



BUILDING CHEMISTRY

LAB 2

FOUNDATIONS OF QUANTITATIVE CHEMICAL ANALYSIS DETERMINATION OF SODIUM HYDROXIDE CONCENTRATION WITH ACID–BASE TITRATION METHOD

THEORETICAL BACKGROUND

Quantitative analysis is the determination of the absolute or relative abundance (often expressed as a concentration) of one, several or all particular substances present in a sample. It is often expressed in moles or grams. Quantitative analysis can be carried out using different methods and techniques. The choice of an appropriate test procedure depends on the qualitative composition of the material, expected accuracy and the precision of the test results, or the duration of the analysis.

Depending on the measurement technique, two kinds of quantitative analysis can be distinguished: chemical (classical) and instrumental analysis.

Nowadays, in analytical laboratories the instrumental methods are widely used. However, among the sophisticated state-of-the-art equipment, classical measuring and research equipment still plays an important role.

The advantage of the instrumental methods lies in a higher precision and sensitivity of the equipment. However, in many instances, instrumental techniques are not suitable for unconventional material tests, especially when it comes to environmental samples. In practice, chemical and instrumental methods are complementary. Standards, required in instrumental methods, are analyzed with the use of classical chemical methods.

Quantitative chemical analysis

Classical chemical quantitative analysis is based on chemical methods, where the residue precipitation, neutralization, oxidation, reduction and complexation reactions occur.

The classical analysis is divided into gravimetric and titration methods, and the test is carried out by measuring the weight and volume of the substance.



Gravimetric analysis

In gravimetric procedures, a sparingly soluble solid component is separated from the other components with the use of an appropriate filtration technique or the process of vaporization.

The weight of the residue constitutes the analytic signal.

Gravimetric analysis is based on a very precise determination of the weight of a substance, after obtaining a sparingly soluble chemical compound with the use of an appropriate precipitant. The substance is then dried or calcined, and weighed. In practice, the precipitated chemical compound should be non-soluble in the tested sample. During the calcination process, it is possible for a different chemical compound with precisely defined chemical composition to be produced. Based on the weight of the residue, and stoichiometric relationships, it is possible to calculate the percentage of the compound in the tested substance.

Precipitation is the creation of a solid state material from a solution and it is the basis for the gravimetric analysis. A molecule can be also obtained from a compound with the use of the electrode reaction in a process called electrolysis.

Apart from the precipitation process, the methods that use compounds' volatility are also used in gravimetric analysis. The technique is commonly used in Building Materials Engineering, e.g. determination of crystal water in salts (gypsum), or CO₂ in carbonates (limestone).

Gravimetric analysis is also used for compounds present in a material in macroscale, i.e. in larger amounts. Those techniques characterize themselves with high precision (up to 0,1%). It is a disadvantage, however, that these methods are time-consuming. The application of gravimetric methods is widespread and allows for all the cations and anions to be determined (metals and non-metals).

Quantitative analysis – titration

Quantitative analysis consists in accurate dosing of a standard solution of a reagent of known concentration (called titrant), which reacts with an indicated agent in a stoichiometric way. The amount of the indicated agent is calculated based on the measured volume and the concentration of a solution. The analytical signal in this instance is the volume of the titration solution.

Titration requires the sample to be in a liquid form (solution). During the analysis, mainly ion reactions take place.



The process is used to determine the concentration of an analyte with the use of a titrant of a very precise volume. Titration method is based on the determination of analyte's volume with the use of the standard solution of titrant. The process of adding small portions of titrant with the use of a burette into a beaker filled with analyte is called titration.

Equivalence point EP

The equivalence point EP is the point at which the number of moles of the titrant is equivalent to the number of moles of the analyte.

$$n_{\text{molesA}} : m_{\text{molesB}} = V_A \cdot c_A : V_B \cdot c_B$$

where: V – volume of solution

c – mole concentration

It is more precise to use equivalent concentration c_n .

