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Review Article

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REVIEW ON TITRIMETRIC ANALYSIS

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ABSTRACT

Titrimetric analysis covers a quite large group of methods which have a long tradition in quantitative analysis. Owing to their advantageous characteristics, they are still used in the laboratories as definitive methods, especially when they can be used with instrumental endpoint detection. Titrimetic analysis is referred to as volumetric analysis for transferring liquid volumes, and solution reaction stoichiometry in analyzing solution are all topics with which we will be concerned in our discussion of titrimetric analysis.

Keywords: Titrimetric analysis, Primary Standard, Secondary Standard, Indicator, Precipitation Titrations, Complexation Titrations.

INTRODUCTION

For Origin of titrimetric analysis we can date back around middle of 18th century along with industrial development. In1835, Gay- Lussac devised volumetric method for the first time and the term 'titration' originated- Before we take up titrimetric analysis, let us try to relate it in a broader sense to main branches of chemistry. Analytical Chemistry is the branch of chemistry which implies to all experimental sciences. This branch guides us to develop and apply new methods and techniques to identify the nature and composition of matter.[1] This is the basis of chemical analysis which is an art of recognizing different substances and determining their constituents. Chemical analysis involves various technologies, develops procedures, provides tools and makes use of variety of instruments and finally the interpretation of the results is obtained. So wherever chemical processes are employed; whether simple problems like analysis of elements and the compounds derived from them using chemical reactions, use of alternative methods of analysis, or the development of high profile instruments; the chemical analysis is indispensable. It enables us to answer few basic problems like: What is happening in a chemical reaction? Will the course of reaction same every time or everywhere? What are the quantities of reagents required? Various methods are used to identify the composition of a substance and to determine the exact amounts of the confirmed constituents. Thus the Chemical analysis is subdivided in two broader categories:

1. Qualitative analysis
2. Quantitative analysis

Qualitative analysis

As the name indicates; qualitative analysis deals with the identification of elements, ions or compounds present in a sample while quantitative analysis deals with the determination of how much of one or more constituents is present. Basically it is the answer to two questions; what is it and how much is it? In general qualitative proceeds quantitative.[2]

Quantitative analysis

Mainly includes gravimetric analysis and volumetric analysis. In gravimetric analysis, the substance to be determined which we call analyst, is converted into an insoluble compound using a suitable reagent, which is collected, dried and weighed. The weights of compounds obtained are then correlated with the amount of substance originally present using stoichiometric equation. It is important that the formulae of the compound should be correctly known. Volumetric analysis is concerned with measurements by volumes. It can be a. determination of the concentration of analyte by volume in a solution as by titration which is also called titrimetric Analysis**.**

TITRIMETRIC ANALYSIS

The definite volume of the analyte (i.e.; the substance to be determined) is allowed to react with a suitable reagent whose standard solution can be prepared and the volume of the solution consumed for complete reaction is used to find out the concentration of analyte solution. At this point**,** it is necessary to know definitions of some useful terms. In titrimetric analyses, the solution of accurately known concentration i.e.; standard solution is called the titrant and the substance to be determined is called titrand or analyte. The volume of the titrant added is measured with a special type of glassware called burette which is graduated and has a stopcock at one extreme end to control the flow of titrant. The process of determining analyte by adding the small increments of standard solution untill the reaction is just complete; the reacting ratio of the two being known from stoichiometry or otherwise is called titration. eg. determination of a substance A by adding increments of substance B (almost always as a standardized solution) with provision for some means of recognizing the point at which all of A has reacted, thus allowing the amount of A to be found from the known amount of B added up to this point, the reacting

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ratio of A and B being known from stoichiometry or otherwise. The reverse process incremental addition of A to B is seldom applied, except in standardization titrations. The point in a titration at which the amount of titrant added is chemically equivalent to the amount of substance titrated i.e. The point at which the completion of the reaction occurs is called the equivalence point or theoretical or stoichiometric end point. The point at which the completion of a reaction is practically observed is called end point. The point in a titration at which some property of the solution (as, for example, the colour imparted by an indicator) shows a pronounced change, corresponding more or less closely to the equivalence-point.[2-5]

