Titrimetry | Overview☆

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Introduction

Titrimetry refers to a group of methods of quantitative analysis in which an analyte is determined basing on its stoichiometric reaction with a reagent of established concentration introduced to a sample gradually, in small portions until the analyte is consumed quantitatively. The end of the reaction can be detected visually, using a properly selected indicator or with the use of an instrumental method. The content of the analyte in the sample is calculated basing on properly measured amount of the reagent consumed in the reaction with the analyte, the reagent solution concentration and the reaction stoichiometry.

Titrimetry is one of the oldest analytical techniques. Its continued popularity stems from the simplicity of equipment and execution, wide applicability, and high accuracy and precision (greater than most instrumental techniques), all of which make it particularly applicable to the determination of major and minor components of samples. Skilled titrimetric analysis should give results with a precision lower than 0.2% at the 1×10^{-2} mol L^{-1} level.

Titrimetry may be classified with respect to the types of reaction that are involved. The major reactions are acid–base reactions (acid–base titrimetry), redox reactions (redox titrimetry), complexing reactions (complexometric titrimetry), and precipitation reactions (precipitation titrimetry). Titrimetry may also be classified by the nature of the measurement of the end point of titration. The use of electrical measurements gives rise to potentiometric and amperometric titrations. Measurement of heat changes is used in thermometric titrimetry, and of absorbance in photometric and turbidimetric titrations. Radiometric titrations measure changes in radioactivity during the titration. This article discusses the titrations that use the visual end point detection.

Titrimetric Analysis

Basic Terms in Titrimetric Analysis

Titrant—a standard solution of exactly known concentration of a reagent.

Titration—a process of determination of an analyte in which a titrant is gradually added to a sample solution until the reaction with the analyte is completed.

Volumetric titration—a type of titration in which the amount of titrant consumed in the reaction with an analyte is measured volumetrically.

Gravimetric titration—a type of titration in which the amount of titrant consumed in the reaction with an analyte is measured gravimetrically (usually applied when a greater accuracy than in the volumetric titration is required).

Coulometric titration—a type of titration in which a reagent is generated electrochemically.

☆*Change History*: April 2018. Kozak introduced Abstract, Section 2.1 and Supplementary material; made changes in Sections 1–7; moved a part of section Redox titrations to Supplementary material; introduced Figs. 1, 3, (4B)–(6B); made changes in Figs. 2, (4A)-(6A); removed Figs. 5–8 (previous numbering of the figures); introduced Table 2; moved Table S1 (previous number 3) to Supplementary material; made changes to Table 3 (previous number 4); removed Tables 2 and 5 (previous numbering; the information was introduced into the text); removed some positions from References and Further reading; introduced new positions to Further reading.

Primary/secondary standard—an ultrapure compound/a compound whose purity was established by a chemical analysis, used as the reference material in titrimetric analysis.

Standardization—a process in which the concentration of titrant solution is established for example, by titrating it against a weighed quantity of a primary (or a secondary) standard.

The equivalence point—the point in a titration (the stage of the titration) in which the amount of the dispensed titrant is equivalent to the amount of an analyte, according to the stoichiometry of the reaction.

The end point—the point in a titration (the stage of the titration) in which a change of a physical property of the titrated sample solution (e.g., the change of color) associated with achieving the equivalence point is observed. The end point of titration can be detected visually or instrumentally (by measuring e.g., conductivity, pH or absorbance).

Indicator—a substance added to a titrated sample whose change of physical property appears at or close to the equivalence point and indicates the end point of titration.

Titration curve—a plot showing the relationship between a p-function of an analyte (or a reagent, in back titrations) concentration ($-\log[X]$, where $[X]$—analyte concentration), or a signal registered by an instrument, and a volume of titrant introduced to a sample (Fig. 1A and B, respectively), usually applied to identify the end point in titrations with instrumental detection.

Titration error—the difference between the amount of titrant added to the sample to achieve the end point of titration and the theoretical amount of titrant necessary to obtain the equivalence point.

Back titration—a type of titration in which two different titrants are used. At the first stage, a measured volume of titrant I is added to a sample in excess. After the reaction with an analyte is completed, the excess of the titrant I is titrated with the titrant II. Back titration is applied to the analyte-reagent reactions of slow rate.

Basic Equipment for Titrimetric Analysis

The accuracy and precision of titrations is critically dependent on the use of correct experimental technique by the analyst. As in most analytical procedures, accurate measurement of the amount of sample (or sample aliquot) is necessary, but it is most important in titrimetry if an accuracy of <0.2% is to be achieved. Thus, proper use of a pipette, buret, and balance, and a careful sample preparation procedure is crucial. Measurement devices of high quality, such as class A flasks, pipettes and burets should be used. The simple equipment used for volume measurements in titrimetric analysis is shown in Fig. 2.

Preparation of Titrant Solution

Titrimetric analysis depends upon the availability of titrant solutions. They can be prepared directly using primary standards, or standardized by titration of weighed quantity of a primary (or secondary) standard dissolved in an appropriate solvent or of another titrant solution. The primary standard should be characterized by a high purity, be stable at normal conditions, should not contain of hydrate water (or show a stable composition with hydrate water), be soluble and have a large molar mass to decrease the effect of small weighing errors. It is also possible to buy concentrated standard solutions, which can be used after dilution. Selected primary standards used in titrimetric analysis are given in Table 1.

The Course of Titration

Conventional volumetric titration is carried out with the use of a setup consisting of a buret positioned vertically (with the use of a buret stand and a clamp) above an Erlenmeyer flask. The scheme of the setup is presented in Fig. 3A. The end of the buret is placed in the mouth of the Erlenmeyer flask. The Erlenmeyer flask is usually located on a white background to allow the proper detecting of the end point of titration.

