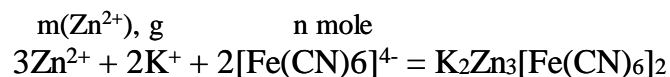
$$1 \text{ L} = 1000 \text{ mL} = 1 \cdot 10^3 \text{ mL}$$

$$V(\text{Zn}^{2+}) \text{ mL} \cdot 1 \text{ L} / 1000 \text{ mL} = 10 \cdot 10^{-3} \text{ L}$$

$$V_{\text{av}}(\text{K}_4[\text{Fe}(\text{CN})_6]) \cdot 1 \text{ L} / 1000 \text{ mL} = V_{\text{av}}(\text{K}_4[\text{Fe}(\text{CN})_6]) \cdot 10^{-3} \text{ L}$$

$$= \underline{\hspace{2cm}} \cdot 10^{-3} \text{ L}$$

16. Calculate the mass of the zinc ions in an aliquote, which has been titrated in consideration of the reaction specifics during the titration:



$$\begin{array}{ccc} n=3 \text{ mole} & & 2 \text{ mole} \\ \hline & & \end{array}$$

$$M(\text{Zn}^{2+})=63\text{g/mole}$$

$$m(\text{Zn}^{2+})=n \cdot M$$

$$=3 \text{ mole} \times 63\text{g/mole}$$

$$m(\text{Zn}^{2+}) = \frac{3 \text{ mole} \cdot 63 \text{ g/mole} \cdot n[\text{Fe}(\text{CN})_6]^{4-} \text{ mole}}{2 \text{ mole}}$$

Based on $V_{\text{av}}(\text{K}_4[\text{Fe}(\text{CN})_6])$ and $c(\text{K}_4[\text{Fe}(\text{CN})_6])$ calculate $n([\text{Fe}(\text{CN})_6]^{4-})$:

$$n([\text{Fe}(\text{CN})_6]^{4-}) = c(\text{K}_4[\text{Fe}(\text{CN})_6]) \cdot V_{\text{av}}(\text{K}_4[\text{Fe}(\text{CN})_6])$$

$$n([\text{Fe}(\text{CN})_6]^{4-}) =$$

$$m(\text{Zn}^{2+}) =$$

17. Calculate mass concentration of the Zn^{2+} in the sample solution:

$$\rho(\text{Zn}^{2+}) = \frac{m(\text{Zn}^{2+})}{V(\text{sample})} = \underline{\hspace{2cm}} =$$

Evaluation table.

$C(\text{K}_4[\text{Fe}(\text{CN})_6]) = \dots\dots\dots \text{mol/L};$

$V(\text{sample}) = \dots\dots\dots \text{L}$

No titration	of	$V(\text{K}_4[\text{Fe}(\text{CN})_6]), \text{L}$	$V_{\text{av}}(\text{K}_4[\text{Fe}(\text{CN})_6]), \text{L}$	$m(\text{Zn}^{2+}), \text{g}$	$\rho(\text{Zn}^{2+}), \text{g/L}$
1					
2					
3					
4					
5					

Practical lesson 22

Gravimetric analysis. Basic practical skills in gravimetric analysis. Problem solving and situational tasks. Laboratory work "Determination of the water content in a compound". Test control.

Gravimetry (precipitation method) is used for quantitative determination of sulfates in potable water. What substance should be used as precipitator for sulfates? A. BaCl_2 B. KCl C. MgCl_2 D. NaCl E. NH_4NO_3

Solve the tests :

1. What conditions are necessary for formation of crystal precipitate?

- A. Slow precipitation from the hot diluted solutions.
- B. Fast precipitation from the hot diluted solutions.
- C. Slow precipitation from the cold diluted solutions.
- D. Fast precipitation from the hot concentrated solutions.
- E. Slow precipitation from the cold concentrated solutions.

2. Which method is method of gravimetric analysis?

- A. An particulate method.
- B. A neutralisation method.
- C. The Faience-Hodakov method.
- D. A polarimetric method.
- E. Method of Mhor.