The end-point may be represented by the intersection of two lines or curves in the graphical method of end-point determination. In an ideal titration, end point and equivalence points should coincide while practically (in reality) this doesn't happen. End point is generally a little ahead of equivalence point. The completion of the titration is accompanied by some physical change in the reaction mixture which can be identified visually or with the help of some instrumental techniques. This physical change could be:

1. A colour change produced by the titrant itself (e.g.; pink colour of $KMnO_4$)
2. A colour change produced by an additional reagent called 'indicator'
3. A sudden change in properties like conductance, pH, e.m.f., shift in Absorption maxima or variation inabsorbance etc.

Since in a titration we measure the quantity of one reactant that is required to consume all of another reactant, we have beenconcerned about completion of chemical reaction, achieving chemical equivalence in a reaction, so we put restrictions onsystem. Now what type of systems i.e., reactions can be studied titrimetrically. Definitely not all in the universe. Therefore some criteria have to be set which must be fulfilled for a given set of reactants/reactions so that they can be analysed titrimetrically. These criteria are:

1. The reaction must be simple and well defined i.e., stoichiometric. This means one should be able to present the reaction with a balanced chemical equation. The reaction must proceed by a definite chemistry.There should be no complicating side reactions.
2. The reaction must approach completion at the equivalence point. In other words, chemical equilibrium favors products.
3. The reaction should be instantaneous or very fast. In some cases a catalyst may be employed to increase the speed of the reaction.
4. There should be a discernible change in some property of the solution when the reaction is complete. This may be a change in the colour of the solution or any other physical property.
5. In case the titrant does not produce a visible change, an indicator should be available which by a change in physical properties (colour change or precipitation) is able to sharply define the end point.

A few rules of thumb for designing a successful titration are:

- The titrant should either be a standard or should be standardized.
- The equivalence point must be stable and well defined and able to be detected.
- The titrant's and sample's volume or mass must be accurately known.
- The end point should not be too far from the equivalence point.

There are many different types of titrations that differ by the titrant used and substances that can be determined. While every titration is different, they all share similar characteristic, several important terms will discuss. In Titrimetric analysis, we often talk about standard solutions. Standard solution is the one whose concentration is known. The chemicals which are used to prepare these standard solutions are of two kinds: Primary Standard and Secondary Standard.

Primary Standard

A Primary Standard substance is a compound of sufficient purity from which a standard solution can be prepared by direct weighing of a quantity of it followed by dissolution in a defined volume of a solvent. The solution obtained is thus a primary standard solution. A compound should satisfy following criterion to act as a primary standard:

1. It should be pure. In case slight impurities are present then the impurity level should not be too high and its percentage should be known
2. It should be stable upto moderate temperatures required for drying and it should be stable indefinitely at room temperature i.e., it should not be altered in air during weighing. This means it should not be hygroscopic, oxidized by air or affected by CO_2. Its composition should be unchanged during storage.
3. The substance should be capable of being analysed for impurities by known reactions.
4. It should have a high relative molecular mass so that weighing errors are minimum or negligible.
5. The substance should be readily soluble under the conditions in which it is employed.
6. The reaction with the standard solution should be stoichiometric and instantaneous. The titration error should be negligible.

A solution prepared from a primary standard substance whose concentration is known from the weight of the substance in a known volume of the solution is called primary standard solution A standard solution prepared from a primary standard substance whose concentration is known from the weight of that substance in a known volume (or weight) of the solution.

Secondary standard

A Secondary standard substance is a substance whose actual active content is found by comparison against a primary standard through chemical reactions. Thus a secondary standard solution is one in which the concentration of the dissolved solute has not been found from the weight of the compound dissolved but by reaction (titration) of a volume of the solution against measured volume of a primary standard solution i.e. its concentration or titre has been obtained by standardization, or which has been prepared from a known weight of a secondary standard substance. e.g. $KMnO_4$ is not a primary standard but $K_2Cr_2O_7$ is.