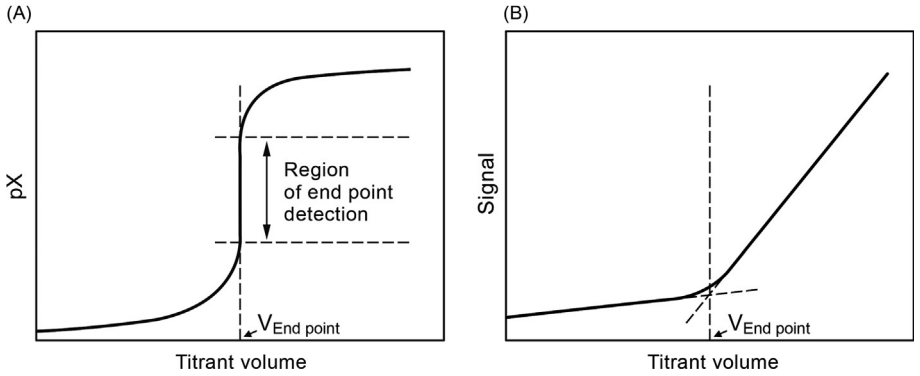

Fig. 1 Examples of titration curves obtained in titrimetric analysis with a visual (A) and an instrumental (B) detection, and the ways of the end point determination.

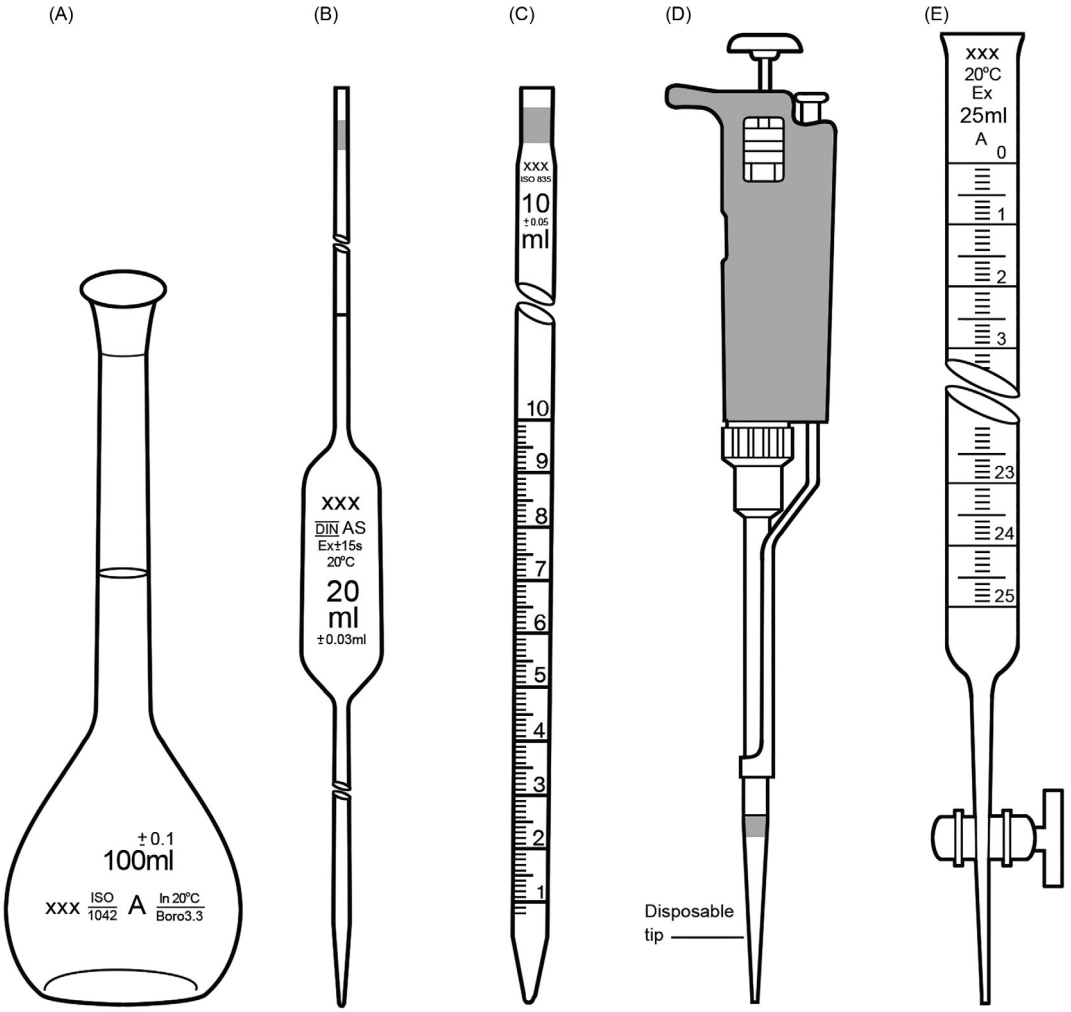

Fig. 2 Selected pieces of equipment used in titrimetric analysis; (A) volumetric flask, (B) volumetric pipet to deliver a single, defined volume of a solution, (C) measuring pipet to deliver any volume up to the pipet maximum capacity, (D) automatic pipet with disposable tip to deliver a single specified volume (or a selected volume, in case of variable-volume automatic pipets) of solution (motorized and computer-controlled pipets are also available); (E) buret to measure any delivered volume up to the buret maximum capacity; information on the volumetric pipet: XXX—manufacturer; A—class of the glassware; S—rapid delivery; DIN—standard according to which the class was determined; Ex ± 15s—calibration to deliver the specified volume and waiting time; 20°C—temperature at which the calibration applies; 20 ± 0.03 mL—rated and tolerance volumes.

