A Review of Titration:

Theory and Practice

HANNA® instruments

The Theory of Titration

CONTENTS

The Theory of Titration

1. GENERAL REVIEW OF TITRATION THEORY

1.1 Introduction to Titration

A titration is a quantitative, volumetric procedure used in analytical chemistry to determine the concentration of an analyte (the species being measured) in solution. The concentration of the analyte is determined by slowly adding a titrant (reagent) to the solution. As the titrant is added, a chemical reaction occurs between the titrant and the analyte.

Titration reactions are relatively fast, simple reactions that can be expressed using a chemical equation. The titration reaction continues as the titrant is added until all of the analyte is consumed and the analyte reacts completely and quantitatively with the titrant.

The point at which all of the analyte has been reacted is called the equivalence point, also known as the theoretical or stoichiometric endpoint. This point is accompanied by an abrupt physical change in the solution, which sharply defines the endpoint of the reaction. The physical change associated with the titration endpoint can be produced by the titrant or an indicator and can be detected either visually or by some other physical measurement.

Titrations cannot be used to determine the quantity of all analytes. The chemical reaction between the titrant and analyte must fulfill four requirements:

- The reaction must be fast and occur within approximately one second after the titrant is added
- The reaction must go to completion
- The reaction must have well-known stoichiometry (reaction ratios)
- A convenient endpoint or inflection point

Titrations are highly precise and can provide many advantages over alternative methods. Titrations are quickly performed and require relatively simple apparatus and instrumentation.

1.2 Uses of Titrations

Titrations can be used in many applications, including:

- Acid content of plant effluents, food (e.g.: cheese and wine), plating and etching baths, petroleum products, drugs
- Base content of fertilizer (containing ammonia), bleach, minerals
- Hardness in water
- Metal content of alloys, minerals, ores, clays, waters, plating baths, paints, paper, plant materials, biological fluids, petroleum products
- Moisture content in foodstuffs, petrochemicals, pharmaceutical products, and plastics
- Redox reagent concentrations such as available chlorine in potable water, peroxide, traces of oxidants and reductants in food, reductants in high temperature or high pressure boiler water, vitamin analysis

1.3 Advantages and Disadvantages of Titrations

Some advantages of titrations as an analytical technique are:

- More precise results than many instrumental methods, such as measurement by electrode, the accuracy of the measurement is up to 0.1%
- Simple methods, reasonable capital costs, and easy training

- Suitability to measure major components of a mixture or product
- Automation can reduce time and labor spent on each analysis

Some disadvantages of titrations are:

- Time it takes to prepare standards and titrants
- Good technique is required to achieve precise results (training and practice required)
- Not suitable for determining trace or minor components of a mixture or product
- Limited dynamic range; it may require additional sample preparations (dilution) and repeat analyses

2. TYPES OF TITRATIONS

2.1 Titrations According to The Measurement Method

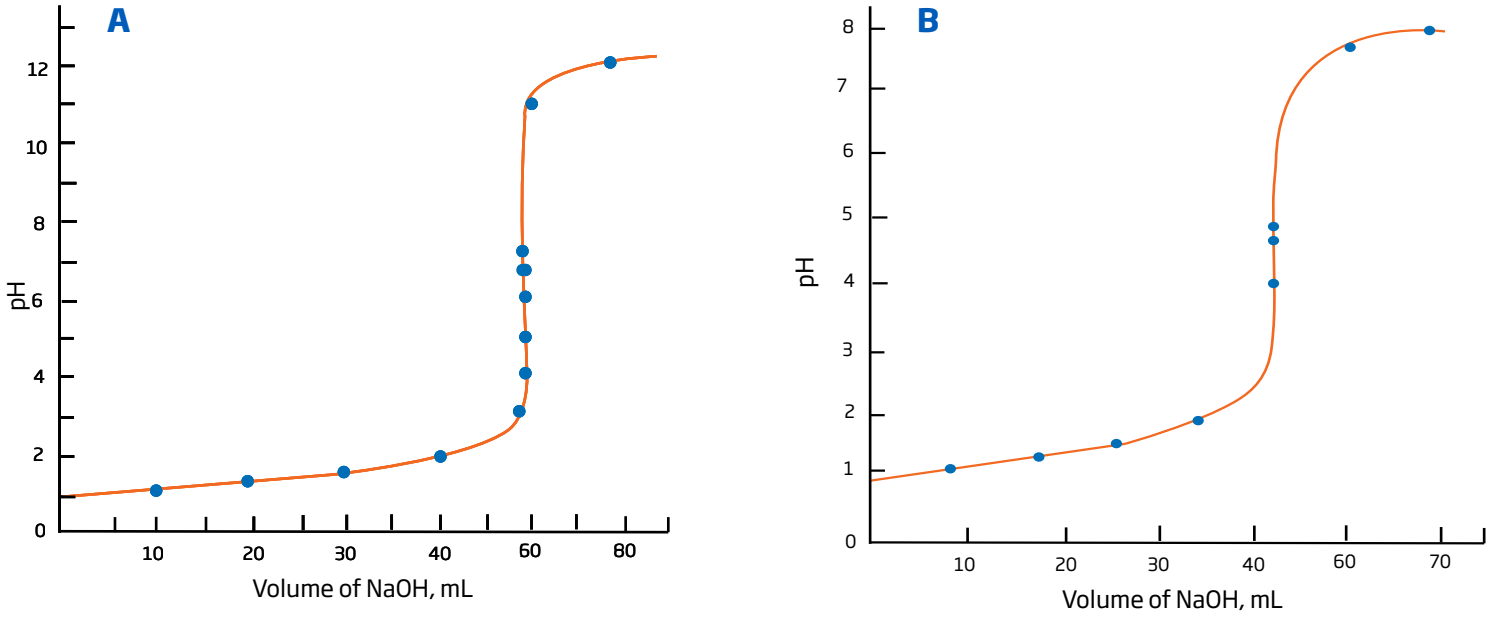
2.1.1 Potentiometric Titrations

Potentiometric titrations are performed by measuring the voltage across the solution using an electrode system. An electrode system consists of an indicator electrode and a reference electrode. As titrant is added the variations in the potential of the indicator electrode, with respect to the reference electrode, are monitored to show the progress of the titration.