Titrant

Titrant is a substance added from the burette. Titrant used and reaction that proceeds usually defines name of the titration - like acid-base (or alkalimetric) titration if we use strong acid (or strong base) as a titrant, or redox when the reaction that proceeds is of a redox type. Name can be also much more specific - like permanganometric titration

(also known as manganometry or permanganometry) when titrant is potassium permanganate.[6]

Titre (titer)

The reacting strength of a standard solution, usually expressed as the weight of titrated substance equivalent to 1 ml of the standard solution. One should not confuse it with total volume of the titrant used.

Titration fraction (or Titration percentage)

Titration fraction tells us how far we have proceeded with the titration. At the equivalence point we have added stoichiometric amount of titrant and titration fraction equals 1 (or 100%, when it is expressed as titration percentage). It may seem that more convenient will be to use titrant volume to measure titration progres. That's not a case. For example it is much easier to say "pH at 50% titration equals pK_a of monoprotic weak acid" then to calculate each time volume of titrant added to get to the same point.

Note that in the case of polyprotic acids 100% titration may either mean that only first proton was fully neutralised, or that acid was completely neutralised. Thus depending on the definition used fully titrated phosphoric acid is titrated either 100% or 300%. We will use the latter number throughout the site.[7]

Indicator

A compound having a physical property (usually color) that changes abruptly near the equivalence point of a chemical reaction (Table **1**).[8]

Table 1. Different types of indicator use in tritemetric analysis in given

Indicator	Color on Acidic Side	Range of Color Change	Color on Basic Side
Methyl Violet	Yellow	0.0 - 1.6	Violet
Bromophenol Blue	Yellow	3.0 - 4.6	Blue
Methyl Orange	Red	3.1 - 4.4	Yellow
Methyl Red	Red	4.4 - 6.2	Yellow
Litmus	Red	5.0 - 8.0	Blue
Bromothymol Blue	Yellow	6.0 - 7.6	Blue
Phenolphthalein	Colorless	8.3 - 10.0	Pink
Alizarin Yellow	Yellow	10.1 - 12.0	Red

Direct Titration

One in which the analyte is treated with titrant, and the volume of titrant required for complete reaction is measured.

Back Titration

One in which an excess of standard reagent is added to react with analyte. Then the excess reagent is titrated with a second reagent or with a standard solution of analyte.

Standardization.

The process of finding the concentration or the reacting strength of a solution by titrating with a known amount of the substance which is pure or has a known reaction value.

Titration Equivalence Point

Equivalence point is where the titration should really end - titration fraction equals exactly 1, we have added stoichiometric amount of titrant to titrated substance. That's not necessarily where we end titration.

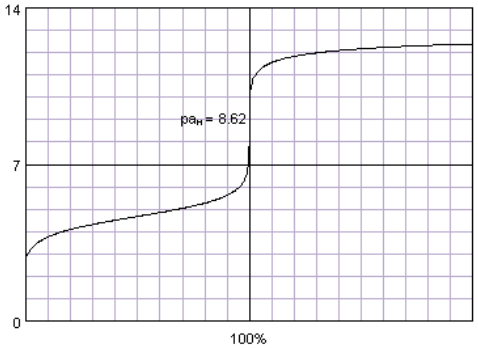
Titration End Point

End point is where the titration ends in practice. The closer the end points to the equivalence point the better, but it is often not easy to find a good method of equivalence point detection. However, very often we can easily spot a point very close to the equivalence point and that's where the end point will be. For example in alkalimetric titration of a strong acid with a strong base equivalence point is at pH 7.00, but the most popular and convenient indicator used - phenolphthalein - starts to change color at pH slightly above 8 (in the lab practice change can be observed much closer to 9). In permanganate titrations we don't use any special indicator, as the permanganate solution is strongly colored and excess of titrant added is easily visible (especially if we put white paper sheet behind the flask). In both cases we can't see the color without adding small excess of titrant which introduces small positive error in the titration As long as this error is in the same range as the burette precision (and precision with which we can read the volume) we can safely ignore it.

