

Volumetric analysis –selected tasks

Libuše Kadlecová

1. Introduction

Volumetric analysis (also **titration determination** or **titration**) is generally one of the **quantitative methods** that deal with determination of **quantity (amount) of particular elements (components) in tested (analysed) material (sample)**. It is preceded by qualitative analysis, when only composition of analysed sample is tested.

Volumetric analysis is carried **in liquid media** and is one of **direct chemical methods**. Next to the direct chemical methods there are instrumental analytical methods used for quantitative determination by means of indirect physico-chemical measurements.

Stoichiometric analytical reactions are used for quantitative determination in volumetric analysis. The requirements for such identification include unidirectionality of the reaction, sufficient rate, no disturbing side reactions and easy identification of the end of reaction, also called **achievement of point of equivalence**.

2. Methods of volumetric analysis - titration

The principle of titration is based on exact measurement of volume of titration solution (reagent). The titration reagent is added from burette to exactly known volume of analysed sample (in titration flask) until the status of quantitative chemical reaction is achieved (point of equivalence). Equivalent amount of analysed substance in the volume of analysed sample or directly the substance concentration is calculated using the stoichiometric relationships of the chemical reaction, from the measured volume of titration reagent spent during titration, from its concentration and the volume of analysed solution.

Titration can be performed as:

- **Direct titration**, where titration reagent is added directly to solution of determined substance until the point when substance amounts of both reagents are equivalent.
- **Indirect titration**, where surplus of titration reagent is added to the solution of determined substance first, and subsequently the formed product is titrated.

- **Back titration**, where an exact volume of titration reagent is added in excess to the solution of determined substance, quantitative reaction runs over and then the remaining surplus of titration reagent is titrated by another titration reagent.

Methods of volumetric analysis are classified according to principle of chemical reaction, on which the titration determination is based:

- **Acid-base titration:** determination of acid or alkaline substances by titration with a hydroxide or an acid, respectively; principle is a neutralization reaction

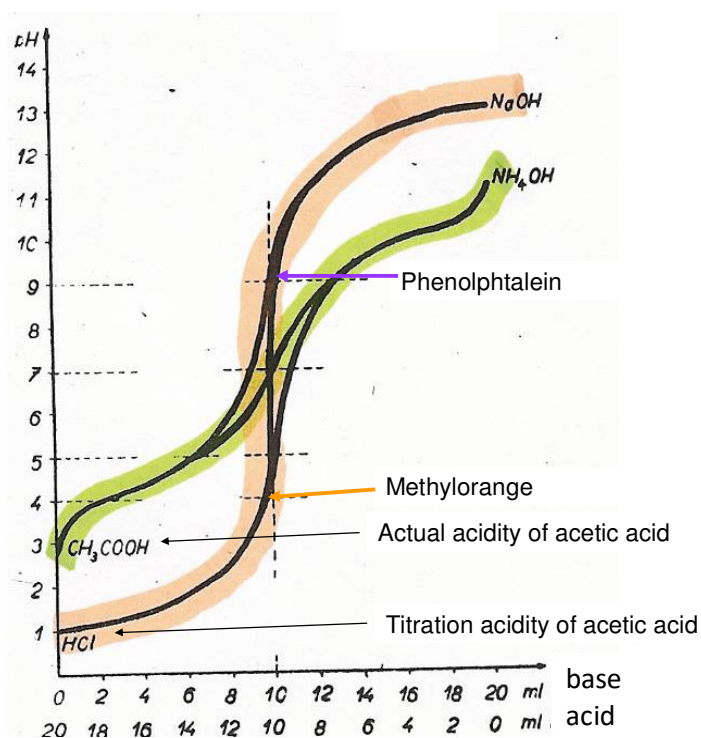
$$\text{H}_3\text{O}^+ + \text{OH}^- \rightleftharpoons 2 \text{H}_2\text{O}$$
- **Complex-forming:** titration where cation of the determined metal is bound to a soluble complex ion, so that the free cation goes away from the solution (see complex compounds).
- **Precipitation:** titration based on production of slightly soluble compounds, titrated substance goes away from solution because it is precipitated (see solubility product). An example is argentometry, based on formation of insoluble salts with cation Ag^+ : titration reagent is AgNO_3 ; it is suitable for determination of Cl^- , Br^- , I^- , CN^- , SCN^- etc.
- **Redox:** titrated substance is oxidized or reduced by oxidizing or reducing titration reagent.

Particular types of titrations can be named according to character of the solution of titration reagent (alkalimetry – volumetric solution is hydroxide, acidimetry - volumetric solution is acid, manganometry – volumetric solution is KMnO_4 etc.). If the end of titration is investigated with some way of instrumental indication, then the titration can be called for example potentiometry, conductometry etc.