Potentiometry is the measurement of a potential under conditions of zero current flow. The measured potential can then be used to determine the analytical quantity of interest, generally a component concentration of the analyte solution. The potential that develops in the electrochemical cell is the result of the free energy change that would occur if the chemical phenomena were to proceed until the equilibrium condition has been satisfied.

There are many types of titrations where potentiometry can be used,e.g., pH electrodes for acid-base titrations, platinum ORP electrodes in redox titrations, ion selective electrodes, such as chloride or fluoride for a specific ion titration, and silver electrodes for argentometric (silver-based) titrations. An example of potetiometric titrations are shown below. Figure 1 "A" is the pH of a solution vs. the volume of titrant and "B" is the potential from a chloride electrode vs. the volume of $AgNO_3$.

Figure 1



2.1.2 Amperometric Titrations

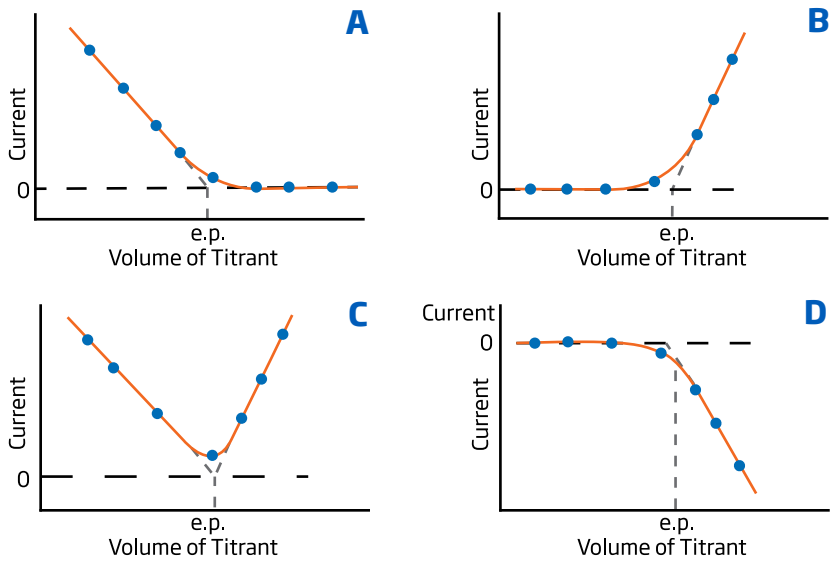
An amperometric titration is performed by placing two electrodes (often a metal ISE and a reference electrode) into the sample solution and holding the potential of the metal electrode at a selected voltage. The current that flows, due to the oxidation or reduction of a reactant or product, is plotted vs. volume of titrant to provide the titration curve and locate the equivalence point. Changes in the current are due to changes in the concentration of a particular species (being oxidized or reduced at the electrode).

Generally, the reaction between the analyte and titrant forms a new species. Depending on the titration, the reactants are electroactive and the products are not, or vice-versa. Amperometric titration curves look like two straight lines intersecting at the equivalence point, this is due to the change in the electroactivity of the solution.

Many metal ions can be amperometrically titrated using a precipitation, complexation or redox reaction. Some metal ions and species that can be determined in this manner include silver, barium, halides, potassium, magnesium, palladium, molybdate, sulfate, tungstate, zinc, bismuth, cadmium, fluoride, indium, thallium, iodine, and gold.

Figure 2 shows four amperometric titrations and their endpoints. In graph "A" the analyte is electroactive and gives current, but the reacted species does not. In "B" the reactant is not active but the titrant is. In "C" both the analyte and titrant are active and both give current flow. Graph "D" shows the same situation as "B"; however, the current has an opposite sign (the titrant is reduced).

Figure 2



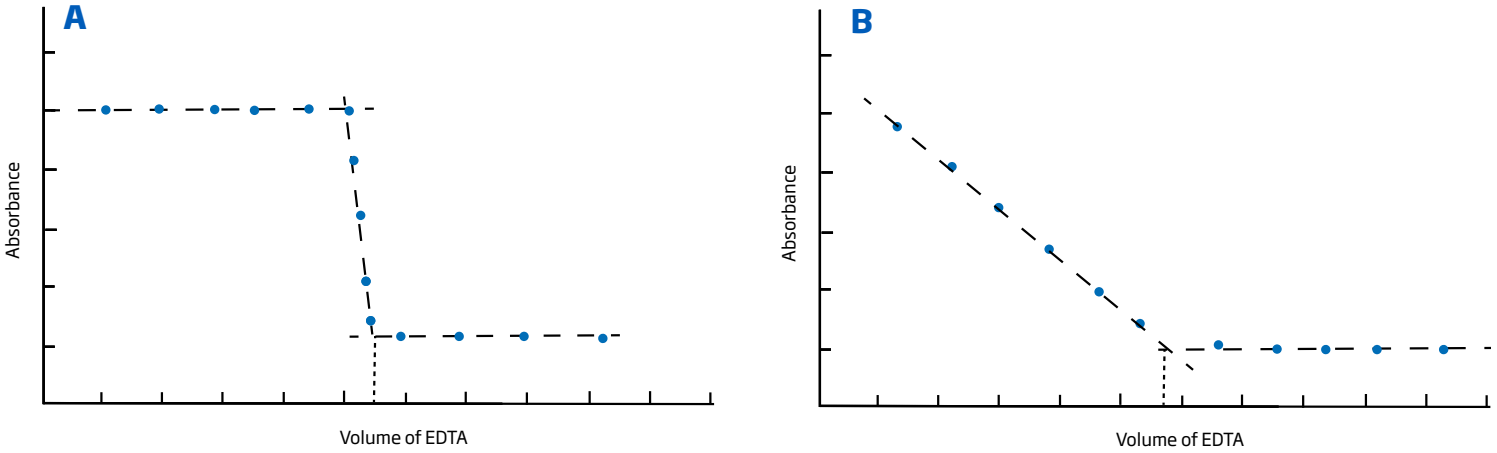
2.1.3 Spectrophotometric Titrations

The name comes from the method used to detect the endpoint of the titration, not its chemistry. Highly colored indicators that change color during the course of the titration are available for many titrations. More accurate data on the titration curve can be obtained if the light absorption is monitored instrumentally using a light source, a simple monochromator and a photodetector, rather than visually determining the color or light absorption change. Light absorption by either an indicator or by one of the reactants or products can be used to monitor the titration.

