Ministry of Health of the Republic of Belarus
Educational institution
"Gomel State Medical University"

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METHODOLOGICAL MANUAL

for conducting the laboratory class with the first-year students
of the Faculty of International Students
studying in the specialty 7-07-0911-01 "Medical business" (FIS)
English-speaking students
in the discipline "Medical chemistry"

Topic 2: **INTRODUCTION INTO VOLUMETRIC ANALYSIS**

Time: 2 hours

Gomel, 2023

THE TRAINING AND EDUCATIONAL GOALS, MOTIVATION TO STUDY THE TOPIC

The purpose of the class:

To form knowledge about the principles and classification of titration analysis methods; to develop skills of working with measuring laboratory glassware; to teach to perform calculations in titration analysis, to prepare and standardize solutions; to familiarize with the role of titration analysis in biomedical research and clinical analysis.

The tasks of the class:

As a result of the class, the student ***must know:***

1) the principles of volumetric analysis;
2) the requirements for reactions applied in titration analysis;
3) the classification of titration methods and types of solutions applied for titration analysis;
4) the concept of titrants and ways of their preparation;
5) the requirements for standard compounds which are used for primary standards preparation;
6) the role of titration analysis in biomedical research and clinical analysis.

The student ***must be able to:***

1) choose the method of titration analysis for research, a suitable working solution, standard solution, a method for fixing the equivalence point;
2) carry out the titration analysis;
3) perform typical calculating based on the Equivalent Law involving the rules of significant figures;
4) perform static treatment of experimental data.

Motivation to study the topic:

Volumetric (titration) analysis is a widely-used quantitative analytical method which is applied to determine amounts of elements, species or compounds present in a sample. As the name implies, this method involves the measurement of volume of a solution of known concentration which is used to determine the concentration of the analyte (an element, species or compound that is the subject of analysis).

The method is easy to use if the quantitative relationship between two reacting solutions is known. It is particularly well-suited to acid-base and oxidation-reduction reactions.

Titrations are routinely used in clinical and biological studies to test important nutrients, naturally produced chemicals, such as cholesterol, sugars, vitamins and urea, and administrated drugs in the body fluids of patients undergoing hospital treatment require monitoring. Titrations permit concentrations of the unknown substance to be determined with a high degree of accuracy.

NECESSARY EQUIPMENT

1. Methodological manual for students on the topic "Introduction into volumetric analysis".
2. Reference materials of physico-chemical constants for the 1st year education international students.
3. Chemical reagents and equipment necessary for laboratory work.

CONTROL QUESTIONS ON THE TOPIC OF THE CLASS

1. Basic terms of titration analysis.
2. Classification of titration methods of analysis.
3. Calculations in titration analysis.

COURSE OF THE CLASS

The theoretical part

1. BASIC TERMS OF TITRATION ANALYSIS

Volumetric analysis is a method of quantitative analysis in which a solution with accurately known concentration of one substance is used to determine the concentration of another substance in another solution. Volumetric analysis is also known as titration.

In a titration experiment, a solution with the precisely known concentration of substance, called a titrant, is added gradually and carefully to solution with unknown concentration of another substance, called an analyte, until the chemical reaction between the two solutions is complete:

$$\mathbf{T + A \rightarrow products}$$

Figure 1 shows the scheme of the titration unit.

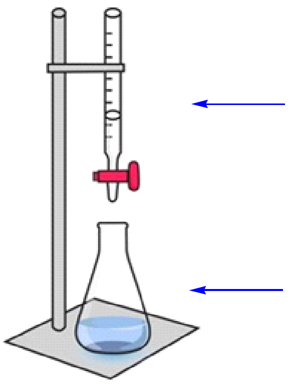

Figure 1 – Setup for a typical titration

In other words, titration is fulfilled up to the equivalence point or endpoint. Since the stoichiometry of the reaction is known, it is possible to determine the concentration of the unknown substance by performing appropriate calculations in volumetric analysis.

The endpoint of titration is the moment of the reaction when the number moles of equivalent of titrant becomes equal to the number mole of equivalent of analyte.

There are two types of titrants in volumetric analyses:

1) primary standards (standard solutions);
2) secondary standards (working solutions).

The method of preparing *the primary standard* is to dissolve an accurately weighed amount of the substance and dilute it to a measured volume. In this way, the concentration can be accurately calculated. Primary standards are prepared by dissolving standard compounds that must meet the following requirements:

– the substances have to be chemically pure, i.e. presence of impurities is less than 0.05-0.1 %;

– be stable in pure state and in solutions;

– have a well-known composition agreeable to the chemical formula;

– to have a high molar mass to minimize weighing errors.

Not many substances can meet these requirements, and therefore the number of substances suitable for primary standards is limited.

Secondary standard is prepared with approximately known concentration of substance and then is titrated using a primary standard, to define its exact concentration.