In EP the equivalent weight of analyte is equal to equivalent weight of titrant:

$$V_A \cdot c_{nA} = V_B \cdot c_{nB}$$

hence:

$$c_{nA} = V_B \cdot c_{nB} / V_A \text{ [eq/dm}^3\text{]}$$

The equivalence point can be determined with the use of visual or instrumental methods. Visual methods are based on the change of the indicator color once the equivalence point is reached.

In instrumental methods EP can be determined with:

- potentiometric titration – based on the changes of the electrode potential during the titration;
- conductometric titration – based on the changes in the substance's conductivity.

Types of titrations:

- acid-base titration – based on a neutralization reaction; acid + base. Titrant reacts with the analyte changing the solution's pH. The change is determined with the pH indicators or pH-meters. During the titration process, the solution's conductivity also changes. This phenomenon can be measured with an electrical conductivity meter;
- redox titration – based on a reduction-oxidation reaction between an oxidizing agent and a reducing agent, which causes the change of color of redox indicator or a change of conductivity;



- complexometric titration – relies on the formation of a complex between the analyte and the titrant. In general, they require specialized complexometric indicators that form weak complexes with the analyte;
- precipitation titration – based on a reaction, where the analyte and the titrant form an insoluble precipitate.

Based on the titration method the following types of titration are distinguished:

- direct titration, where the titrant is being added to the analyte in small amounts until the reaction goes to completion,
- back titration, where an excess amount of a reagent is added to the analyte, and then such excess of an added reagent is determined.

The titration methods have following advantages:

- the determination of an absolute amount of a compound,
- ease of use,
- promptness,
- extent,
- precision and reproducibility.

Acid-base titration

Acid-base titration is a common laboratory method of titrimetry (titration) based on neutralization, e.g. reaction of binding H^+ ions (from acid) with OH^- ions (from base) into weakly dissociated water molecules.



The endpoint of titration can be determined visually based on the color changes of the indicators, potentiometrically through pH determination, or with the use of conductometric measures, determining solution's conductivity.

With acid-base titration, acid (alkalimetry) and base (acidimetry) can be determined, as well as the salt of weak acids and strong bases or salts of weak bases and strong acids. In alkalimetry, NaOH is a commonly used as a standard solution. In acidimetry, the same role plays HCl. The more titrant is added, the more changes in the concentration of hydrogen and hydroxide ions occur. Titration of a strong acid with a strong base (and vice versa) in EP $nH^+ = nOH^-$ the solution is neutral and $pH=7$. Titration of a weak acid with a strong base (and vice versa) causes neutralization, as well as the hydrolysis of the formed salt, and the solution in EP demonstrates acidity or basicity.

Color indicators in acid–base titration

Indicators are the halochromic chemical compounds added in small amounts to a solution so that the pH (acidity or basicity) of the solution can be determined visually. Oftentimes, weak acids (HInd) or weak bases (IndOH) are used as indicators, because their non-dissociated molecules present themselves with different colors than anions or cations in these compounds. Commercial indicators are produced as sheets of paper, and water or alcohol solution.

Indicator	Color of the solution		Change of color with pH
	acidity	basicity	
Methyl orange	red	yellow	3,1 – 4,4
Phenolphthalein	colorless	purple-pink	8,3 – 10,0
Bromothymol blue	yellow	blue	6,2 – 7,6
Methyl red	red	yellow	4,2 – 6,3

Three types of acid-base titration can be distinguished: titration of a strong acid with a strong base, a weak base with a weak acid, acid with base of different strengths. In all three cases the titrant is a standard solution of a strong base or a strong acid.

Titration of a strong acid (or base) with a strong base (or acid)

During the titration of a strong acid with a strong base neutralization process occurs. Strong acids and strong bases are fully dissociated in the solution, and the base cations and acid anions do not hydrolyze. The pH in EP is neutral ($pH=7$). For example:



Figure 1 presents the titration curves for different concentrations of titrant and analyte.