In the first titration curve, Figure 3 "A", the absorption of a metal-indicator complex is being monitored. The absorption is constant while the metal is complexed by the EDTA titrant. The metal indicator complex was stripped, causing a sharp break in the titration curve. The point where all the metal is complexed and stripped from the indicator is the equivalence point. This point is marked by "e.p." on the graph.

In the second titration curve, Figure 3 "B", the metal complex is being measured while being titrated with EDTA. The new complex being formed is not colored and does not absorb light. The extrapolated intersection of the two lines determines the equivalence point.

Figure 3



2.2 Titrations According to The Reaction Type

2.2.1 Acid-Base Titrations

Acid–base titrations are the most common type of titrations. They are based upon a reaction between an acid and a base, a stoichiometric neutralization, or the exchange of protons. Virtually all acid-base titrations are carried out using a strong acid or a strong base as the titrant. The endpoint of a titration carried out with a weak acid or a weak base would be difficult to detect due to a small change in pH at the equivalence point.

Chemical indicators can be used to determine the endpoint. The indicator will change color to signify that the end of the titration has been reached. The color of the indicator is dependent upon the concentration of ions in the solution. An acid-base indicator is composed of a conjugate weak acid-weak base pair, where the two forms exhibit different colors depending on the pH of the solution. For an indicator, the acid ionization constant K_a is usually written as:

$$K_a = \frac{[H_3O^+][In^-]}{[HIn]}$$

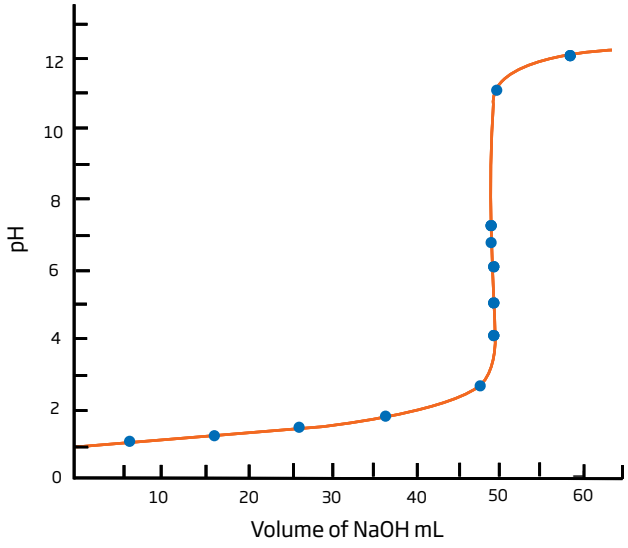
HIn is the acid form of the indicator and In^- is the base form. At the center of the change region, the ratio of [In^-] to [HIn] is one, [H_3O^+]=K_a and pH=pK_a. The color change region is usually ±1 pH unit around this point. Table 1 contains a list of some aqueous acid-base chemical indicators, as well as the pH range, the pK_a and the expected color (acid and base form). When choosing the proper indicator you should select one that has a pK_a as close to the endpoint of the titration.

Table 1

pH Range	Indicator	pKa	Acid Form	Base Form
0.0 - 1.6	Methyl Violet		Yellow	Blue
1.2 - 2.8	Thymol Blue	1.65	Red	Yellow
3.2 - 4.4	Methyl Orange	3.46	Red	Yellow
3.8 - 5.4	Bromocresol Green	4.90	Yellow	Blue
4.8 - 6.0	Methyl Red	5.00	Red	Yellow
5.2 - 6.8	Chlorophenol Blue	6.25	Yellow	Red
6.0 -7.6	Bromothymol Blue	7.30	Yellow	Blue
6.6 - 8.0	Phenol Red	8.00	Yellow	Red
8.0 - 9.6	Thymol Blue	9.20	Yellow	Blue
8.2 - 10.0	Phenolphthalein	9.50	Clear	Pink
9.4 -10.6	Thymolphthalein		Clear	Blue
10.1 - 12.0	Alizarin Yellow R		Yellow	Red
11.4 - 12.6	Indigo Carmine		Yellow	Blue

When chemical indicators are not suitable, a potentiometric pH titration can also be used. The pH of the solution is plotted versus the volume of titrant added. Figure 4 shows a traditional strong acid-strong base titration curve. The graph shows the volume of NaOH added to an acidic solution and the resulting pH of the solution. Note the abrupt change in the pH at the equivalence point.

Figure 4

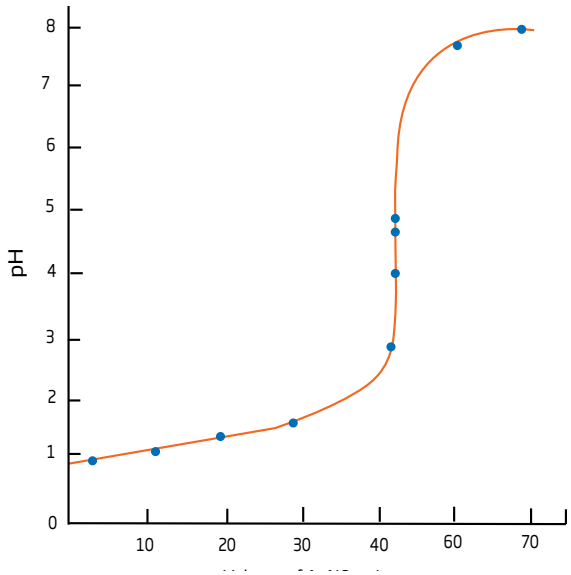


2.2.2 Argentometric Titrations

Argentometric titrations use silver (nitrate) as the titrant and are generally precipitation titrations, as many silver salts are insoluble. These titrations are commonly used to titrate and determine the concentration of bromide, chloride, cyanide, iodide, and sulfide.