3. For determination a content of water in drugs and medicinal substances use:

- A. A volatilization gravimetric method.
- B. A particulate gravimetry method.
- C. Method of Mhor.
- D. A precipitation gravimetric method.
- E. A permanganatometric method.

4. To advantages and lacksof the gravimetric analysis it is necessary to note:

- A. High accuracy and duration of the analysis.
- B. High sensitivity and duration of the analysis.
- C. High selectivity and duration of the analysis.
- D. Low sensitivity and expressive of the analysis.
- E. Low sensitivity and high accuracy.

5. At the requirement which concern to the weighed (gravimetric) form is:

- A. Exact conformity of structure to the chemical formula.
- B. The content of a defined element should be whenever possible big.
- C. The content of a defined element should be whenever possible smaller.
- D. Insignificant hygroscopicity of the weight form.
- E. High chemical firmness of the weight form.

6. Which a precipitant choice at first?

- A. Are flying substances.
- B. Are group reagents.
- C. Do not form supersaturated solutions.

- D. Have small molarity weight.
- E. Have big molarity weight.

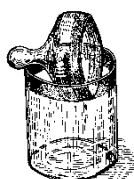
Laboratory work № 13

DETERMINATION OF THE WATER CONTENT IN A COMPOUND

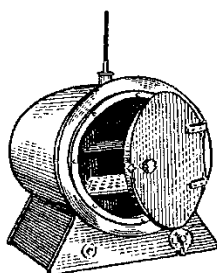
1. Procedure

2. Weight the container with the technical (laboratory) weight with accuracy $\pm 0,01\text{g}$.
3. Weight the container with the analytical balance weight with accuracy $\pm 0,0001\text{g}$.
4. Add 2 g of the compound into container,
5. Weight the container with the sample of compound
6. Place the container with the sample of compound into oven and dry it during an hour.

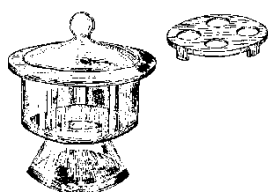
container



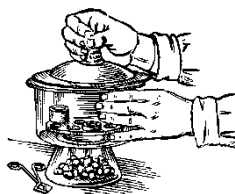
Oven



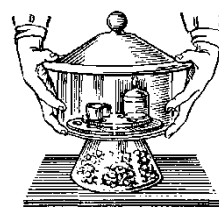
7. In an hour place the container to the exsiccator for cooling.
8. After cooling weight the container with the sample of compound after heating.
9. Write down the mass .
10. To make sure of the complete water vaporization, repeat again the procedure of heating, cooling , weighting . The difference with the previous heating must be no more than 0,0005g.



Dessicator and ceramic



Dessicator opening



Dessicator transferring

plate for it

Do the calculations of $\omega(\text{H}_2\text{O})$ by the formula:

$$\omega(\text{H}_2\text{O}) = \frac{m(\text{water})}{m(\text{compound})} \cdot 100\%$$

Results and calculations

Empty container mass _____. Sample mass _____.

Container mass with sample _____. Mass after heating _____.

Water mass _____.

$$\omega(\text{H}_2\text{O}) = \frac{m(\text{water})}{m(\text{compound})} \cdot 100\% = \text{_____} =$$

Practical lesson 23

Calculations based on the results of the gravimetric analysis.

Solve the problems:

1. Calculate the optimal weight of copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), which need to be taken to determine content of water in the compound by the method of indirect volatilization gravimetric.
2. What weight seeds need to be taken to determine a moisture, if permissible moisture content in seeds is 4%, and determining the content of a moisture transmitting by the method of indirect volatilization gravimetric?
3. Calculate the moisture roots of a dandelion, if desiccation 5.1123 g of to constant mass weight decreased to 0.4528 g.
4. Calculate the minimum weight of medicinal product piracetham (substance), necessary for the determination of volatile substances by indirect volatilization gravimetric with relative error not more 8%, if the loss weight during drying (removal of volatile substances) is about 0.5%.
5. Find the best original mass of Calcium carbonate for gravimetric determination of calcium in the form of CaO (a gravimetric form) - the relative error of determination is not more 0.2 %. Precipitable form – a crystal residue, so for optimum weight of gravimetric form to take 0.5 g
6. Calculate the optimal mass of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ for gravimetric determination of aluminum in the form oxyquinolinathe aluminum ($\text{Al}(\text{C}_9\text{H}_6\text{ON})_3$) (gravimetric form) with relative error of determination is not more 0.2 %.