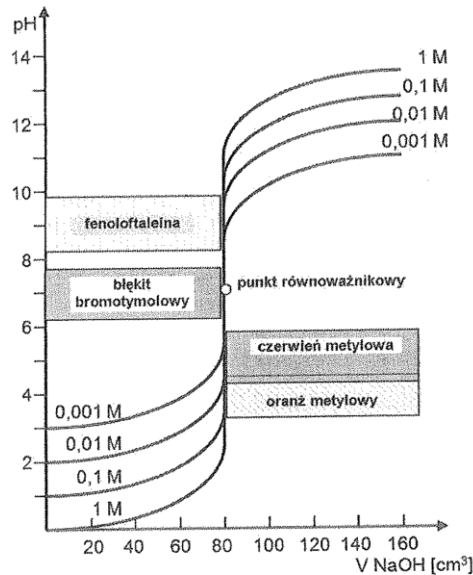


Fig. 1 Titration curves for titration of strong acids (HCl) with strong bases (NaOH), with different concentration ratio

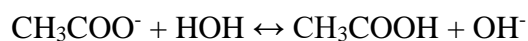
The graph shows that the more diluted the solution, the smaller is the pH change when close to the EP, which decreases the precision of determination of the EP. The titration of highly diluted solutions requires a very precise indicator. A highly concentrated solution demonstrates distinct changes of the pH when close to the EP, which means that the addition of a small amount of NaOH causes rapid changes in substance's pH. In this situation, various indicators can be used, such as: methyl orange, methyl red or phenolphthalein. For highly diluted solutions the more appropriate indicators would be either methyl red or bromothymol blue, because the color change occurs in the range of around pH=7. In titration of a strong base with a strong acid the titration curves will constitute a mirror reflection of the curves for strong acid – the test solution (analyte), and strong base – titrant.

Titration of a weak acid with a strong base

An example of the titration of a weak acid with a strong base: acetic acid and sodium hydroxide



At the same time a reverse reaction occurs – hydrolysis of the formed salt:



Hence the solution demonstrates basic reaction (pH > 7).



Titration of a weak base with a strong acid

During the titration of a weak base with a strong acid the neutralization, and hydrolysis and salt formation occur.

Example: ammonia and hydrochloric acid



As a result of hydrolysis of ammonium cation:



It can be concluded that the solution demonstrates acid reaction in the equivalence point ($\text{pH} < 7$).



PRACTICAL SESSION

DETERMINATION OF SODIUM HYDROXIDE CONCENTRATION WITH ACID–BASE TITRATION METHOD

Equipment: burette, pipette, Erlenmeyer flask, beakers, graduated cylinder

Reagents: NaOH, HCl, methyl orange or phenolphthalein

PROCEDURE

1. Use the pipette to place 10 cm³ of NaOH solution of an unknown concentration in the Erlenmeyer flask (250 ml volume) and add distilled water up to 100 ml.
2. Add a small amount of the indicator (pinch of methyl orange or a view drop of phenolphthalein).
3. Place the flask underneath the calibrated burette.
4. With the use of the burette, keep adding small volumes of the titrant (HCl) until the indicator changes its color in reaction to the titrant saturation threshold, reflecting arrival at the endpoint of the titration.
5. Perform three marks.
6. Note the chemical equation of performed reaction.

CALCULATION

Molar concentration of the NaOH solution:

$$C = V_{mv} \cdot 0,1 \text{ (mol/dm}^3\text{)} / V_{NaOH}$$

Percent concentration of the NaOH solution:

$$C_p = \frac{V_{mv} \cdot 0,1 \text{ (mol/dm}^3\text{)} \cdot 40 \text{ (g/mol)}}{1000 \text{ (g/dm}^3\text{)} \cdot V_{NaOH}} \cdot 100\%$$

Weight of NaOH:

$$m_{NaOH} = V_{mv} \cdot 0,1 \text{ (mol/dm}^3\text{)} \cdot 40 \text{ (g/mol)}$$