At the beginning of a volumetric (direct) titration the buret is filled with a titrant solution to the zero position at the top. A sample solution for analysis is measured with the use of a pipet (Fig. 2B) (or by weighing) and delivered into the flask. Depending of the type of titrimetric reaction, a small portion of an indicator is placed into the flask, if necessary. The indicator in solid phase should be dissolved in the sample solution.

During the titration, the titrant is added gradually, in small portions (drops), to the flask containing sample which is swirled continuously (by hand or using a magnetic stirrer). At the beginning of titration, the titrant can be added more quickly, but approaching to the end point of titration (which e.g., can be observed as a transient color change in the portion of the solution where the drop of titrant is added), the dispensed portions (drops) should be added so slowly to allow for the detection of the end point after adding of each single drop. When the end point of titration is observed (as e.g., the change of color of the sample solution), the titration with visual detection is considered as completed. The volume of the consumed titrant is measured using the buret scale. The proper position of an eye for reading the level of meniscus of a transparent solution is indicated in Fig. 3B. The detection of the endpoint, when using a 50 or 25 mL burette, should be possible to within 0.02 mL.

Acid–Base Titrimetry

Acid–base (neutralization) titrations include reactions in which acid is used as a sample and base as a titrant, and vice versa. Acid–base titrations are widely used in chemical analysis to determine acidic or basic substances or to monitor the progress of

Table 1 Selected primary standards used in titrimetric analysis

Compound	*Formula*	*Type*	*Type of titration*
Anhydrous sodium carbonate	Na_2CO_3	Weak base	Acid–base
Sodium borate (borax)	$Na_2B_4O_7 \cdot 10H_2O$	Weak base	Acid–base
Sulfamic acid	NH_2SO_3H	Strong acid	Acid–base
Potassium hydrogen phthalate	$KHC_8H_4O_4$	Weak acid	Acid–base
Potassium hydrogen biiodate	$KH(IO_3)_2$	Strong acid	Acid–base
Silver nitrate	$AgNO_3$		Argentimetric
Sodium oxalate	$Na_2C_2O_4$	Reductant	Redox
Arsenic(III) oxide	As_2O_3	Reductant	Redox
Potassium dichromate	$K_2Cr_2O_7$	Oxidant	Redox
Ammonium hexanitrocerate (IV)	$(NH_4)_2Ce(NO_3)_6$	Oxidant	Redox
Potassium iodate	KIO_3	Oxidant	Redox
Potassium bromide	$KBrO_3$	Oxidant	Redox
Calcium carbonate	$CaCO_3$	Source of calcium ions	Complexometric
Zinc oxide	ZnO	Source of zinc ions	Complexometric
Ni, Zn, Cu metals	Ni, Zn, Cu	Source of metal ions	Complexometric
Anhydrous disodium EDTA	$C_{10}H_{14}N_2O_8Na_2$	Complexing agent	Complexometric

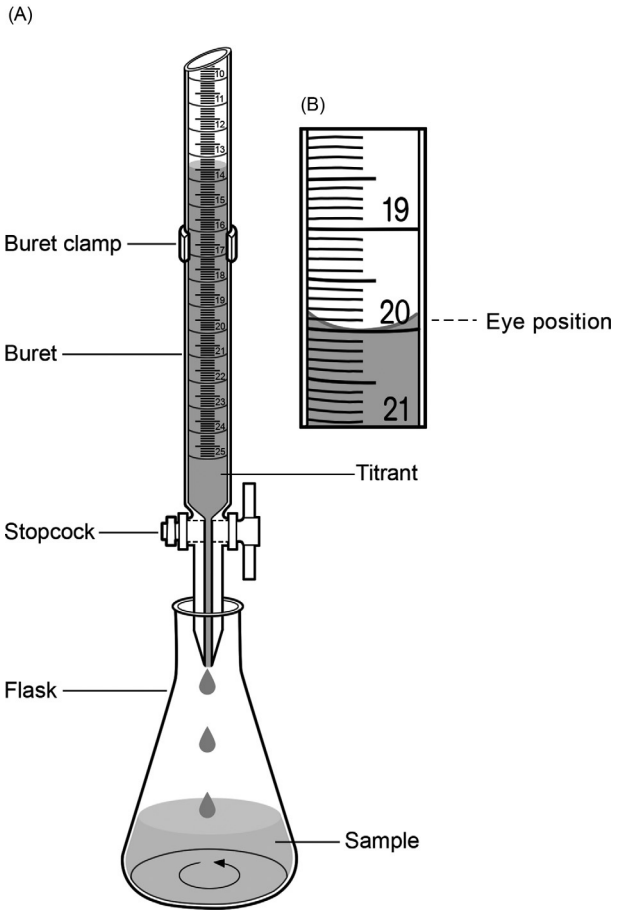

Fig. 3 Typical set up for manual, volumetric titration (A) and the proper eye position for reading the level of meniscus of a transparent solution, the volume of 20 mL corresponds to the end point of titration (B); flask—usually Erlenmeyer flask (250 or 100 mL).

reactions that produce or consume hydrogen ions. Analysis of a titration curve enables also determination of acidic and basic components in a mixture and their p*K* values.

Indicators used for the detection of the end point of the acid–base titrations are usually organic compounds (weak organic acids or weak organic bases) which change their colors within a defined pH range. The change of the color is connected with dissociation

(and/or the change of the structure) of the compound. Many indicators show a complete color change in the range of about two pH units ($pK \pm 1$). Selected acid–base indicators and their transition ranges are given in Table 2.