Precipitable form, the composition of which coincides with the a gravimetric form is a crystalline precipitate, that why a mass of gravimetric form can take to equal is 0.5 g.

7. What a volume of 2% solution ($\rho = 1\text{g/ml}$) of 8- oxyquinoline taken from 10% of the excess, required for complete deposition of Magnesium 8-oxyquinolinathe ($\text{Mg}(\text{C}_9\text{H}_6\text{ON})_2$) with 100 ml solution, wich containing 50 mg of magnesium chloride?
8. Obtained the following results definition of loss in a mass (in %) for drying substances to glucose: 9.78, 9.29, 10.05, 10.11, 9.76, 9.12. Decide the question about present of error (a card error) for the Q-test.

METHOD OF IMPLEMENTATION OF PRACTICAL WORK

Dry residue of extracts

n a flat-bottomed dish about 50 mm in diameter and about 30 mm in height, introduce rapidly 2.00 g or 2.0 ml of the extract to be examined. Evaporate to dryness on a water-bath and dry in an oven at 100-105 °C for 3 h. Allow to cool in a desiccator over *diphosphorus pentoxide R* or *anhydrous silica gel R* and weigh. Calculate the result as a mass percentage or in grams per litre.

Work 1. Definition of the dry residue in tinctures.

In weighed weighing bottle or flat-bottomed dish (preliminary finished to constant weight) introduce 2.0 ml of the tincture to be examined. Evaporate to dryness on a water-bath and dry in an oven at 100-105 °C for 3 h. Allow to cool in a desiccator over *diphosphorus pentoxide R* or *anhydrous silica gel R* and weigh. Calculate the result as a mass percentage or in grams per litre.

Results of definition write down under the form:

$$m_{\text{dish}} =$$

$$m_{\text{dish+tinct}} =$$

$$m_{\text{tinct}} =$$

$$m_{\text{dish + residue}} =$$

$$m_{\text{residue}} =$$

The dry residue of tincture count under the formula:

$$W = \frac{m_{\text{residue}}}{m_{\text{tinct}}} \cdot 100\%$$

$$W_{W/V} = \frac{m_{residue}}{V_{tinct}} \cdot 100\%$$

Loss on drying of extracts

In a flat-bottomed dish about 50 mm in diameter and about 30 mm in height, weigh rapidly 0.50 g of the extract to be examined, finely powdered. Dry in an oven at 100-105 °C for 3 h. Allow to cool in a desiccator over *diphosphorus pentoxide R* or *anhydrous silica gel R* and weigh. Calculate the result as a mass percentage.

Work 2. Definition loss on drying of drugs.

In weighed weighing bottle or flat-bottomed dish (preliminary finished to constant weight) introduce 1.0 ml of the substance to be examined (lactose, glucose, analginum). Dry in an oven at 100-105 °C for 3 h. Allow to cool in a desiccator over *diphosphorus pentoxide R* or *anhydrous silica gel R* and weigh. Calculate the result as a mass percentage.

Results of definition write down under the form:

$$m_{dish} =$$

$$m_{dish + substance} =$$

$$m_{substance} =$$

$$m_{dish + drying substance} =$$

$$m_{loss} =$$

The loss on drying count under the formula:

$$W = \frac{m_{loss}}{m_{substance}} \cdot 100\%$$

Work 3. Definition of Acid-insoluble ash

The Acid-Insoluble Ash Limit Test is designed to measure the amount of ash insoluble to diluted hydrochloric acid.

