Volumetric analysis

The following methods are distinguished in the chemical quantitative analysis:

- classical
- instrumental

Classical methods include:

- Weight
- volumetric

Volumetric methods are divided into:

- titration methods (allowing for the determination of the component (unknown concentration/amount) by measuring the volume of the standard solution that has been used for the reaction)
- gasometric methods (allowing for the determination of an ingredient by measuring the volume of released or absorbed gas in a given reaction).

Titration analysis is the method of quantifying the concentration of known substance in tested solution. Small portions - "titrations" of the chemically equivalent amount of the reagent in the form of a standard solution are introduced to a solution containing the substance to be determined.

A standard solution called a titrant is defined as a solution with a well-known concentration or titer.

The titer defines the number of grams of a given substance contained in 1 cm^3 of the solution or the number of grams of the substance determined corresponding to 1 cm^3 of this solution.

The concentration of the standard solutions is expressed in their molarity. A one-molar solution is a solution that in 1 dm^3 contains 1 mole of the substance.

Important advantages of titration methods are high speed of determinations, the possibility of unlimited repetitions and application in many types of reactions. This way we increase the accuracy of results. The moment at which the entire determined component has completely reacted with the standard solution is called the equivalence point. In order to recognize it, a color changing indicator is added into the solution when the reaction is completed between the titrated solution and the titrant. The identification of the equivalent point can be carried out:

- Optical methods (visual, colorimetry, nephelometry)
- Instrumental, for example measuring changes in the electrode potential (potentiometric titration) or conductivity of the solution (conductometric titration).

The moment in which the indicator changes color is called the endpoint of the titration and should coincide with the equivalent point. In practice, they do not coincide and the difference between them is called the titration error.

The so-called titration curve is the image of the changes taking place during the titration. It is a graph in which on the abscissa axis (X) the volume of the used solution nominated on the ordinate axis (Y) is applied to the numerical values of the bound parameter (designated ions, Ox-red potential). The titration curve can be calculated theoretically based on the reaction equation or experimentally determined. Near the equivalent point, the curve should show a distinct change, e.g. a sharp bend, an inflection point.

All titration methods are divided according to types of reactions into:

- Alkacymetry – is based on acid-base reactions and includes methods for determining bases using standardized acid solutions (acidimetry) and acid determination using standard alkaline solutions (alkalimetry)
- Precipitometry - uses reactions in which ions combine to give a sparingly soluble compound (argentometry).
- Redoximetry - uses red-ox reactions, where methods based on titration with oxidant solutions are called oxidimetry while solutions of reductors - reductometry (manganometry, iodometry).
- Complexometry - based on creating readily soluble complex compounds between the solution of the substance determined and the standard solution (complexonometry)

Alkacymetry - gathers methods based on acid-base reactions, they are also called neutralization methods. In addition to acids and bases, salts of weak acids and strong bases and salts of strong acids and weak bases can also be determined by alkacymetric methods because according to Brönsted's theory their anions are bases (or cations, respectively, are acids). In the most of alkacymetry determinations there is no neutral pH at the equivalence point.

The main types of alkacymetric determinations are:

- Titration of a strong acid with a strong base - at the equivalence point and after exceeding it, pH changes rapidly in the range of 3-10, therefore in this type of determination any pH indicator from methylene yellow (2,9-4,0) to thymaphthaline can be used (9,3 -10).

- Titration of a weak acid with a strong base - a salt forms which, when hydrolyzed, gives the solution an alkaline character. phenolphthalein changing its color at pH> 7 will be a suitable pH indicator in this type of determinations.
- Titration of a weak base with a strong acid - at the point of equivalence, the pH of the solution will be acidic. Methyl orange or methyl red that changes its color at pH <7 should be selected.

Manganometry

Covers the determination of reducers using $KMnO_4$ standard solution.

Potassium permanganate has a very high oxidizing potential and therefore belongs to the oxidants most commonly used in laboratory practice. Its solutions have such a strong color that the need to use indicators is eliminated. The reduction course of $KMnO_4$ depends on the pH of the environment. The strongest oxidizing properties are found in the acidic solution, where the reduction to manganous salts appears.

$$MnO_4^- + 8H^+ + 5e^- = Mn^{2+} + 4H_2O$$

In an neutral or weakly acidic environment as well as in a basic solution manganese is reduced from $KMn0_4$ to MnO_2 (brown color)

$$MnO_4^- + 2H_2O + 3e^- = Mn0_2 + 4OH^-$$

However, in a strongly alkaline environment, reduction to manganate occurs. In this environment $KMn0_4$ exhibits the weakest oxidizing properties.

$$Mn0_4^- + e^- = MnO_4^{2-} \text{ (green colour)}$$

The determination of hydrogen peroxide can be an example of manganometric determinations.