In acid–base titrimetry, strong acids (HCl, $HClO_4$, H_2SO_4) and strong bases (NaOH, KOH) are used as titrants. They are prepared by diluting concentrated solutions and standardized against anhydrous sodium carbonate (Na_2CO_3) or borax ($Na_2B_4O_7 \cdot 10H_2O$), and oxalic acid ($H_2C_2O_4$), potassium hydrogen phthalate ($KHC_8H_4O_4$) or potassium hydrogen iodate ($KH(IO_3)_2$), respectively.

In acid–base titrimetry, the essential reaction is between H^+ and OH^-, giving water. The pH at the equivalence point depends on the dissociation constants of reactants and products. Thus, the titration of a strong, that is, almost completely dissociated acid with strong, almost completely dissociated, base reaches equivalence at pH 7.0. For this type of titration, an abrupt change of pH in a wide range is obtained for the volume of titrant corresponding to the equivalence point of titration (Fig. 4). As a the change of pH corresponds to adding a small portion (a drop) of the titrant, and achieving the equivalence point of titration, indicators which transition range of color is contained in this range of pH can be used to indicate the end point of titration. In case of titration of a strong acid (e.g., HCl) with a strong base (e.g., NaOH), and vice versa, several indicators can be used, among them bromocresol green, bromothymol blue or phenolphthalein (Fig. 4).

The extent of the pH change also depends on the concentration of the analyte and titrant. Fig. 4 shows how the pH change decreases with decreasing concentration of HCl and NaOH. Indicators for such titrations are chosen to change color very close to the pH corresponding to the equivalence point of titration (e.g., bromothymol blue).

If a weaker, that is, less dissociated acid, such as acetic acid, is titrated with a strong base (NaOH), the equivalence pH is >7.0, the weaker the acid, the higher the equivalence pH. Likewise, if a weak, that is, less dissociated, base (e.g., ammonia) is titrated with a strong acid (HCl), the equivalence pH is <7.0, and the equivalence value of pH decrease with increasing weakness of the base. For the titration of a weak acid or a weak base, the pH change corresponding to the equivalence point is not as sharp as for a strong acid or strong base titration. Therefore, there is a less number of indicators that can be applied to the proper end point detection. The change of pH during the course of such titrations is illustrated in Fig. 5. It can be noticed that from the indicators presented in Fig. 5, only phenolphthalein and bromocresol green can be applied to detect the end point during the titrimetric determination of acetic acid and ammonia, respectively.

Some acids are polybasic, that is, they give rise to more than one hydrogen ion. Phosphoric acid, for example, dissociates gradually giving three hydrogen ions.

$$H_3PO_4 \rightleftarrows H_2PO_4^- + H^+ \quad (1)$$

$$H_2PO_4^- \rightleftarrows HPO_4^{2-} + H^+ \quad (2)$$

$$HPO_4^{2-} \rightleftarrows PO_4^{3-} + H^+ \quad (3)$$

The change in pH on titration with NaOH is shown in Fig. 6. The first dissociation (Eq. 1) occurs most easily, and titration with NaOH gives an equivalence point at pH 4.5. Further titration, of the second, more strongly bound hydrogen ion (Eq. 2), also gives rise to an equivalence point, at pH 9.6. The third hydrogen ion does not give rise to a sharp endpoint. Thus, phosphoric acid may be determined by titration to the first or second endpoints in the presence of bromocresol green or thymolphthalein, respectively.

Similar situation is observed during the titration of sodium carbonate with hydrochloric acid:

$$Na_2CO_3 + HCl \rightleftarrows NaHCO_3 + NaCl \quad (4)$$

$$NaHCO_3 + HCl \rightleftarrows NaCl + H_2O + CO_2 \quad (5)$$

Two changes of pH can be observed in titration curve. The titration can be carried out to the first end point in the presence of phenolphthalein or, to more clear—the second end point, in the presence of methyl orange.

Table 2 Selected acid–base indicators

Indicator	*Transition range, pH*	*Color change*	
Methyl orange	3.1–4.4	Red	Orange
Bromocresol green	3.8–5.4	Yellow	Blue
Methyl red	4.2–6.3	Red	Yellow
Bromothymol blue	6.2–7.6	Yellow	Blue
Phenolphthalein	8.3–10.0	Colorless	Red
Thymolphthalein	9.3–10.5	Colorless	Blue