Titration Curve

Titration curve is a plot of changes of some selected solution property during titration. Property selected depends on the titration. In the case of alkalimetric titration we look for the changes in solution pH, in the case of complexometric titration we will usually trace changes in metal concentration (using its logarithm or minus logarithm on the plot, as concentration can change even 10^{10} times), during redox titrations we are interested in the redox potential in the solution and so on. Most titration curves have the same shape - plateau in the first part, sharp rise (or fall) near equivalence point (inflection point of the curve), followed by the second flat part. The most important part of the curve is the one where the changes are the fastest - close to the inflection point. Thanks to the fact that changes occur so fast there, and are so large, they are usually easily detectable. That in turn helps us detect titration end point.[9]

Acetic acid titrated with sodium hydroxide. Titration curve generated with bate - pH calculator.



Sometimes depending on the titration type and solution property selected titration curve can have different shape. For example if we use conductometry to localize end point of alkalimetric titration, we measure not the solution pH, but its conductance and titration curves are in this case V shaped.

Concentrations of Standard solutions

Titrimetric Calculations can be done using two concentration units: Molarity and Normality.

Molarity

Molarity is defined as no. of moles of solute (or analyte) dissolved per litre of the solution. Molar is abbreviated as M

$$Molarity = \frac{Moles}{Liter}$$

$$Moles = Molarity \times Liters$$

For relatively small quantities encountered in titrations, where mL are used

$$Millimoles = Molarity \times mL$$

Where molarity is expressed in mmol/mL

Now for a reaction where an analyte A reacts with the Titrant T to give the product P

$$A + T \rightarrow P$$

Since the reaction is in 1:1 ratio

No. of m moles of A = No. of m moles of T

$$Molarity\ (A) \times mL\ (A) = Molarity\ (T) \times mL\ (T)$$

or $$M_AV_A = M_TV_T$$

However the reactions most often are not in 1:1 ratio.

$$aA + tT \rightarrow P$$

thus every mmol of A ~ a/t mmoles of T

or $$Molarity\ (A) \times mL\ (A) = Molarity\ (T) \times mL\ (T) \times a/t$$

or $$tM_AV_A = aM_TV_T$$

where,

t = no. of mmol of titrant in balanced chemical equation

a = no. of mmol of analyte in balanced chemical equation

Normality

For such cases where reactions are not on 1:1 basis, the calculations are quite often based on normality. Normality of a solution is equal to the number of equivalents of the substance per litre of the solution.

Symbol N stands for Normal just as M stands for Molar.

$$Normality = \frac{milli\ equiv}{mL}$$

i.e. $$Milliequiv = Normality \times mL$$

Equivalents are based on the same concept as moles but the number of equivalents will depend on the no. of reacting units supplied by each molecule or the number with which it will react. e.g.

In 1 mole of HCl, one mole of H^+ is present therefore no. of reacting units is 1.

In 1 mole of H_2SO_4, two moles of H^+ are present therefore no. of reacting units is 2.

The no. of equivalents can therefore be calculated from no. of moles as

$$Equiv = mol \times no.\ of\ reacting\ units\ per\ molecule$$

Equivalent Weight is therefore defined as that weight of a substance (in g) that will furnish one mole of reacting unit. Thus

$$Equivalent\ weight\ of\ HCl = \frac{Mol\ wt}{1}$$

$$Equivalent\ weight\ of\ H_2SO_4 = \frac{Mol\ wt}{2}$$

Thus no. of equivalents can be calculated as

$$No\ of\ Equiv = \frac{wt\ of\ substance\ (g)}{Equivalent\ wt\ of\ the\ substance}\ (g/euqiv)$$

Normality of a solution is therefore

$$Normality = No.\ of\ equivalents\ /\ litre$$

$$Normality = \frac{wt\ of\ the\ substance\ (g)}{equivalent\ wt\ of\ the\ substance\ (g/equi) \times L}$$