Argentometric titrations can be done with Mohr's indicator (when all of the chloride has reacted, a red silver chromate precipitate is formed) or the titration can be easily followed with a silver ISE (or chloride ISE for chloride titrations) and a reference electrode. Figure 5 shows the titration of 50 mL of 0.1N NaCl with 0.1N $AgNO_3$. The potentiometric signal is from a chloride ISE and is plotted as pCl (- log [Cl^-]).

Figure 5



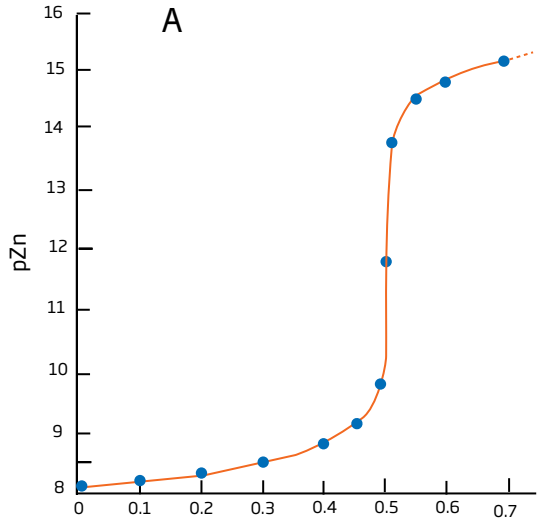
2.2.3 Complexometric Titrations

A complex is a species where a central metal ion is covalently bonded to one or more electron donating groups called ligands. In a complexometric titration, metal ions are titrated using a titrant that binds strongly to it. Often these titrants contain EDTA or CDTA, polydentate ligands that form very stable coordination compounds with metal ions. The complexation reaction must be fast in order to be useful for direct titration. Some metal ions react too slowly with EDTA for a direct titration.

An indicator electrode that responds to the metal ion can be used to monitor the titration progress. The titration curve will appear similar to a usual potentiometric titration. Complexation indicators change color at the endpoint as all metal ions are "consumed", or complexed, by the titrant.

The titration curve will appear similar to a potentiometric titration when using an indicator electrode that responds to the metal ion (see Figure 6).

Figure 6



2.2.4 Ion Selective Titrations

The most popular ion selective titration is an acid-base titration. The hydrogen ion concentration is specifically measured and monitored during the titration process to locate the equivalence point. Using an ion selective electrode (ISE) as the indicator electrode, the potentiometric signal (in mV) is used to directly follow a specific ion's concentration (or activity).

Examples of ISE titrations include titrating fluoride with an aluminum titrant using a fluoride ISE, chloride with silver nitrate using a chloride ISE, sodium with a sodium ISE, etc. The equivalence point can be determined by plotting the mV value vs. the amount of titrant added.

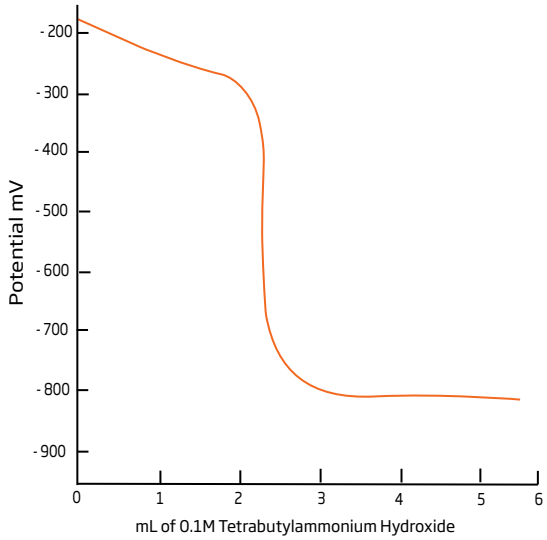
2.2.5 Non-aqueous Solvent Acid-Base Titrations

Non-aqueous solvents must be used to titrate very weak acids and bases due to the inherent leveling effect water has on all acids and base dissolved in it. A wide variety of weak acids and bases can be titrated using non-aqueous solvents. Mixtures of acids or bases can often be individually analyzed in a single sequential titration.

Titration of Acids

Weak acids with pK_a's up to about 11 can be titrated in non-aqueous solvents. These include carboxylic acids, enols, phenols, imides, sulfonic acids, and inorganic acids. Water or lower alcohols are suitable for titrating medium to strong acids (pK_a less than 5). Titrating a weaker acid with a strong base titrant requires a solvent less acidic than water or ethanol/methanol. Solvents such as acetone, acetonitrile, t-butyl alcohol, dimethylformamide, isopropanol and pyridine have been found to work well for acid-base titrations of strong, medium and weak acids/bases. Titrants include alcoholic potassium hydroxide and various sodium or potassium alkoxides in a 10:1 mixture of benzene/methanol. The best titrants are quaternary ammonium hydroxides (such as tetrabutylammonium hydroxide) due to good solubility of tetraalkylammonium salts of the titrated acids and the clean potentiometric titration curve obtained (see Figure 7).

Figure 7



Titration of Bases

Weak bases with pK_b's up to about 11, which do not ionize with water, can be titrated in non-aqueous solvents. These bases include aliphatic and aromatic amines, basic nitrogen heterocycles, alkali metal and amine salts of acids, and many other organic basic compounds. Titrating a weak base with a strong acid titrant requires a basic solvent that is as weak as possible. Water and alcohols allow the titration of medium strength bases such as aliphatic amines (pK_b = 4 to 5), but not the titration of weaker bases such as pyridine (pK_b = 8.8). Glacial acetic acid works well for weak bases and has been used extensively. Less basic solvents such as acetone, acetonitrile, and nitromethane extend the range of titrable compounds.

The endpoint for non-aqueous titrations are usually determined potentiometrically using a pH glass electrode, a modified calomel or double junction reference electrode with a low-flow rate reference junction. Good potentiometric titration curves are obtained in most solvents, except those with very low dielectric constants such as benzene, chloroform and others, when high electrical resistance of the solvent causes unstable potentials.

2.2.6 Precipitation Titrations

Precipitation titrations allow for faster analysis compared to the old gravimetric analysis, where a precipitate is formed, filtered, dried and weighed to analyze a compound. Typically silver halides, silver thiocyanate and a few mercury, lead, and zinc salts are titrated using this method. The chemical reactions must form an insoluble salt and precipitate out quickly in order to be analyzed by this method. When the reaction is not quick, a back titration can be used. A measured excess of the precipitating reagent (titrant) is added to force the reaction to occur, and then unreacted titrant is then titrated with a standard solution of another reagent.