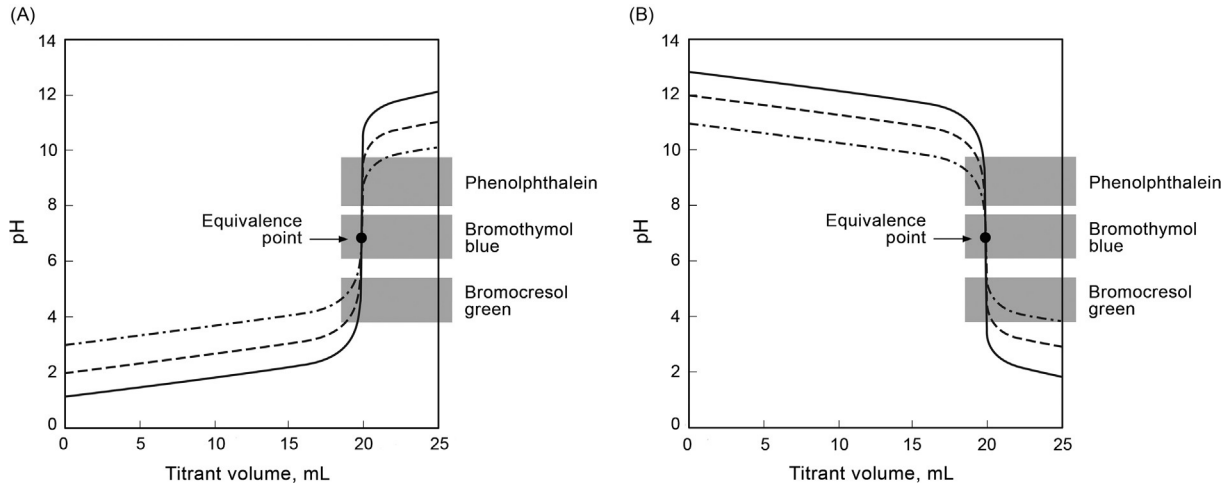

Fig. 4 Titration curves for titration of 20 mL of hydrochloric acid of various concentrations with sodium hydroxide solutions of the same concentration (A) and 20 mL of sodium hydroxide of various concentrations with hydrochloric acid solutions of the same concentration (B): concentrations: 0.1 (_____), 0.01 (- - - -) and 0.001 (- · - ·) mol L^{-1}, and the transition range for the selected end point indicators.

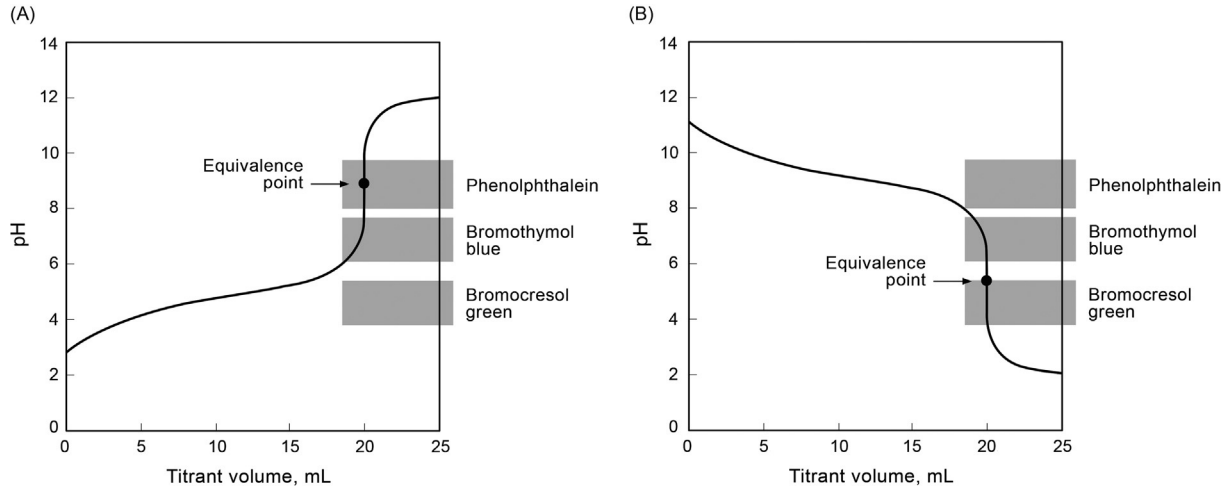

Fig. 5 Titration curve for titration of 20 mL of 0.1 mol L^{-1} acetic with 0.1 mol L^{-1} sodium hydroxide solution (A) and 20 mL of 0.1 mol L^{-1} ammonia with 0.1 mol L^{-1} hydrochloric acid solution (B), and a transition range for selected end point indicators.

Precipitation Titrimetry

In precipitation titrimetry an analyte and titrant react to form a precipitate. In precipitation titrimetry, the most widely used titrant is silver nitrate (a primary standard in argentometric titrations). Its use is mainly restricted to the determination of chloride, bromide, iodide, cyanide, and thiocyanate, although in principle any species that is precipitated by silver ions could be determined.

In precipitation titrations, the change of the titration curve at the equivalence point region depends on the solubility constant of the formed compound (the change increases with decreasing the solubility of a compound), and on the concentrations of an analyte, and titrant. Indicators (e.g., potassium chromate, iron(III), or fluorescein compounds) are usually selected individually for a method.

Mohr and Volhard methods are the examples of precipitation titrations used for determining the halide ions in aqueous solutions. In Mohr method, chloride ions are titrated directly at a pH 7–10 using $AgNO_3$ as the titrant and potassium chromate as an indicator. The Volhard method is an example of an indirect (back-titration) procedure, in which the measured excess of precipitant ($AgNO_3$, used as titrant I) is added to the acidic sample solution and the unreacted Ag^+ ions are titrated with potassium thiocyanate (titrant II), using iron(III) as an indicator. Volhard method can be also used for the determination of for example, Br^-, I^-, AsO_4^{3-}, SCN^- and other ions, taking into account the method modifications.