H_20_2 behaves as a reducer against KMnO4. In an acidic environment, it reduces $KMn0_4$ to Mn_2^+, with oxygen being released. After oxidation of all hydrogen peroxide, the excess of $KMnO_4$ stains the titrated solution pink (equivalence point)

$$5H_2O_2 + 2Mn0_4^- + 6H^+ = 5O_2 + 2Mn^{2+} + 8H_2O$$

Iodometry

It is a section of redoximetry analysis where iodine is used.

There are two types of iodometric determinations depending on whether the I_2 + 2e- = 2I- system is used as an oxidizer or reducer.

In the first type of iodometric determinations, a titration with iodine solution is used. In this way, we can determine reducers, i.e. substances whose Ox-red potential is lower than the potential of Ox-red I_2 / 2I-. These substances are: SO_3^{2-}, $S_2O_3^{2-}$, S^{2-}, As_2O_3, SO_4^{2+}.

The second type is the determination of oxidants (substances showing a higher ox-red potential than the I_2 / 2I- system). In this case, the measured substance oxidizes the equivalent amount of iodides to any iodine, which is titrated with the standard solution of sodium thiosulphate. The method is used for the determination of: Cl_2, H_2O_2, Cu^{2+}, Fe^{3+}, MnO^{4-}.

Starch glue is used as the indicator in both types of iodometric determinations. It gives an additive compound with a very intense sapphire color with iodine. Iodometric determinations are among the most accurate titrimetric determinations due to the high sensitivity of these reactions.

Complexometry

The basis of this titration analysis is the reaction of the formation of a persistent hard-dissociating, soluble complex.

The most important section is complexonometry, which covers methods based on the use of so-called complexons. Ethylenediaminetetraacetic acid, abbreviated as EDTA, has the greatest practical importance among complexones.

EDTA forms very stable, easily soluble in water chelate connections with numerous two-, three- and tetravalent cations. An important feature of these compounds is that one complexone molecule always binds only one metal cation, regardless of its valence.

Complexes of cations with EDTA differ in durability. The highest durability is demonstrated by the complexes of tetravalent cations, and the smallest monovalent cations.

The indicators used in complexonometry are: metal markers and ox-red indicators. Metal markers are colorless or colored compounds having the ability to create in specific conditions of the titration a colored complex with ions of determined metal or used to back-titrate the excess of complexon. As the reaction progresses, the amount of metal-indicator complexes decreases in solution, and the number of more stable metal-complexon complexes increases. The released indicator has a different color than in the complex with metal, and because close to equivalent point there is a sharp drop in the concentration of metal ions, therefore a visual detection is possible.

Precypitometry

It is based on the separation of the substance to be determined in the form of sparingly soluble sediment using a standard solution of the corresponding second substance. The amount of the component to be determined is calculated on the basis of the volume of the standard solution used.

The decisive role in this method is played by the solubility of the precipitate formed.

The source of errors in precipitometry can be:

- high solubility of sediments
- adsorption mainly of ions from which it was created
- occlusion - growing of sediment particles
- creation of colloidal solutions

The most commonly used method in precipitometry is argentometry. It is based on the formation of sparingly soluble sediments of silver salts with group I anions, and others such as PO_4^{3-} and CrO_4^{2-}. Main solution in argentometry is standard solution of $AgNO_3$.

An example of argentometric determinations can be the Volhard method, used to determine chloride ions that are among others in body fluids. This method is based on acidifying the sample with HNO_3 and adding the $AgNO_3$ to this mixture. Under these conditions, all the chloride is precipitated as an AgCl solid and some excess of $AgNO_3$ will remain in the solution. This excess is titrated with the standard solution of NH_4SCN (ammonium sufocyanate) in the presence of Fe^{3+}. The chloride content is calculated from the difference between the addition and the titrated amount of $AgNO_3$.

Practical application of titration analysis

The analytics provides information that allows the assessment of the quality of products in the food, pharmaceutical and cosmetics industries. It also allows to assess the status of biological fluids. The methods used in analytics allow for continuous monitoring of changing concentrations of chemical compounds.