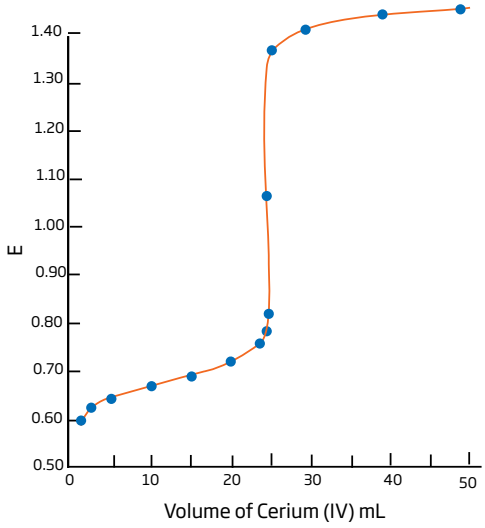
2.2.7 Redox Titrations

There are a number of oxidation-reduction reactions that can be used to determine unknown concentration by titration. If the reaction goes to completion, is fast and has an analytical signal available to follow it, a titration can be performed. The term "fast" means that each addition of titrant is reacted completely and the sensing electrode is able to detect the change in solution in less than one second.

Redox titrations are potentiometric titrations where the mV signal from a combination ORP (redox) electrode (usually with a platinum indicator electrode) is used to follow the reaction of oxidant/ reductant. The electrode potential is determined by the Nernst equation and is controlled by the oxidant reductant ratio.

Visual indicators such as Ferrion are also available. The oxidized and reduced form of the indicator will have different colors and can be used to determine the end point. Various reductants can be determined by titrants with oxidants such as potassium permanganate, potassium chromate or iodine. Commonly used reductants that are used as titrants include sodium thiosulfate, and ferrous ammonium sulfate.

Figure 8



As with Acid-Base titrations the potential changes dramatically at the equivalence point.

2.2.8 Karl Fischer Titration

This method is based on a well-defined chemical reaction between water and the Karl Fischer reagent. The chemistry provides excellent specificity for water determination. The method can be used to determine free and bound water in a sample matrix. The Karl Fischer method is widely considered to produce the most rapid, accurate and reproducible results and has the largest detectable concentration range spanning 1 ppm to 100%.

The determination of water content is one of the most commonly practiced methods in laboratories around the world. Knowledge of water content is critical to understanding chemical and physical properties of materials and ascertaining product quality. Water content determination is conducted on many sample types including pharmaceuticals and cosmetics, foods and natural products, organic and inorganic compounds, chemicals, solvents and gases, petroleum and plastic products as well as paints and adhesives. The KF method is verifiable and can be fully documented. As a result, Karl Fischer titration is the standard method for analysis of water in a multitude of samples as specified by numerous organizations including the Association of Official Analytical Chemists, the United States and European Pharmacopoeia, ASTM, American Petroleum Institute, British Standards and DIN.

2.3 Titrations According to The Titration Sequence

2.3.1 Back Titrations

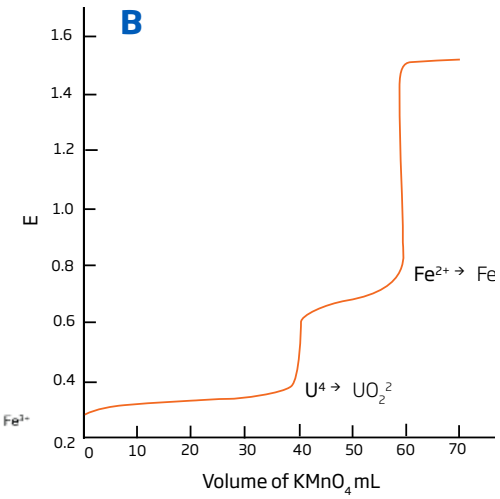
Back titrations are generally used when a reaction is too slow to be directly accomplished using a "direct" titration, where the reaction goes to completion within a few seconds. In a back titration, a large excess of a reagent is added to the sample solution, helping a slow reaction to go to completion. The unreacted, excess reagent is then titrated. The difference in the total volume of the first reagent added and amount determined from the second titration is the quantity of reagent required to complete the first reaction.

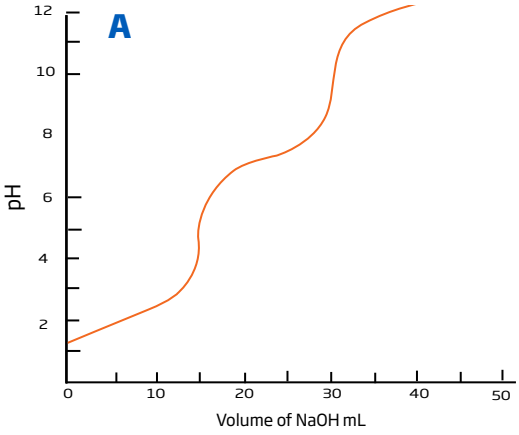
2.3.2 Multiple Endpoint Titrations

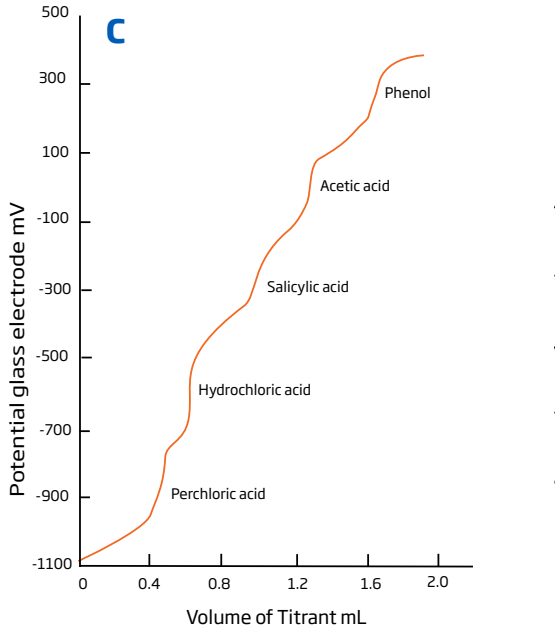
Under certain conditions, some titrations can exhibit more than one equivalence point and be titratable to the individual endpoints to determine the concentration of each individual component. Examples of these types of titrations include acid-base (where different strength acid or bases are in a mixture), redox (where each species has a different reduction potential), complexometric (where different species are separately titratable), and acid-base using polyprotic acids (the pKa of the different protons varies enough to separate them).

