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

Department of General and Bioorganic Chemistry

Author:
A.K. Dovnar, senior lecturer of the Department
of General and Bioorganic Chemistry

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

Topic 2: Introduction into volumetric analysis

Time: 2 hours

Approved at the meeting of the Department
of General and Bioorganic Chemistry
(Protocol No. 9 dated 31.08.2024)

2024

THE TRAINING AND EDUCATIONAL GOAL, TASKS, MOTIVATION TO STUDY THE TOPIC

Training purpose:

– formation of students' basic professional competence for solving diagnostic, research and other tasks of professional activity based on knowledge about the essence of titration analysis methods;

– formation of students' skills in working with measuring utensils; training in performing calculations in titration analysis, preparation and standardization of solutions;

– familiarization with the role of titration analysis in biomedical research and clinical analysis.

Educational goal:

– to develop your personal, spiritual potential;

– to form the qualities of a patriot and a citizen who is ready to actively participate in the economic, industrial, socio-cultural and social life of the country;

– learn to observe academic and labor discipline, the norms of medical ethics and deontology;

– to realize the social significance of their future professional activities.

Tasks:

As a result of the training session, the student should

know:

– formulation of the Equivalent Law of and its mathematical expression;

– the essence and classification of analysis methods;

– the essence of the titration process, the concept of the equivalence point and ways of fixing it;

– the concept of titrants and ways of their preparation;

– reactions used in titration analysis;

– the role of titration analysis in biomedical research and clinical analysis;

be able to:

– perform calculations in titration analysis based on the Equivalent Law;

– choose the method of titration analysis for research, a suitable working solution, standard solution, a method for fixing the equivalence point;

– carry out the titration analysis;

– perform static treatment of experimental data;

possess:

– skills in calculating the results of titration analysis based on the Equivalent Law;

– the methodology of titration analysis.

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. Training tables:
a) Periodic Table of chemical elements by D.I. Mendeleev;
b) table of solubility of acids, bases and salts.
3. Reference materials of basic physico-chemical constants.
4. 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. The Equivalent Law. 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.

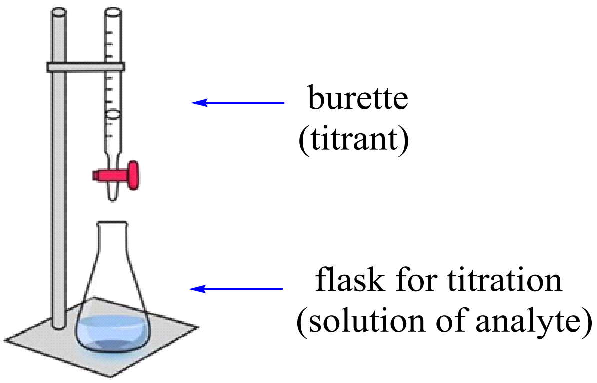

Figure 1 – Setup for a typical titration

In other words, titration is fulfilled up to the equivalence point or endpoint.

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

Upon reaching the equivalence point, titration is completed and the volume of the titrant solution used for this reaction is fixed. The equivalence point is determined by chemical methods, using indicators (substances that change their color in the area of the equivalence point) or using devices that record a change in some property of the medium during titration (physico-chemical methods: potentiometric, conductometric, photocolorimetric, etc.).

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

Various methods of titration analysis can 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 hardly 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:
$Mg^{2+} + H_2Y^{2-} \rightarrow MgY^{2-} + 2H^+$;

In complexometry, the disodium salt of ethylenediaminetetraacetic acid (Na_2-EDTA, Trilon B) is most often used. Trilon B is highly soluble in water and forms stable complexes with most metal ions in a ratio of 1:1, regardless of the degree of oxidation of the metal ion, which is very convenient.

▪ *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. THE EQUIVALENT LAW. CALCULATIONS IN TITRATION ANALYSIS

Calculations of the mass or concentration of the analyzed substance in titration analysis are based on the Equivalent Law.

The Equivalent Law: *the number moles of equivalents for reactants are equal to the number moles of equivalents for products (the amounts of equivalents for reactants and products are identical).*

For a hypothetical reaction: aA + bB → cC + dD the Equivalent Law may be represented as:

$$\boldsymbol{n_e(A) = n_e(B) = n_e(C) = n_e(D)}$$

where $n_e(X) = \frac{m(X)}{M_e(X)}$ is the number moles of equivalent of substance (the amount of equivalent substance), mol.

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 equivalent of 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 (for condition of complete neutralization)?

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

$$V(NaOH) = \frac{V(H_2SO_4) \times C_N(H_2SO_4)}{C_N(NaOH)}, \text{ where } C_N(H_2SO_4) = \frac{C_M(H_2SO_4)}{f_e(H_2SO_4)} = \frac{0.245}{0.5} = 0.49N$$

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

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, at the equivalence point: $n_e(H_3PO_4) = n_e(NaOH)$

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

$$m(H_3PO_4) = \frac{M_e(H_3PO_4) \times C_N(NaOH) \times V(NaOH)}{1000} = \frac{32.67 \times 0.2000 \times 25.50}{1000} = 0.1666g$$

Answer: *m* (H_3PO_4)*= 0.1666 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 HCl working solution titration with standard borax 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:

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

According to the Equivalent Law in equivalence point:

$n_e(HCl) = n_e(Na_2B_4O_7)$

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

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

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

Control over the assimilation of the topic

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

METHODOLOGICAL RECOMMENDATIONS FOR THE ORGANIZATION AND PERFORMING OF INDEPENDENT WORK OF STUDENT (IWS)

The time allotted for independent work can be used by students for:

– preparation for laboratory classes;
– taking notes of educational literature;
– performing tasks for self-control of knowledge;
– preparation of thematic reports, abstracts, presentations.

The main methods of organizing independent work:

– studying topics and problems that are not covered in the classroom;
– writing an abstract and making a presentation;

– performing tasks for self-control of knowledge.

List of tasks of IWS:

1. Calculate the equivalence factor (f_e) and the equivalent molar mass (M_e) for individual substances: $Al(OH)_3$; 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 (f_e) and the equivalent molar mass (M_e) 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. An acid with mass of 9 g was neutralized by 8 g of sodium hydroxide. Calculate the equivalent molar mass of an acid.

Answer: 45 g/mol

4. The equal volumes of hydrogen gas were released from an acid as a result of its interaction with 0.69 g of Ca and 1.13 g of Zn. Calculate M_e of zinc when M_e of calcium is 20 g/mol.

Answer: 38.75 g/mol

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. 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

7. 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 %

The control of the IWS is carried out in the form of:

– evaluation of an oral answer to a question, message, report or presentation;

– individual conversation.

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.

2. Филиппова, В. А. Общая химия : учеб. пособие для студентов лечеб. фак-та, обуч. на англ. яз. : в 2 ч. = General Chemistry : Educational guaidance for students medical department in English medium / В. А. Филиппова, А. В. Лысенкова, Л. В. Чернышева. – Гомель : ГомГМУ, 2009. – Ч. 1. – 192 с. URI: https://elib.gsmu.by/handle/GomSMU/2679.

3. Chang, Raymond. Chemistry / R. Chang. – 4th ed. – USA : University Science Books, 1991. – 1065 p.