3. Titration curves

Concentration of hydrogen ions in titration solution changes according to character of equilibrium reactions between titrated substances and titration reagents during acid-base (neutralization) titrations in water solutions. pH of these solutions can either be calculated from their concentrations, dissociation constants, ionic product of water, or the pH can be measured with pH-meters during the time of titration. Diagram of relationship between pH and amount of added titration reagent is called titration curve (see figure below).

During titration of strong acid with strong hydroxide or vice versa, the resulting salt rises gradually till the point of time, when the titration solution in point of equivalence contains neutral salt and its pH is 7. In case of titration of a weak acid with strong hydroxide the pH of the point of equivalence is moved towards higher values of pH, whereas in case of titration of a weak hydroxide with strong acid the point of equivalence will be moved towards lower values of pH. It is obvious that the biggest change of pH occurs in the point of equivalence. Difference between the terms **titration acidity** and **actual acidity** should be obvious from the measured relationships, too. Titration acidity of a strong acid and a weak acid is approximately the same if the number of proton dissociating groups in the acid molecule and the acid concentration are the same, while the actual acidity is different. pK of weak acids and bases are possible to find out from these relationships (see below).



4. Determination of point of equivalence and indicators

Point of equivalence in chemistry denotes the end of titration – state, where the substance amount of titration reagent (its substance (molar) concentration multiplied by volume spent during titration) is equivalent to the substance amount of determined substance.

5. Indication ways of point of equivalence

- **Visual indication:** subjectively observed change in the appearance of titration solution, such as change of colour, formation of precipitate, and fluorescence. The most often employed is colour change of a suitable organic dye, an **indicator**, added to titration solution. The change of colour occurs just at the moment of when the point of equivalence is achieved.
- **Instrumental indication:** some physical quantities of titration solution are measured by instruments (for example conductivity of the solution, pH etc.) in dependence on the volume of added titration reagent – again, we get the titration curve. Quantity is chosen so that the essential change in the titration curve (e.g. a turning point, break) occurs in the point of equivalence. Consumption of titration reagent is determined from a certain point of this change.

Indicators are substances that react either with the determined substance or with surplus titration reagent. The forms of indicator before and after the reaction have different colours. One form transforms to the other form in the point of equivalence. Indicators are usually substances of the same character as titration reagent or titrated substance. There are many various indicators according to character of titration (see below).

Acid-base indicators (for titration of acids and hydroxides). These are weak organic acids or bases. The acid form ($HInd$), which exists at higher concentration H^+ (lower pH), has different colour than the basic form (Ind^-). Indicator acid and base forms constitute together a conjugate pair with ionization constant K_{HInd} .



Ratio of concentrations of both forms reaches a steady state according to concentration of ions in titration solution – protolytic equilibrium

$$K_{HInd} = \frac{[H^+] \cdot [Ind^-]}{[HInd]} \quad \frac{[Ind^-]}{[HInd]} = \frac{K_{HInd}}{H^+}$$

By mathematic adaptation of the relationship above (negative logarithmic conversion) gives the equation

$$pH = pK_{HInd} - \log \frac{[HInd]}{[Ind^-]}$$

The acid form is present in titration solution during titration determination of an acid, titrated by a basic titration reagent. Both forms are actually present in the point of equivalence. The acid form essentially disappears immediately behind the point of equivalence (it reacts with surplus of basic titration reagent to the basic form). It is obvious that the colour of indicator changes step by step in certain short range around the point of equivalence. Ratio $\log \frac{HInd}{Ind}$ can take the value approximately from -1 to +1 during titration. That is why **the interval of pH for colour transitions of the acid-base indicators (function area) is within 2 pH units.**

Examples of acid-base indicators:

- **Methyl orange, function area pH 3.0–4.4; red/orange;**
Sodium 4-[4-(dimethylamino) phenylazo]benzenesulphonate
- **Methyl red, function area pH 4.4 – 6.2; red/yellow;**
2-(4-dimethylaminofenylazo) benzoic acid
- **Phenol red, function area pH 6.8 – 8.4; yellow/red;**
phenolsulphophthaleine, 3,3-bis(4-hydroxyphenyl)-sulphophthalide)
- **Phenolphthalein, function area pH 8.2 – 10.0; colourless/red-violet;**
3,3-bis(4-hydroxyphenyl)-1(3H)-isobenzofuranone

Indicators of complexometric titrations – **metallochromic**, are substances forming complexes with the determined metal ion. Complex with metal has a different colour than the form of free indicator. Before point of equivalence only the complex form with metal is present. Immediately before point of equivalence, when there is already lack of free ions of determined metal in solution, complexometric titration reagent begins to react with metal ion bound in the complex with indicator and thereby indicator is displaced in free form.

Examples of metallochromic indicators: **eriochrome black T** (transition from violet to blue), **xylene orange** (from red or violet to yellow), **murexide** (from yellow or red to violet).

Indicators of precipitation titrations form coloured precipitation and eventually soluble coloured complexes with surplus of titration reagent immediately behind point of equivalence. These indicators can cause the change of precipitation colour in consequence of adsorption or desorption on particles of precipitate or solution in point of equivalence (see argentometry, solubility product).