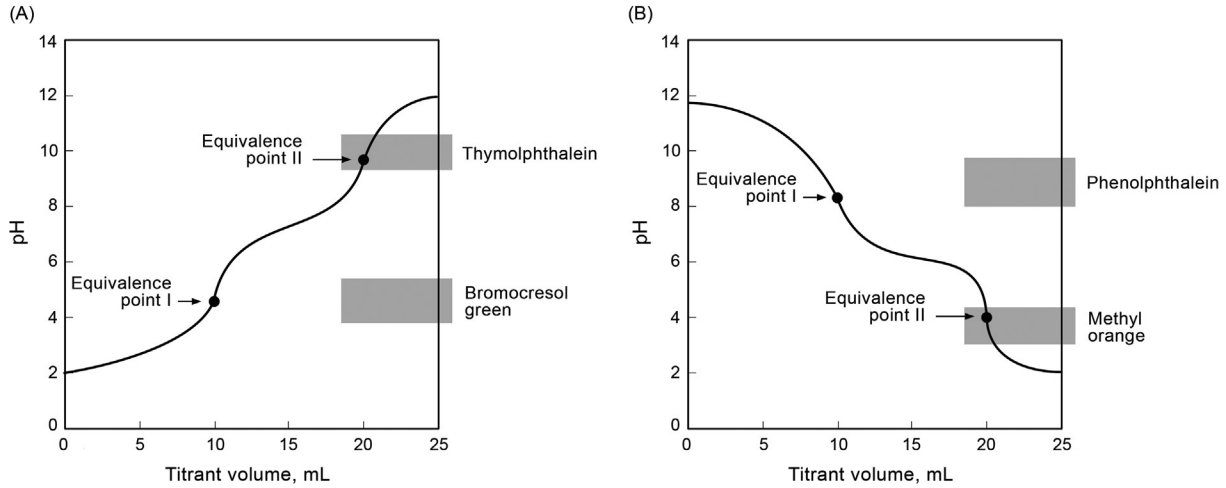

Fig. 6 Titration curve for titration of 10 mL of 0.1 mol L^{-1} H_3PO_4 with 0.1 mol L^{-1} NaOH (A) and 10 mL of 0.1 mol L^{-1} $Na_2C_2O_3$ with 0.1 mol L^{-1} HCl (B), and a transition range for selected end point indicators.

Redox Titrimetry

In redox titrimetry, a reducing agent is titrated with an oxidizing agent, or vice versa. The common oxidizing titrants are potassium permanganate ($KMnO_4$), potassium dichromate ($K_2Cr_2O_7$), cerium(IV) sulfate ($Ce(SO_4)_2$), iodine (I_2), potassium iodate (KIO_3), and potassium bromate ($KBrO_3$). The most important reducing titrants are iron(II) salts, ammonium iron(II) sulfate ($(NH_4)_2Fe(SO_4)_2{\cdot}6H_2O$), sodium thiosulfate ($Na_2S_2O_3{\cdot}H_2O$), and arsenic(III) oxide (As_2O_3).

The stoichiometry of the reaction between one of these titrants and a particular analyte is established by combining the appropriate half-reactions. For some of the titrants above, the half-reactions are as follows.

Oxidants:

$$MnO_4^- + 8H^+ + 5e^- \rightleftarrows Mn^{2+} + 4H_2O \ (\text{acidic conditions},\ E^0 = +1.52\ \text{V}) \tag{6}$$

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \leftrightarrows 2Cr^{3+} + 7H_2O \ (E^0 = +1.33\ \text{V}) \tag{7}$$

$$Ce^{4+} + e^- \rightleftarrows Ce^{3+} \ (E_f^0 = +1.44\ \text{V}\ H_2SO_4\ 0.5\ \text{mol}\ L^{-1}) \tag{8}$$

$$I_2 + 2e^- \rightleftarrows 2I^- \ (E^0 = +0.54\ \text{V}) \tag{9}$$

$$BrO_3^- + 6H^+ + 6e^- \rightleftarrows Br^- + 3H_2O \ (E^0 = +1.45\ \text{V}) \tag{10}$$

Reductants:

$$Fe^{3+} + e^- \rightleftarrows Fe^{2+} (E_f^0 = +0.68\ \text{V}\ H_2SO_4\ 0.5\ \text{mol}\ L^{-1}) \tag{11}$$

$$S_4O_6^{2-} + 2e^- \rightleftarrows 2S_2O_3^{2-} \ (E^0 = +0.09\ \text{V}) \tag{12}$$

E^0 is a constant known as the standard potential, which is the idealized potential when [Ox] = [Red]. A similar parameter, but measured under actual experimental conditions, is known as the formal potential (E_f^0), and is more useful for application in redox titrimetry. For example, iron(II) can be determined by titration with dichromate, so combination of the appropriate half-reactions (7) and (11), so as to achieve a charge and mass balance, gives the overall reaction (13):

$$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \leftrightarrows 2Cr^{3+} + 6Fe^{3+} + 7H_2O \tag{13}$$

The driving force for each half-reaction is measured by its oxidation potential, E, measured in V, which is given by the Nernst equation:

$$E = E^0 + \frac{0.059}{n} \log \frac{[Ox]}{[Red]} \tag{14}$$

where n is the number of electrons involved in the above half-reaction, and [Ox] and [Red] are the concentrations (or better, activities) of the oxidized and reduced forms of the species, respectively. Redox titration curve shows the changes of the redox potential during the course of titration. The range of the changes depends on the differences between potentials of reagents and the

on concentrations of the solutions. The final oxidation potential increases with the strength of the oxidant used. Sometimes, it is possible to make a simple calculation of the equivalence potential (E_{EP}) as follows. For the reaction that can be written as in (15):

$$Fe^{2+} + Ce^{4+} \rightleftarrows Fe^{3+} + Ce^{3+} \tag{15}$$

then

$$E_{EP} = \frac{E^{o}_{f}\left(Ce^{4+}/Ce^{3+}\right) + E^{o}_{f}\left(Fe^{3+}/Fe^{2+}\right)}{2} = \frac{1.44 + 0.68}{2} = 1.06\ V \tag{16}$$

For more complex systems, however, especially those involving oxoanions, such simple calculations are not valid.