Figure 9 shows three different types of multiple endpoint titrations. "A" shows the titration of a polyprotic acid. The different acid strengths of the first and second proton can be determined. "B" illustrates a mixture of two different metal redox species, where the different redox potentials allow the species to be separated. "C" is the titration of a solution containing strong, weak, and very weak acids.

Figure 9







3 INTRODUCTION TO TITRATION APPARATUS AND TYPICAL TITRATION PROCEDURE

3.1 Manual Titration

Apparatus required for manual titration include:

- Volumetric Burette, for precisely controlled delivery of titrant to the reaction vessel
- An Erlenmeyer, or similar flask, that facilitates constant mixing or swirling required to ensure solution homogeneity
- Volumetric pipettes for the precise addition of samples and indicator solutions
- Titrant solutions of known concentration
- A visual or instrumental indicator for detecting the completion of the reaction

A typical manual titration consists of the following steps:

1. A volumetric pipette is typically used to add a known volume of sample to the flask
2. An indicator solution or instrument probe is added to the flask
3. A burette is used to measure the addition of titrant to the flask and dispense titrant in a controlled manner
4. Titrant is added via the burette until the method indication signals the reaction endpoint
5. The concentration of analyte is calculated based on the concentration and volume of titrant required to reach the endpoint

3.2 Automatic Titration

Automatic titrators are high-precision analytical instruments that deliver the titrant, monitor the physical change associated with the titration reaction, automatically stop at the endpoint and calculates the concentration of the analyte. Automatic titrators are best for repetitive titrations and high-accuracy analyses.

An automatic titrator must have an accurate liquid dispensing system. In high accuracy systems like the HI 900-series titrators, the liquid dispensing system consists of a stepper-motor driven piston syringe burette capable of accurately and precisely dispensing very small volumes of titrant, a valve system to switch between titrant intake and outlet and a dispensing tip. These three main subsystem components must be as accurate as possible, with very low gear backlash in the burette pump, minimal piston seal

flexing, precision ground inner diameter of the glass syringe, a low dead volume valve, minimal evaporation/permeation, and chemically resistant tubing.

Apparatus required for automatic titration include:

- An automatic titrator, equipped with a burette
- A beaker
- An electronic stirring system, either a propeller stirrer or a magnetic stir bar and stir plate
- Volumetric pipettes for the precise addition of samples
- Standard titrant solutions of known concentration
- An electrode system that can be used to determine the endpoint of the titration

A typical automatic titration consists of the following steps:

1. Set up the automatic titrator according to the manufacturer's instructions
2. A volumetric pipette is typically used to add a known volume of sample to the beaker
3. Submerge the propeller stirrer or add the stir bar to the beaker, and turn on
4. Start the titration, the titrator will automatically stop at the endpoint and determine the concentration of the analyte

4 TITRATION RESULTS

4.1 Accuracy

The factors most critical to achieving accurate results with the HI 900 titration systems are the concentration of the sample, size of the sample and having an optimized set of method parameters.

4.2 Repeatability

Repeatability, or the agreement between replicate determinations, is expressed quantitatively as the relative standard deviation (RSD).

4.3 Sources of Error

One of the advantages of volumetric analysis is excellent accuracy and precision. The sources of error can be grouped into sampling, titrant and standards, chemical reactions, endpoint determination and calculations.

4.3.1 Sampling Errors

- Selection of a non-homogeneous or non-representative sample
- Sample changed or was contaminated during collection, storage or transfers
- Poor technique when transferring sample to beaker or flask
- Errors in the balance, calibrate and check balance regularly

4.3.2 Errors with Titrant and Standard

4.3.2.1 Preparation Errors

Incorrect preparation due to:

- Poor technique in weighing the salt or when transferring to volumetric glassware
- Low-purity of salts or water used to make titrant and standard
- Dirty or wet glassware

- Improper storage of titrant or standard which allows water gain, evaporation or deterioration
- Failure to standardize frequently to adjust for change in titrant
- Failure to flush titrator tubing with a volume of titrant before standardizing
- Volume errors from pipettes and volumetric flasks, grade A glassware is required
- Balance errors when weighing out salts, calibrate and check balance regularly

4.3.2.2 Dispensing Errors

Incorrect dispensing due to:

- Dead valve volume and leaking valve
- Inaccuracy in motor drive and gear lash/ backlash
- Poor burette/ piston seal
- Non-uniform diameter of burette glass cylinder
- Chemical incompatibility with tubing or bubble generation
- Density/ temperature changes in titrant

4.3.3 Chemical Reaction Errors

- Inappropriate solvent or sample resulting in side reactions
- Poor mixing of the titrant and solvent or sample in the titration vessel
- Reaction between titrant and sample is not rapid
- Reaction does not go to completion
- Reaction has side reactions

4.3.4 Endpoint Determination Errors

Most manual titrations use a visual indicator to indicate when the endpoint is reached and the titration should be stopped. Automatic titrators use instrumental methods to determine the end of a titration and the equivalence point. There are two predominant methods used to determine the equivalence point, first derivative and second derivative.

The inflection point of the titration curve (mV vs. Volume) is normally assumed to be the equivalence point. The first derivative is often used to determine the inflection point. The maximum value of the first derivative (dmV vs. dV) corresponds to the theoretical equivalence point. During a titration it is rare to have a data point exactly at the first derivative maximum, the maximum value is determined by interpolating the first derivative data points.

The second derivative (d2mV vs. dV^2) can also be used to determine the equivalence point, and can offer advantages over the first derivative method. Second derivatives have increased sensitivity to smaller inflection points and easier numerical evaluation of the actual equivalence point. The value where the second derivative is equal to zero is the equivalence point. The second derivative requires fewer points located near the equivalence point, where data is often not obtained or not as reliable.