Relation between normality and molarity

$$equiv = mol \times no.\ of\ reacting\ units\ per\ molecule\ (n)$$

Dividing both sides by L

$$equiv\ /L = mol/L \times no.\ of\ reacting\ units\ per\ molecule\ (n)$$

$$Normality = Molarity \times n$$

Where n is no. of reacting units per molecule or stoichiometry factor. From here only we can deduce that

$$Equivalent\ wt\ of\ the\ substance\ \left(\frac{g}{equiv}\right) = \frac{Mol\ wt\ (g/mol)}{n\ equi/mol}$$

Thus our earlier equation

$$tM_AV_A = aM_TV_T$$

can be written as

$$N_AV_A = N_TV_T$$

STEPS IN THE PROCESS OF A TITRATION

- primary standard solution preparation
- titrant preparation
- titrant standardization
- analyte titration with the titrant solution
- data analysis

VOLUMETRIC CALCULATIONS

Simple, based upon law of equivalents which states that at the end point or equivalence point, the number of equivalents of the substance titrated is equal to the number of equivalents of the titrating reagent used.[10] Thus if V_1 ml of the solution 1 of the normality N_1 requires V_2 ml of solution 2 of normality N_2 for reaction completion (indicated by end point), then No. of gram

$$Equivalents\ in\ V_1\ ml\ solution\ 1 = \frac{N_1 \times V_1}{1000}$$

and

$$Equivalents\ in\ V_2\ ml\ solution\ 2 = \frac{N_2 \times V_2}{1000}$$

By law of equivalence,

$$\frac{N_1 \times V_1}{1000} = \frac{N_2 \times V_2}{1000}$$

$$N_1V_1 = N_2V_2$$

This normality formula is the key relation in all volumetric calculations.

Calcultion of Normality

In the volumetric exercise V_1, V_2 and one of the normalties are invariably known. The unknown normality is calculated by using formula

$$N_1V_1 = N_2V_2$$

$$Unknown\ Normality = \frac{Known\ Normality \times Vol\ of\ the\ solution}{vol\ of\ the\ solution\ of\ unknown\ Normality}$$

Calculation of Strength of Solution

Strength in grams/litre can be found by relation

$$Strength = Normality \times Equivalent\ weight$$

A development of profound importance in practical analysis was the realisation that titrimetric procedures could be carried out with greater speed and convenience if the concentrations of the two reacting solutions were such that the reaction with the analyte was complete when comparable volumes of sample and titrant solutions had been brought together. More specifically, if volumes V_1 and V_2 of these solutions were mixed the reaction would be stoichiometric when

$$N_1V_1 = N_2V_2$$

where 'N_X' the 'normality' of the solution designated the number of 'gram equivalents' per litre. The principle involved in all titration methods is to balance a chemical reaction between titrant and titrand.

CLASSIFICATION OF REACTIONS IN TITRIMETRIC ANALYSIS

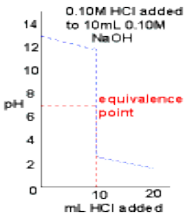
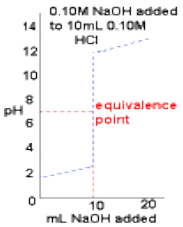
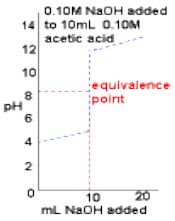
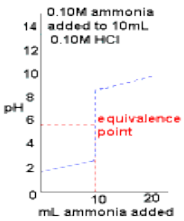
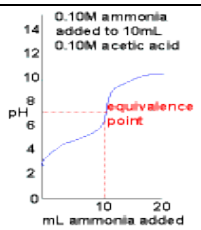
- Neutralisation(Bronsted acid-base) Titrations
- Reduction –Oxidation (Redox) Titrations
- Precipitation Titrations
- Complexation Titrations