Indicators for redox titrations will be chosen to change the color reversibly by oxidation or reduction at a potential as close as possible to the equivalence potential (diphenylamine, ferroin). The exceptions are starch used for iodine indication or $KMnO_4$ used as a self-indicating reagent.

Redox titrations are still used, for example, for the determination of analyte/titrant: Fe(II), Fe(III), $H_2O_2/KMnO_4$, nitrite/Ce $(SO_4)_2$, Cu(II), O_2, acids/$Na_2S_2O_3$. Table 3 summarizes some applications of redox titrations.

Complexometric Titrimetry

Complexometric titrations are used mainly to determine metal ions by use of complex-forming reactions. Although many complexing agents (cyanide, thiocyanate, fluoride, 1,2-diaminoethane, etc.) can be used for this purpose, in practice the titrants are almost always compounds having the iminodiacetic acid functional groups. The most widely applied are ethylenediaminetetraacetic acid, H_4Y (Fig. 7) and the dihydrate of the sodium salt, $Na_2H_2Y \cdot 2H_2O$ (better soluble in water).

EDTA fulfills most of the conditions for a good complexometric titrant. It forms sufficiently stable complexes with most metal ions (except the alkali metals which form too weak complexes), all the complexes have exact 1:1 stoichiometry (regardless of the charge of the cation), the reaction with most metal ions (except Cr^{3+}) is rapid, the complexes are water soluble and colorless (unless the metal ion itself is colored). The reaction between a typical metal ion and EDTA (H_4Y) can be written as:

$$Me^{n+} + H_4Y \rightleftarrows MeY^{(4-n)-} + 4H^{+} \tag{17}$$

that is, as a competition between the metal ion and hydrogen ions for binding with Y^{2-}. The stability of binding of Me^{n+} with Y^{2-} is measured by its stability constant K_{MeY}, which is the equilibrium constant for the reaction:

$$Me^{n+} + Y^{4-} \rightleftarrows MeY^{(4-n)-} \tag{18}$$

$$K_{MeY} = \frac{\left[MeY^{(4-n)-}\right]}{\left[Me^{n+}\right]\left[Y^{4-}\right]} \tag{19}$$

where "square brackets" denote concentrations (or better, activities). Values of stability constants for selected complexes of metal ions with EDTA (valid at 20°C, at ionic strength of 0.1) are as follows $Me^{n+}/\log K_{MeY}$: Ag^{+}/7.20, Mg^{2+}/8.69, Ca^{2+}/10.70,

Table 3 Selected examples of redox titrations

Analyte	*Titrant*	*Indicator*	*Remarks*
Iron(III)	$KMnO_4$	Self-indicating	$SnCl_2$ reduction
H_2O_2	$KMnO_4$	Self-indicating	–
Iron	$K_2Cr_2O_7$	Diphenylamine sulfonic acid	In iron ore, $SnCl_2$ reduction
Ethanol	$K_2Cr_2O_7$	*N*-Phenylanthranilic acid	Add excess oxidant, heat, back-titrate with iron(II)
Oxalate	$Ce(SO_4)_2$	Nitroferroin	Add excess oxidant, heat, back-titrate with iron(II)
Nitrite	$Ce(SO_4)_2$	Ferroin	Add excess oxidant, back-titrate with iron(II)
Antimony(III)	I_2	Starch	–
Copper(II)	$Na_2S_2O_3$	Starch	Iodide oxidized to iodine
Acids	$Na_2S_2O_3$	Starch	$5I^{-} + IO_3^{-} + 6H^{+} \rightarrow 3I_2 + 3H_2O$
Available chlorine	$Na_2S_2O_3$	Starch	Oxidation of I^{-} to I_2
O_2	$Na_2S_2O_3$	Starch	Add a mixture of Mn^{2+}, NaOH and KI, dissolve the precipitated $Mn(OH)_3$ with H_2SO_4, Mn^{3+} oxidizes I^{-} to I_2
Magnesium(II)	$Na_2S_2O_3$	Starch	Precipitate Mg^{2+} with 8-quinolinol, add excess $KBrO_3$/KBr to brominate precipitate, determine excess $KBrO_3$ by oxidation of I^{-} to I_2
Phenol	$Na_2S_2O_3$	Starch	Add excess $KBrO_3$/KBr to brominate phenol, determine excess $KBrO_3$ by oxidation of I^{-} to I_2

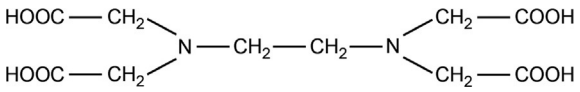

Fig. 7 Ethylenediaminetetraacetic acid, H_4Y.

Mn^{2+}/13.79, Fe^{2+}/14.33, Pb^{2+}/18.00, Ni^{2+}/18.62, Cu^{2+}/18.80, Al^{3+}/16.13, Fe^{3+}/25.1, Bi^{3+}/27.9.[1] Generally metals forming weaker complexes require less acidic (i.e., higher pH) conditions for complex formation. Metals forming stronger complexes can be titrated at lower pH values, at which the weaker complexing metals do not react, thus selective titration of Fe^{3+} or Bi^{3+} can be carried out in the presence of Mg^{2+} and Ca^{2+} or Pb^{2+}, respectively at pH 1–2. The reaction of metal ions with EDTA (Eq. 17) generates H^+. Thus, to prevent a pH change during the titration, the solution must be adequately buffered.

A titration curve in complexometric titrations shows relationship between pMe and the titrant volume. The change of the pMe in the end point region increases with the increase of the stability constant of the formed complex. Titration with visual detection is possible for a complex of stability constant higher than 10^7. The change in titration curve depends also on the concentration of sample and titrant solution analogously to other titration types.