Errors in determining the endpoint can result from:

- Incorrect signals from the sensor
- Sensor drift
- Sensor or instrument has slow response, keep sensors in good condition
- Inappropriate setting on the titrator

5 CALCULATIONS

The main variables used in calculating a result from a titration are the sample volume, the concentration of the titrant, and the volume of titrant required to reach the equivalence point. At the equivalence point, an equal number of equivalents of the analyte and titrant has been added.

5.1 Sample Calculation

By Mass

$$C\ sample = \frac{V\ titrant \times C\ titrant \times Ratio \times FW\ analyte}{m\ sample} \times 100$$

C sample	Sample Concentration (g/100g)
V titrant	Volume of titrant (L)
C titrant	Titrant Concentration (eq/L)
Ratio	Equivalence ratio of analyte/ titrant (mol analyte/ eq titrant)
FW analyte	Formula Weight of the Analyte (g/mol)
m sample	Mass of sample (g)

By Volume

$$C\ sample = \frac{V\ titrant \times C\ titrant \times Ratio \times FW\ analyte}{V\ sample} \times 100$$

C sample	Sample Concentration (g/100mL)
V titrant	Volume of titrant (L)
C titrant	Titrant Concentration (eq/L)
Ratio	Equivalence ratio of analyte/ titrant (mol analyte/ eq titrant)
FW analyte	Formula Weight of the Analyte (g/mol)
V sample	Volume of Sample (mL)

5.2 Standardize Titrant

Titrant standardization is the second most important calculation in titrations. A primary standard is titrated in order to determine the concentration of the titrant. This is essentially a typical titration calculated in "reverse", where the concentration of the solution is known and the titrant is the unknown.

By Mass

$$C\ titrant = \frac{m\ standard \times Ratio}{FW\ standard \times V\ titrant}$$

C titrant	Titrant Concentration (N)
m standard	Mass of Standard (g)
Ratio	Equivalence ratio of titrant/standard (eq titrant/ mol standard)
FW standard	Formula Weight of the Standard (g/mol)
V titrant	Volume of Titrant (L)

By Volume

$$C\ titrant = \frac{V\ standard \times (1\ L/1000\ mL) \times C\ standard}{V\ titrant}$$

C	titrant Concentration of titrant (N)
V	standard Volume of Standard (mL)
C	standard Concentration of standard (eq/L)
V	titrant Volume of Titrant (L)

5.3 Blank Titration

In a blank titration a pre-titration is performed, often times on the solvent to be used for the sample titration, and the titrant volume required to reach the endpoint is noted. This blank value nullifies error due to titrant required to react with the components of the titration solution matrix. The basic titration equation can be used for a blank titration, with the single modification that the volume of titrant used in the blank titration should be subtracted from the regular titration titrant volume.

$$C\ sample = \frac{C\ titrant \times (V\ sample - V\ blank) \times Ratio \times FW\ analyte}{m\ sample} \times 100$$

C Sample	Sample Concentration (g/100g)
C titrant	Titrant Concentration (eq/L)
V sample	Volume of Titrant required for the sample (L)
V blank	Volume of Titrant required for the blank (L)
Ratio	Equivalence ratio of analyte/ titrant (mol analyte/ eq titrant)
FW analyte	Formula Weight of the Analyte (g/mol)
m sample	Mass of sample (g)

5.4 Multiple Endpoint Titration

Some titrations have two or more endpoints, each corresponding to the equivalence point for a specific reaction. Multiple endpoint titrations are similar to a blank titration in that the volume of titrant required to reach the first endpoint is subtracted from the titrant volume used to reach the next sequential endpoint.

$$C\ sample\ 1 = \frac{V\ titrant\ 1 \times C\ titrant \times Ratio \times FW\ analyte\ 1}{m\ sample} \times 100$$

$$C\ sample\ 2 = \frac{(V\ titrant\ 2 - V\ titrant\ 1) \times C\ titrant \times Ratio \times FW\ analyte\ 2}{m\ sample} \times 100$$

$$C\ sample\ 3 = \frac{(V\ titrant\ 3 - V\ titrant\ 2) \times C\ titrant \times Ratio \times FW\ analyte\ 3}{m\ sample} \times 100$$

C sample 1	Sample 1 Concentration (g/100g)
C sample 2	Sample 2 Concentration (g/100g)
C sample 3	Sample 3 Concentration (g/100g)
V titrant 1	Volume of titrant required to reach the first end point (L)
V titrant 2	Volume of titrant required to reach the second end point (L)

V titrant 3	Volume of titrant required to reach the third end point (L)
C titrant	Concentration of titrant (N)
Ratio	Equivalence ratio of analyte/ titrant (mol analyte/ eq titrant)
FW analyte 1	Formula Weight of the Analyte 1 (g/mol)
FW analyte 2	Formula Weight of the Analyte 2 (g/mol)
FW analyte 3	Formula Weight of the Analyte 3 (g/mol)
m sample	Weight of Sample (mL)

5.5 Back Titration

The equation used in back titration calculations is also similar to the equation for a blank titration. Instead of subtracting the initial amount of titrant needed to react with the blank, the amount of second titrant needed to react with the excess titrant added in the first titration is subtracted from the amount of the first titrant added. The difference between the two amounts is the amount of titrant necessary to reach the first equivalence point.

$$C\ sample = \frac{(C\ titrant\ 1 \times V\ titrant\ 1 - C\ titrant\ 2 \times V\ titrant\ 2) \times Ratio \times FW\ analyte}{V\ sample} \times 100$$

C sample	Sample Concentration (g/100mL)
C titrant	1 Concentration of titrant 1 (N)
V titrant	1 Volume of titrant 1 (L)
C titrant	2 Concentration of titrant 2 (N)
V titrant	2 Volume of titrant 2 (L)
Ratio	Equivalence ratio of analyte/ titrant (mol analyte/ eq titrant)
FW analyte	Formula Weight of the analyte (g/mol)
V sample	Volume of sample (mL)

6. GLOSSARY

Acid - A chemical species that can donate one or more protons (hydrogen ions).

Acid - Base Titration - Stoichiometric neutralization titrations, based upon the reaction that occurs between an acid and base.