Indicators of redox reactions are substances that have different colour in reduced form than in oxidized form. The first surplus of oxidized titration reagent converts reduced form of the indicator to the oxidized one immediately behind the point of equivalence, (examples **benzidine** or **diphenylamine** – conversion from colourless to blue). Number of redox indicators behave in an irreversible way, such as some of colour substances (for example **methyl red**), which after the first surplus of oxidized reagent get themselves oxidized, then break down and decolourization develops. The colour of the reduced form cannot be obtained back by reduction.

6. Preparation of titration reagents

The titration reagent of an exact concentration can be prepared by exact weighing out of the substance, dissolution and refilling of distilled water up to the mark on volumetric flask. This way of preparation is used, when the substance is stable, standard and chemically pure. A very common way of preparation of a titration reagent is that the reagent is prepared at an approximate concentration and then by means of this titration reagent is titrated an accurate volume of a standard solution that has the exact concentration equivalent to what should be in the titration reagent – it means **standardization of titration reagents**. By this way **titration factor f** of the titration reagent is determined as a ratio of theoretical volume of titration reagent in ml and actual volume of titration reagent in ml. This titration factor is used for adjustment of the substance (molar) concentration to calculate concentration of substance from titration determination:

$$f = \frac{\text{volume of theoretical consumption of titration reagent (ml)}}{\text{volume of actual consumption of titration reagent (ml)}}$$

If concentration of titration reagent is exact, $f = 1$.

If concentration of titration reagent is more diluted, $f < 1$.

If concentration of titration reagent is more concentrated, $f > 1$.

7. Titration

Burette is rinsed out with distilled water and titration reagent of known concentration is filled into burette using a funnel. The volume of solution of the analysed substance (sample) is exactly measured off in a pure titration flask and a few drops of suitable indicator are added as well. Titration flask is gently rotated and at the same time a small volume of titration reagent is carefully added from burette step by step. When we get near to the end of titration, the

change of titrated solution (colour, turbidity etc.) becomes evident. In this time it is needed to add the titration reagent very slowly drop by drop till a stable change of titrated solution is achieved. Titration is repeated three times. The first titration is route-identification, it serves for testing (checkout) of colour transition of indicator or other changes (it is easily over-titrated, meaning more volume of titration reagent is consumed). Average consumption of the second and third titrations is used to calculate the concentration. Colour solution is better to observe against a white background, whereas arising white turbidity is better seen against a black background.

8. Calculation of substance (molar) and mass concentration from titration determination

Calculation of concentrations determined by means of a titration goes out from the state where chemical reaction runs over quantitatively in stoichiometric ratio and the corresponding substance amounts of the titration reagent and titrated substance are equal in the equivalence point. If X mols of titration reagent react with Y mols of titrated substance in solution, then generally the following equation is valid

$$\frac{n_x}{X} = \frac{n_y}{Y}$$

After substituting the product of concentration and volume instead of the substance amount n , then this relationship is valid

$$\frac{c_x \cdot V_x}{X} = \frac{c_y \cdot V_y}{Y}$$

where n_x substance amount of substance x (titration reagent)

n_y substance amount of substance y (titrated substance)

X number of reacting molecules of substance x

Y number of reacting molecules of substance y

c_x concentration of substance x

c_y concentration of substance y

V_x volume of solution substance x

V_y volume of solution substance y

Example

For titration of 10 ml of NaOH solution 8 ml of sulphuric acid was used, of concentration exactly $c = 0.1$ mol/l. What will be the molar and mass concentration of titrated NaOH solution?

Solution

Chemical equation of titration is



Titration reagent H_2SO_4 ($X = 1$ mol), titrated compound NaOH ($Y = 2$ mols).

By adaptation of the above relationship we get

$$Y \cdot c_x \cdot V_x = X \cdot c_y \cdot V_y$$

After substitution

$$2 \cdot 0.1 \cdot 8 = 1 \cdot c_y \cdot 10$$

$$c_y = \frac{2 \cdot 0.1 \cdot 8}{1 \cdot 10} = 0.16 \text{ mol/l}$$

Molar concentration NaOH $c_y = 0.16$ mol/l.

Conversion to mass concentration ($M_{r \text{NaOH}} = 40$)

$$w = \frac{m}{V} = M_r \cdot \frac{n}{V} = 40 \cdot 0.16 = 6.4 \text{ g/l}$$

Mass concentration NaOH $w = 6.4$ g/l.

References:

Karlíček R. et al. (2001): Analytická chemie pro farmaceuty. (Analytical chemistry for pharmacists – in Czech). Karolinum, Publisher Charles University.

Kraml J. et al. (1999): Návody k praktickým cvičením z lékařské chemie a biochemie. (Guide to practise from medical chemistry and biochemistry – in Czech) Karolinum, Publisher Charles University.

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