The most common indicators in complexometric titrations are organic dyes which function by forming a colored complex with the metal ion being titrated. During the reaction, EDTA replaces the indicator to form a more stable complex with metal and when the reaction is completed the change for the color is observed. The new color corresponds to the color of the free ligand of indicator (at a given pH). To observe a distinct change of the color at the end point of titration, the stability constant of the complex metal-indicator should be not lower than 10^4–10^5 and be appropriately lower than the stability constant of the formed complex metal-EDTA. The ratio of these stability constants should be 10^4–10^5.

The example of an indicator is Eriochrome Black T (H_2Ind^-) which behaves as an acid/base indicator and as a metal ion indicator. It can be used in the titration of several cations (Mg^{2+}, Zn^{2+}, Cd^{2+}). Its behavior as a week acid can be described in a following way:

$$\underset{\text{Red}}{H_2Ind^-} \xrightarrow{pH\ 6.3} \underset{\text{Blue}}{HInd^{2-}} \xrightarrow{pH\ 11.5} \underset{\text{Orange}}{Ind^{3-}} \tag{20}$$

The titration is usually carried out at pH 10. During the determination of Mg^{2+}, the reaction with the indicator (21) and then, with the titrant (22) occurs:

$$Mg^{2+} + \underset{\text{Blue}}{HInd^{2-}} \rightarrow \underset{\text{Red}}{MgInd^-} + H^+ \tag{21}$$

$$\underset{\text{Red}}{MgInd^-} + H_2Y^{2-} \rightarrow \underset{\text{colorless}}{MgY^{2-}} + \underset{\text{blue}}{HInd^{2-}} + H^+ \tag{22}$$

Hence, the change of the color from red (excess of $MgInd^-$) to blue ($HInd^{2-}$) is observed at the end point of titration.

The Eriochrome Black T can be also applied to determine the sum of Ca^{2+} and Mg^{2+} (at pH 10) (the method also used for the determination of water hardness). Ca^{2+} cannot be determined with the use of Eriochrome Black T because the complex $CaInd^-$ is too weak to obtain the distinct change of the color at the end point of titration. During the titration of Ca^{2+} in the presence of Mg^{2+} the reactions occur in the following sequence:

$$Mg^{2+} + HInd^{2-} \rightarrow MgInd^- + H^+ \tag{23}$$

$$Ca^{2+} + HInd^{2-} \rightarrow CaInd^- + H^+ \tag{24}$$

$$CaInd^- + H_2Y^{2-} \rightarrow CaY^{2-} + HInd^{2-} + H^+ \tag{25}$$

$$MgInd^- + H_2Y^{2-} \rightarrow MgY^{2-} + HInd^{2-} + H^+ \tag{26}$$

Magnesium forms the least stable complex with EDTA than common multivalent cations present in typical water samples. Hence, it is titrated when the appropriate amount of titrant has been added to complex Ca^{2+} (and all of the other) cations in the sample. Therefore, the end point of titration corresponds to the titration of Mg^{2+} ions.

In complexometric displacement titrations, for example, when no indicator for an analyte is available, magnesium-EDTA complex is introduced into the analyte (Me^{2+}) solution in excess. If the analyte forms more stable complex with EDTA, the following reaction occurs:

$$MgY^{2-} + Me^{2+} \rightarrow MeY^{2-} + Mg^{2+} \tag{27}$$

As a result, Mg^{2+} released in the equivalent amount to Me^{2+}, is titrated with EDTA solution.

If a weaker-complexing metal ($Me_{(W)}$) has to be titrated in the presence of a more strongly complexing metal ($Me_{(S)}$), it is possible to "mask" $Me_{(S)}$ by adding another complexing agent that complexes much more strongly with $Me_{(S)}$ than with $Me_{(W)}$, so that $M_{(W)}$ but not $M_{(S)}$ will react with EDTA.

Nonaqueous Titrimetry

Nonaqueous titrations are normally used for acid–base reactions, but redox reactions may also be applicable. The Karl-Fischer titration of water, in particular, is based upon redox reactions in a nonaqueous medium.

The ionization of a molecule HB in a solvent S is influenced by the solvation of the ions:

$$HB + 2S \rightleftarrows HS^+ + BS^- \tag{28}$$

The ease of dissociation to form HS^+ (solvated H^+) increases with increasing basicity of the solvent, that is, with increasing binding strength between H^+ and the solvent. Thus, an acid that is very weak in aqueous solution will be stronger in a more basic solvent such as pyridine or dimethylformamide, and will give a bigger "pH" change on titration. Phenols, for example, which are too weak acids to be titrated in aqueous solution, can be titrated in pyridine solution with tetrabutylammonium hydroxide in benzene-methanol (9:1, *v*/*v*) as titrant, and thymolphthalein in methanol as indicator. Similarly, bases that are very weak in aqueous solution (e.g., amines) show increased basicity in solvents of greater acidity, such as anhydrous acetic acid. Perchloric acid in acetic acid may be used as the titrant, with crystal violet in acetic acid as indicator.

Because many of the solvents used are aggressive, harmful, volatile, and poses objectionable odor, nonaqueous titrations are normally carried out in a closed environment, which also minimizes the ingress of moisture.

Compounds that may be determined by nonaqueous titrimetry include amines, amino acids, phenols, and Schiff's bases. Carbonyl compounds (by oxidation and titration of the released H^+) can also be determined. Such titrations are especially useful in the pharmaceutical industry.

Appendix: Supplementary Material

Supplementary material related to this chapter can be found on the accompanying CD or online at https://doi.org/10.1016/B978-0-12-409547-2.14419-1.

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Further Reading

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