Activity - A physical property corresponding to the concentration of all ions in a solution. Electrodes respond to activity.

Amperometric Titration - Titrations where the current flow between two electrodes (often a metal electrode and a reference electrode) are used to monitor the titration progress.

Analyte - The chemical species being measured in a titration.

Argentometric Titration - Titrations that use silver (nitrate) as the titrant. These titrations are typically precipitation titrations.

Automatic Titrator - An instrument designed to automatically carry out a titration. It will add the appropriate amount of titrant, determine the endpoint and calculate the results.

Back Titration - A type of titration where an excess amount of titrant is added to a sample, forcing a sluggish reaction to go to completion. The excess reagent is then "back" titrated with a second titrant.

Base - A chemical species that can accept one or more protons (hydrogen ions).

Biamperometric Indication - Uses a double platinum pin electrode to measure the current flow through a titration solution.

Bivoltametric Indication - Uses a double platinum pin electrode to measure the voltage required to maintain a constant current flow through a titration solution while constant voltage is applied across the platinum elements of the electrode.

Burette - A graduated cylindrical piece of laboratory glassware that is used to dispense precise amounts of solution.

Complex Ion - A species where a central metal ion is covalently bonded to one or more electron donating groups called ligands.

Complexometric Titrations - Metal ions are titrated using a titrant that binds strongly to it. The titrants often contain Ethylenediaminetetraacetic Acid (EDTA) or Cyclohexylenedinitrilotetraacetic Acid (CDTA).

Endpoint - The point were a titration is stopped because a physical change in the solution has indicated a completed titration. Titration endpoints typically coincide with the equivalence point. A fixed value endpoint (pH or mV) can be used as well. The titration will stop at the desired point regardless of if the titration is complete.

Equivalence point - The point where the quantity of titrant is stoichiometrically equal to the quantity of analyte.

Formal - The theoretical number of equivalents per liter of the solution. It is used in solutions where the exact concentration of a species may be affected by the other ions present, therefore the stated concentration may not be exactly correct.

Gravimetric Analysis - A quantitative determination of an analyte based on the mass of the solid.

Indicator Electrode - An electrode that responds to the species of interest. The electrode potential is proportional to the concentration or activity of that ion in the solution being measured.

Indicators - Chemical indicators are typically organic dyes that change form under different physical conditions, causing a color change that can be seen by an analyst. Typically used in manual titrations, chemical indicators have been replaced with electrometric indicators, which are used with automatic titrators.

Inflection Point - The point on a titration curve were the second derivative curve changes signs.

Ion Selective Electrode (ISE) - An electrode that responds to a specific ion. The electrode potential is proportional to the concentration or activity of that ion in the solution being measured.

Karl Fischer Titration - A titration that uses a chemical reaction that is specific for determining water.

Manual Titration - A titration that is carried out by hand. The analyst must add the appropriate amount of titrant, determine the endpoint and calculate the results.

Molar - The concentration of a solute in a solution.

Mole (mol) - A quantity of a chemical species. The molecular weight of a substance in grams is equal to the mass of one mole of the substance. One mole is equal to 6.022 x 1023 atoms or molecules.

The Theory of Titration

Monochromator - A device that allows only a narrow range of wavelengths to pass though it by separating the light into different wavelengths.

Multiple Endpoint Titration - A titration that reacts multiple species in solution sequentially using the same titrant. The concentration of each analyte can be determined from their respective endpoints.

Nernst Equation - The fundamental equation relating cell voltage to the concentration of a solution.

Neutralization - A chemical reaction where an acid and a base react to form a neutral salt and water.

Non-aqueous - A solution that does not contain water.

Non-aqueous Titration - A titration that is preformed in non-aqueous solutions, typically used to titrate very weak acids and bases to eliminate the leveling effect water has on all acids and bases dissolved in it.

Normal - The concentration of a solution which accounts for any stoichiometric difference between the various species in a solution.

Oxidation / Reduction Potential (ORP) - The measurement describing whether a species wants to donate or accept electrons from other species in a redox reaction. If a solutions reduction potential is higher than the species it is reacting with, it will typically gain electrons or be reduced. If the potential is lower than the species it is reacting with, it will typically lose electrons or be oxidized.

Oxidant - The species that is accepting electrons in a redox reaction.

Pipette - Scientific apparatus that is used to deliver precise volumes of liquids.

Polyprotic Acid - Acids that are capable of donating more than one proton per acid molecule.

Potentiometric Titration - A titration in which the endpoint is determined by monitoring the voltage of the solution using an electrode.

Precipitation Titration - A titration in which the analyte reacts with the titrant to form an insoluble compound. The endpoint is typically detected with an ISE sensitive to either the analyte or titrant.

Reagent - The chemical added in a titration that causes the given reaction to occur.

Reduction-Oxidation Reaction (redox) - A chemical reaction in which the atoms involved in the reaction have their oxidation numbers changed. Reduction is the gain of electrons, which decreases the oxidation number. Oxidation is the loss of electrons, which increases the oxidation number.

Reductants - The electron donor in a redox reaction.

Reference Electrode - An electrode that supplies a constant electrode potential. It is used in combination with an "indicator" electrode, allowing for the "indicator" electrode potential to be measured.

Relative Standard Deviation (RSD) - A measure of the amount of relative variation in a set of data. It is calculated by dividing the standard deviation by the mean: RSD = (Standard Deviation of X) * 100/ (Mean of X)

Repeatability - The variation in sample measurements taken by a single person or instrument under the same conditions.

Spectrophotometric Titration - A titration in which the endpoint is marked by a change in the color and/or color intensity.

Stoichiometry - The quantitative relationship of the reactants and products in a chemical reaction.

Titrant - The chemical added in a titration that causes the given reaction to occur.

Titration - A quantitative, volumetric procedure used in analytical chemistry to determine the concentration of an analyte in solution. The concentration of the analyte is determined by slowly adding a titrant to the solution. As the titrant is added, a chemical reaction between the titrant and the analyte occurs.

Titration Curve - A graph containing the physical data obtained for a titration. The data plotted is often an independent variable (volume of titrant) vs. a dependent variable (pH of the solution). From the titration curve, the equivalence point or endpoint can be determined.

Thank you for reading!

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