Chemical reactions applied in titration analysis are defined as titrimetric reactions and to be used in the analysis, they have to satisfy some requirements:

1) should be practically irreversible ($K > 10^8$);

2) must run in strict accordance with the equation of the reaction, without by-products formation;

3) have to be fast (equivalent point ought to be reached within several minutes);

4) there must be a reliable way to fix the equivalence point. The equivalence point can be fixed by chemical (using an indicator) and physico-chemical methods (potentiometrically, conductometrically, photocalorimetrically, etc.) [1-3].

2. CLASSIFICATION OF TITRATION METHODS OF ANALYSIS

Titration methods may be classified:

1) according to a type of chemical reaction:

▪ acid-base titration is based on neutralization reaction:

$H^+ + OH^- \rightarrow H_2O$;

▪ precipitation titration is based on the reactions of formation of hard soluble compounds:

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

$Hg_2^{2+} + 2Cl^- \rightarrow Hg_2Cl_2\downarrow$ (mercurometry);

▪ complexation titration is based on the reaction of complex compound formation:

$Mg^{2+} + H_2Y^{2-} \rightarrow MgY^{2-} + 2H^+$;

▪ oxidation-reduction titration based on oxidation-reduction reactions (oxidimetry):

$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$ (permanganatometry),

$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$ (iodometry).

2) according to an analytical technique:

▪ direct titration: gradual addition of a titrant to a test solution up to the equivalence point;

▪ back titration: addition a known excess of titrant 1 to a test solution, then titrates the excess of titrant 1 using a titrant 2.

Back titration is useful if the endpoint of the back titration is easier to identify than the endpoint of the direct titration. It is also useful if the reaction between an analyte and a titrant is very slow.

▪ displacement titration: addition an excess of a reagent to a test solution, then titrates of a product using titrant solution [1,2].

3. CALCULATIONS IN TITRATION ANALYSIS

Calculations in titration analysis are based on the fact that at the equivalence point, the number moles of the equivalent of the analyte is equal to the number moles of the titrant, according to the Equivalent Law:

$$n_e(A) = n_e(T)$$

In practice, the concentration of the analyzed substance in the solution or its mass can be calculated using the following formulas:

1) $C_N(A) \times V(A) = C_N(T) \times V(T)$; **2)** $\frac{m(A)}{M_e(A)} = \frac{C_N(T) \times V(T)}{1000}$

Problem 1. How many milliliters of a 0.610 M NaOH solution are needed to completely neutralize 20.0 ml of a 0.245 M H_2SO_4 solution?

Solution:

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

According to the Equivalent Law: $n_e(NaOH) = n_e(H_2SO_4)$

Since, $C_N(NaOH) \times V(NaOH) = C_N(H_2SO_4) \times V(H_2SO_4)$

$$V(NaOH) = \frac{V(H_2SO_4) \times C_N(H_2SO_4)}{C_N(NaOH)}, \text{ where } C_N(H_2SO_4) = \frac{C_M(H_2SO_4)}{f_e(H_2SO_4)} = \frac{0.245}{1/2} = 0.49N$$

$$V(NaOH) = \frac{20.0 \times 0.49}{0.610} = 16.07 \text{ ml}$$

Answer: *V (NaOH)= 16.07 ml*

Problem 2. How many grams of H_3PO_4 is present in the solution if 25.50 ml of 0.2000 M NaOH solution was used on its titration in the presence of phenolphthalein (for condition of complete neutralization)?

Solution:

$3NaOH + H_3PO_4 \rightarrow Na_3PO_4 + 3H_2O$

According to the Equivalent Law: $n_e(H_3PO_4) = n_e(NaOH)$

$$\frac{m(H_3PO_4)}{M_e(H_3PO_4)} = \frac{C_N(NaOH) \times V(NaOH)}{1000}; \quad M_e(H_3PO_4) = M \times f_e = 98 \times ⅓ = 32.67 \text{ g/mol}$$

$$m(H_3PO_4) = \frac{M_e(H_3PO_4) \times C_N(NaOH) \times V(NaOH)}{1000} = \frac{32.67 \times 0.2000 \times 25.50}{1000} = 0.167g$$

Answer: *m* (H_3PO_4)*= 0.167 g*

The practical part

Safety instructions before laboratory work.

LABORATORY WORK

Standardization of hydrochloric acid solution against borax primary standard

1. This procedure is based on the following chemical reactions:

Being dissolved in water, borax is hydrolyzed by an anion to form a weak boric acid. When the obtained solution is titrated by hydrochloric acid solution, the hydrolysis equilibrium shifts almost completely to the right, since the alkali released during hydrolysis is neutralized by acid. Summing up these two equations, we get:

$$Na_2B_4O_7 + 7H_2O \rightarrow 2NaOH + 4H_3BO_3$$
$$NaOH + HCl \rightarrow NaCl + H_2O \quad | \times 2$$

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

2. Choice of the indicator: at the end point of the titration the medium is a weak acidic because a weak boric acid is prepared as a result of a given reaction. *Methyl orange* is a valid indicator to fix the endpoint of a particular titration since it changes its color in the acidic medium (pH range is 3.1 – 4.4).