Procedure Add carefully 25 ml of dilute hydrochloric acid to the ash (obtained as directed under the Ash Limit Test), boil gently for 5 minutes, collect the insoluble matter on a filter paper for quantitative analysis, wash thoroughly with hot water, and dry the residue together with the filter paper. Ignite it for 3 hours in a crucible of platinum, quartz, or porcelain, which has been prepared as directed in the Ash Limit Test and whose weight is already known. Cool it in a desiccator (silica gel) and weigh

accurately. If the measured amount is larger than the specified value, ignite until a constant weight is obtained.

Work 3. Definition of sulphatic ash.

Heat a platinum dish to redness for 10 minutes, allow to cool in a desiccator and weigh. Unless otherwise specified in the monograph, place 1 g of the substance being examined in the dish, moisten with sulphuric acid, ignite gently, again moisten with sulphuric acid and ignite at about 800°. Cool, weigh again, ignite for 15 minutes and repeat this procedure until two successive weighings do not differ by more than 0.5 mg.

Work 4. Definition of Iron

Iron - one of the most common elements in nature and is also is a part of many medical products. With solution of salt Fe (III) influence of aqueous ammonia

precipitated amorphous precipitate Fe (OH)₃ ($Ks_{Fe(OH)_3} = 6,3 \cdot 10^{-39}$):

$$Fe^{3+} + 3NH_3 + 3H_2O \rightleftharpoons Fe(OH)_3 \downarrow + 3NH_4^+$$

If in the solution present ions of Fe (II), then their pre-effects oxidation by Br₂, H₂O₂, HNO₃. For getting forms of Fe₂O₃, sediment roasting in muffle furnace at 900 ° C:



Sediment Fe₂O₃ is not hygroscopic. During roasting to ensure the access of air.

Definition technique. Based on the approximate content iron in drug and mass precipitable form, calculate the mass. Weighing the required mass of the drug. For this first weighing of the crucible of the samples on the technical and then the analytical weight. Bring a mass in the glass and crucible with he remnants of substance weighed on the analytical weight. The difference between the calculated of mass. The sample in glass wet 5-10 ml of distilled water, add 5-6 5ml of HCl (1:1) and 3-4 ml of 70% HNO₃ and heated almost to boiling. The completeness of oxidation shows a steady orange color solution (sometimes dark brown due to formation of unstable compounds Fe (NO) Cl₂). After oxidation wash off the inside glass of distilled water. In glass add 5-10 ml 10% solution of NH₃ to a noticeable smell of ammonia. Table glasses are raised to 100 ml of hot distilled water, mix and stand for 3-5 minutes, then check the completeness of precipitation by adding 2-3 drops solution of NH₃. Precipitate filtrations through the filter and washed by decantation (three - four times in 20 ml hot water) and then quantitatively transfer to a filter. Precipitate again washed on the filter. Selected 1-2 drops of filtrate, which check the availability chloride ions. Filter with a sediment in drying oven. Removed the filter, carefully not to spill residue, is, containing in a porcelain crucible. Filter heating at 900° C to obtain Fe₂O₃ (as indicated by constant mass of the sample). o iron of calculate

Calculated content of iron in the sample $W(\text{Fe})$, calculate first of gravimetric factor .

$$F(\text{Fe}) = \frac{2 \cdot A_r(\text{Fe})}{M(\text{Fe}_2\text{O}_3)} = 0.6990,$$
$$W(\text{Fe}) = \frac{m(\text{Fe}_2\text{O}_3) \cdot F(\text{Fe})}{m} \cdot 100\%$$

Practical lesson 24

Control of practical skills. Submodule "Quantitative analysis" control: Test control based on test Krok 1. Written control work 2.

Questions for submodule 2.

1. Titrimetric analysis. Requirements to the reactions used in titrimetric analysis. Methods of titrimetric analysis (classification).