Neutralisation (Bronsted Acid-Base) Titration

In order for the titration reaction to go to completion, a strong acid or a strong base is the usual choice for a titrant in acid-base titrations.[11] The levelling effect in aqueous solutions should be kept in mind. (Table **2**)

$$\boldsymbol{HA + B \leftrightarrow HB^+ + A^-}$$

Table 2. Different types a titrant in acid-base titrations shown in given

General Type	Example	Typical Titration Curve	Features of Curve
Strong Acid and Strong Base	HCl added to NaOH		Curve begins at high pH typical of strong base and ends at low pH typical of strong acid. There is a large rapid change in pH near the equivalence point (pH =7).
Strong Base and strong Acid	NaOH added to HCl		Curve begins at low pH typical of strong acid, and ends at high pH typical of strong base. There is a large rapid change in pH near the equivalence point (pH=7).
Weak Acid and Strong Base	NaOH added to acetic acid (CH_3COOH)		Curve begins at a higher acidic pH and ends at high basic pH. The pH change at the equivalence point (pH > 7)is not so great.
Strong Acid and Weak Base	Ammonia (NH_3) added to HCl		Curve begins at low pH and ends at a less high basic pH. The pH change at the equivalence point (pH < 7) is similar to that for Strong Base and Weak Acid.
Weak Acid and Weak Base	Ammonia (NH_3) added to Acetic acid (CH_3COOH)		Curve begins at higher acidic pH and ends at low basic pH. There is not a great pH change at the equivalence point (pH ~ 7) making this a very difficult titration to perform.

Oxidation-Reduction (Redox) Titration

Redox titrations can be used to analyze for any oxidizing or reducing agent. However, many redox reactions are either too slow or have inconsistent stiochiometry. The stability of titrant and analyte solutions can also be a problem. Nevertheless, a wide variety of analytes can be conveniently determined by redox titrations.

$$Ox + Red \leftrightarrow Red' + Ox'$$

Oxidizing Agents

Potassium Permanganate, $KMnO_4$

A strong oxidant

$$MnO_4^- + 4H^+ + 3e^- \longrightarrow MnO_2(s) + 2H_2O$$

Ceric Sulfate, $Ce(SO_4)_2$

Another strong oxidant, just about as strong as permanganate

$$Ce^{4+} + e^- \longrightarrow Ce^{3+}$$

Potassium Dichromate, $K_2Cr_2O_7$

A moderately strong oxidizing agent; oxidizing ability depends strongly on pH, decreasing rapidly assolution becomes more neutral

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

Reducing agents

Ferrous Ammonium Sulfate (FAS or Mohr's salt), $(NH_4)_2Fe(SO_4)_2$

The ferrous ion is a fairly weak reducing agent.

Sodium Thiosulfate, $Na_2S_2O_3$

Thiosulfate is a moderately strong reducing agent:

$$2S_2O_3 \longrightarrow 2S_4O_6^{2-} + 2e^-$$

Precipitation Titration

Precipitation reactions in aqueous solution range from rapid to slow, depending on the identity of the precipitant. Many precipitations are sufficiently rapid and complete to form the basis of quantitation by titration.[12] Precipitation titrimetry has several advantages over precipitation gravimetry.

$$M(aq) + nL(aq) \longleftrightarrow ML_n(s)$$

Complex Formation

Complexometric titrations are based on the reaction between Lewis acids (usually metal cations) and Lewis bases.Lewis acids and bases react to form a complex. The base donates two electrons to form a bond with the acid. Since the proton H^+, is a good Lewis acid, by definition any Bronsted base will be a Lewis base. Lewis bases will possess at least a single lone pair of electrons that it will donate to the Lewis acid. Lewis bases are also sometimes called ligands, and the atom containing the lone pair is the ligand binding site. A special subset of ligands are those that contain more than one binding site on the molecule; these are called chelating agents. Chelating agents form particularly strong complexes-called chelates-with Lewis

acids. By far the most common complexometric titrant is ethylenediamine tetra acetic acid.[13]

$$M(aq) + nL(aq) \longleftrightarrow ML_n(aq)$$

CONCLUSION

A method of quantitative analysis based on the measurement of the volume of a solution with a precisely known concentration of a reagent required for reaction with a given amount of a substance being determined. Among the means used in titrimetric analysis are complexing and precipitation, acid-base, and oxidation-reduction reactions. The main requirements for the reactions used in titrimetric analysis are high speed, the presence of stoichiometric proportions, and the absence of side reactions, which distort the results of analysis.

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