3. Carry out the experiment in the following sequence of operations:

a) take an analytical pipette and pour 10 ml of borax solution into 3 flasks for titration;

b) add two drops of methyl orange into each flask;

c) pour HCl solution into the burette up to the zero mark;

d) titrate borax solution against hydrochloric acid solution up to the endpoint *when yellow color of an initial solution turns red* after adding one drop of HCl;

c) repeat this titration twice, starting from the zero mark of the burette; the results should not differ much from each other;

d) fill in the Table 1 given below with the obtained data.

Table 1 – The results of borax solution titration against HCl solution

№	*V($Na_2B_4O_7$), ml*	*V(HCl), ml*	*V_{av}(HCl), ml*	*C_N(HCl), mol/l*	*T(HCl), g/ml*
1	*10.0*				
2	*10.0*				
3	*10.0*				

4. Calculation of the results of the experiment:

- $V_{av}(HCl) = \dfrac{V_1 + V_2 + V_3}{3}$

According to the Equivalent Law in equivalence point:

$$n_e(HCl) = n_e(Na_2B_4O_7)$$

$$C_N(HCl) \times V(HCl) = C_N(Na_2B_4O_7) \times V(Na_2B_4O_7)$$

- $C_N(HCl) = \dfrac{C_N(Na_2B_4O_7) \times V(Na_2B_4O_7)}{V_{av}(HCl)}$

- $T(HCl) = \dfrac{C_N(HCl) \times M_e(HCl)}{1000}$

Control over the assimilation of the topic

It is conducted in the form of an oral conversation with students.

QUESTIONS FOR SELF-CONTROL OF KNOWLEDGE

1. Define the following terms: a) titration, b) equivalence or end point of titration, c) an analyte.

2. Chemical reactions applied in volumetric analysis are defined as titrimetric reactions. Name the main features of these reactions.

3. Primary standards are prepared by dissolving of standard compounds. What requirements should standard compounds meet?

4. Titration methods are classified by a type of chemical reactions. What types of chemical reactions are applied in volumetric analysis?

5. Define direct, back and displacement titration methods.

6. Calculations in titration analysis.

Exercises for the self – control

1. Calculate the equivalence factors and the equivalent molar masses for the following compounds: $Al(OH)_3$; H_2SO_4; $MgCl_2$; KOH; $Ca_3(PO_4)_2$; $H_4P_2O_7$; P_2O_5; $CuSO_4$.

2. Calculate the equivalence factor and the equivalent molar mass of chromium (III) hydroxide in the following reactions:

$Cr(OH)_3 + HCl \rightarrow Cr(OH)_2Cl + H_2O$;

$Cr(OH)_3 + 2HCl \rightarrow Cr(OH)Cl_2 + 2H_2O$;

$Cr(OH)_3 + 3HCl \rightarrow CrCl_3 + 3H_2O$.

3. What value(s) can the equivalence factor of HNO_3 take in acid-base reactions?

a) ½; b) ⅕; c) 1; d) ⅓; e) ⅛.

4. In which of the reactions given below the equivalence factor of H_2SO_4 is equal to ⅛?

a) $H_2SO_4 + 2KOH \rightarrow K_2SO_4 + 2H_2O$;

b) $H_2SO_4 + KOH \rightarrow KHSO_4 + H_2O$;

c) $H_2SO_4 + Zn \rightarrow ZnSO_4 + S + H_2O$;

d) $H_2SO_4 + HI \rightarrow I_2 + H_2S + H_2O$.

5. How many milliliters of 0.1 M solution of $AgNO_3$ will be used to titrate 5 ml of 0.2 M solution of NaCl?

a) 5 ml; b) 1 ml; c) 2.5 ml; d) 10 ml; e) 100 ml.

6. 9.7770 g of concentrated solution of HNO_3 were diluted by water to get 1 liter of the solution in the volumetric flask. To titrate 25.0 ml of the obtained solution was used 23.40 ml of 0.1040 M of NaOH solution. Determine the percent by mass of nitric acid in its concentrated solution.

Answer: 62.73 %

7. To titrate 5.0 ml of sulfuric acid solution was used 4.12 ml of 0.102 M of NaOH solution. Calculate the normality of the acid solution.

Answer: 0.0841 mol/l

QUESTIONS FOR INDEPENDENT WORK OF STUDENTS (IWS)

1. Application of the titration analysis in biomedical research.

LIST OF SOURCES USED

1. Основы химии для иностранных студентов = Essential chemistry for foreign students : учебно-методическое пособие / С. В. Ткачёв [и др.]. – 5-е изд. – Минск : БГМУ, 2018. – 168 с. – Режим доступа: http://rep.bsmu.by:8080/handle/BSMU/21054.

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