2. Solutions concentration, calculations in the titrimetric analysis.

3. Titrants preparation and standardization. Primary and secondary standard solutions.

4. Direct, back and substitutive titration.

5. Acid-base titration method. Titrants. Primary standard solutions.

6. Indicators of the acid-base titration method. Ways to choose a suitable indicator.

7. Titration curve for the system: strong acid - alkali. Factors, which affect on the value of end-point break.

8. Indicators errors. The reasons of errors. Ways of their elimination and calculation.

9. Acid-base titration in the non-aqueous solutions. Solvents and indicators. Examples of titration.

10. Method of the redox titration. Classification. Requirements to the reactions.

11. Titration curves of the redox titration. Ways to choose a suitable redox indicator. Calculation of the transition interval for the redox indicators.

12. Classification and characteristics of the indicators, which are used in redox titration. Indicatorless methods of analysis.

13. Equilibrium constant of the redox reaction, its effect on the completeness of the reaction.

14. Permanganometric method of titration. Titrants, primary standards, indicators and analytes (reducing and oxidizing agents, indifferent agents) of the method.

15. Iodi- and iodometric titration methods. Titrants, primary standards, indicators and analytes of the method (give an examples).

16. Bromatometric titration method. Titrants, primary standards, indicators and analytes of the method (give an examples).

17. Bromometric titration method. Titrants, primary standards, indicators and analyties of the method (give an examples).

18. Iodine monochloride titrimetry method. Titrants, primary standards, indicators and analyties of the method (give an examples).

19. Dichromatometric titration method. Titrants, primary standards, indicators and analyties of the method (give an examples)

20. Azotometric titration method. Titrants, primary standards, indicators and analyties of the method (give an examples). Conditions of the azotometric titration.

21. Cerimetry. Titrants, primary standards, indicators and analyties of the method (give an examples). Advantages and disadvantages of the method comparing to the permanganometry.

22. Methods of the precipitating titration. Requiremats to the reactions, titration curves.

23. Argentometry, Mohr's method. Titrants, primary standards, indicators and analyties of the method (give an examples).Conditions of the titration.

24. Thiocyanatometric titration (Folgard's method). Titrants, primary standards, indicators and analyties of the method (give an examples).

25. Adsorptive indicators in the argentometry. Fajans method. Titrants, primary standards, indicators and analyties of the method (give an examples).

26. Mercurimetric titration. Titrants, primary standards, indicators and analyties of the method (give an examples).

27. Methods of the compleximetric titration. Requirements to the reactions, titration curves.

28. Chelatometric titration. Indication of the titration endpoint. Principle of the metallochrome indicators action. Give examples.

29. Chelatometric determination of the water hardness.

30. Mercurimetric method of the analysis. Titrants, primary standards, indicators and analyties of the method (give an examples).

31. Gravimetric analysis. Precipitate and gravimetric (weighing) forms, requirements to them.

32. Gravimetric analysis. Steps of the gravimetric determinations. The use of the gravimetric methods for the quantitative determination.

SITUATIVE PROBLEMS

1. Propose a precipitating reagent, indicate the precipitate and the gravimetric (weighing) form, calculate the gravimetric factor of the quantitative determination of:

1. **ZnSO₄**;
2. **Pb(NO₃)₂** ;
3. **AlCl₃** ;
4. **Na₃PO₄** ;
5. **Ba(NO₃)₂** ;
6. **K₃PO₄** ;
7. **Al₂(SO₄)₃** ;
8. **KBr**;
9. **FeSO₄**;

10. CaCl_2 .

2. There are following agents: ammonium buffer solution, secondary standard solutions - NaOH , AgNO_3 , NH_4SCN , H_2SO_4 , $\text{Na}_2\text{S}_2\text{O}_3$, EDTA ($\text{Na}_2\text{H}_2\text{L}$), KMnO_4 ; indicators - phenolphthalein, methyl red, starch, black chromogen, potassium chromate, eosin, ammonium iron alum; in the laboratory. Propose titrant, indicator, write the formula for the calculation of the analyte mass by the titration results for quantitative determination of:

1. ascorbic acid;
2. calcium chloride;
3. sodium thiosulfate;
4. hydrogen peroxide;
5. sodium chloride;
6. acetic CH_3COOH acid;
7. magnesium sulfate;
8. ammonia (NH_3);
9. magnesium sulfate;
10. hydrochloric acid.