Alkacymetry is one of the titration analysis that has been used in the study of the freshness of fats, namely in determining the acid number (acid value) - it is a measure of fat hydrolysis. The acid number is the number of milligrams of standard solution of KOH consumed for the neutralization of free fatty acids contained in 1 gram of fat.

Fresh fats are characterized by low values of the acid number. High acid numbers have rancid fats characterized by a high content of free organic acids.

In the body, fatty acids are formed, among others, by hydrolysis of fat. This process is catalyzed by pancreatic lipase, a pancreatic enzyme whose pH optimum is 7-9. Released fatty acids are a measure of pancreatic lipase activity. We can determine them by alkacymetry by titration with standard solution of NaOH against phenolphthalein.

Amino acids are a group of chemical compounds derived from organic acids, which we can determine using, among others, titrimetric analysis. The Pope and Stevens method is based on the iodometric determination of amino acids with complexes with copper. Ion I- in an acidic environment reduces copper ions that are complexly bound to amino acids and oxidizes itself to I_2. Free I_2 is titrated with the standard solution of sodium thiosulphate. The amount of amine nitrogen is calculated from the amount of sodium thiosulphate used.

Formol titration according to Söerensen is another method for the determination of amino acids. This method involves blocking the amino group of amino acids with two hydroxymethyl groups, while the free carboxyl group is titrated with the standard solution of NaOH with phenolphthalein as an indicator.

The chlorides in body fluids (urine) can be determined using a precipitometric method consisting in precipitation of the determined component in the form of sparingly soluble sediment. An example of this type of determination is the Volhard method. It is based on acidifying the sample with nitric acid (V), then to the mixture prepared in this way, an excess of standard solution of $AgNO_3$ is added. The chloride contained in the solution will precipitate as a precipitate of AgCl in the solution. There will still be some excess of $AgNO_3$, which is titrated with standard NH_4SCN in the presence of Fe^{3+}. The chloride content in the sample is calculated from the difference between the added and the titrated amount of $AgNO_3$.

Chlorides are anions that constitute up to 2/3 of all plasma anions. They are present also in blood cells and skin. These ions are excreted mainly through the kidneys and with sweat. During the day, the body excretes in the urine 90% of chlorides taken with food.

The main role of chloride ions in our body is:

- maintaining the osmotic pressure that determines the displacement of water in the body
- HCl production in the stomach
- maintaining acid-base balance
- activation of salivary amylase
- regulation of kidney function

Parietal cells of the gastric mucosa produce one of the components of the gastric juice, which is hydrochloric acid, which can be determined by the titration method. The chemical examination of gastric juice is based on the determination of the concentration of free HCl and total acidity. Free HCl is determined by titration with 0.1 mol/L NaOH against methylene yellow.

The physiological role of HCl in the stomach is:

- activation of pepsinogen to pepsin
- providing the optimum pH for the pepsin activity
- denaturation of the food proteins and the inhibition of development of bacterial flora

This study allows to find out not only the state of functioning of the stomach mucosa, but also to draw conclusions about the state of nervous and hormonal mechanisms regulating secretory processes.

Due to the constant metabolism, many acid and alkaline compounds are formed in our body which, accumulating in our system, could change the concentration of hydrogen ions. The presence of bases in the tissues and body fluids that can be used to neutralize acids is called the alkaline reserve. The titration method is used most often for the determination of alkaline reserve.

The principle of its determination is based on adding HCl excess to the plasma in order to release CO_2 from bicarbonates. Part of the HCl is bound, the excess is titrated with NaOH against phenol red, the pH at the end of the titration must be the same as in the plasma before the test.

Water is a chemical compound that is used for food, in the pharmaceutical and cosmetics industries. Depending on the purpose, water must meet certain requirements, that is why it is important to examine water by chemical test. Full water analysis includes qualitative and quantitative determinations (water hardness). The hardness of water is the result of calcium, magnesium and other metal salts dissolved in it. Calcium and magnesium occurring in water in the form of bicarbonates form the so-called Carbonate hardness, which is part of the total hardness.

The carbonate hardness is determined by alkacimetric titration against methyl orange as an indicator. The water sample is titrated with the standard solution of HCl against methyl orange up to the change the color from orange to yellow. The change in color corresponds to the content of bicarbonate ions, which in turn allow to determine the degree of hardness. The total water hardness is determined using a complexometric titration with EDTA solution against the eriochrome T black as an indicator. In order to obtain a clear end point prior to titration, carbonates should be removed from the solution by boiling the sample.