NATIONAL OPEN UNIVERSITY OF NIGERIA

SCHOOL OF SCIENCE AND TECHNOLOGY

COURSE CODE: 202

COURSE TITLE: Analytical chemistry

MODULE 1 FUNDAMENTALS OF PRE ANALYSES

UNIT 1: Theory of Errors

1.0 Introduction

Analytical chemistry is a specialised aspect of chemistry that deals with both qualitative analysis (investigating what are the constituent of a given sample) and quantitative analysis (investigation how much of constituents are in the sample). When reporting the quantitative measurement of an experiment, there are normally some controllable and uncontrollable variations that accompany such measurement. These forms of variations are termed **Error**. This unit examines the concept of errors in quantitative analysis in analytical chemistry.

2.0 Objectives

By the end of this unit, students should be able to :

(a) define what an error is;

(b) state various types of errors;

(c) express those errors correctly when reporting; and

(d) report quantitative values to the correct number of significant figures

3.0 Definitions of an Error

Error is a controllable and uncontrollable variation observed when comparing the measured values to the true value. The error affects the accuracy and precision of a measured quantity.

3.1 Types of error

There are basically two types of errors known: systematic errors and random error

3.1.1 Systematic Errors

These are otherwise known as determinate errors because they can be determined and corrected.

Example (a) Using pH meter that has been incorrectly standardised. If the pH buffer used is 14.07 but mistaken for 14.00, therefore a medium measured as 12.48 is actually 12.41 and a value put as 13.74 is actually 13.67. Any measurement with such pH meter must be buffered with a factor of 0.07.

3.1.1.1 Commonly encountered Systematic Errors

Systemic Errors commonly encountered in the course of laboratory exercises include:

(a) Instrumental Error

This occurs when faulty equipment and weight as well as glassware used are not calibrated or wrongly calibrated.

(b) Operative Errors

These are errors traced to the operators (personnel error), either as a result of the in experience of the personnel involved or the operator not been careful enough. It may be mathematical error in the calculation or prejudice in estimating measurement.

(c) Methodic Error

These are errors inherent in the analytical method or procedure used. It is a very serious problem for an analyst. These include errors such as co-precipitation with impurities, incomplete reaction, impurities in the reagents used, etc. The methodical error is also correctable.

3.1.1.2 Prediction and Correction of systematic Error

There are various ways to detect and correct systematic error;

(a) Analyse samples of known composition

Your method should reproduce the known answer; if not there is a problem with the method or equipment used.

(b) Analyse ‘’blank’’ Samples.

Samples containing none of the parameter been sought. If you observe a non zero result, it means your method is responsible for more than what you intended.

(c) Use different analytical methods to measure the same quantity. If the results do not tally, it means there is an error associated with one of the methods.

(d) Let different operators of varying capabilities in different laboratories (using the same method or different methods) carry out the same analyses. Disagreement or Variations of high magnitude indicate error traceable to operators or equipment used.

3.1.2 Random Errors.

These errors are also known as indeterminate errors. They are errors due to the limitations of physical measurement and cannot be avoided. A better experiment or replicated experiment may reduce the magnitude of these types of errors, but cannot eliminate it totally. These types of errors are also called accidental errors. The errors are indicated by small differences in successive measurements made by the same analyst under almost identical experimental conditions. Random errors cannot be predicted or estimated. They can be either positive or negative.

Examples

(a) The type of variation associated with same analyst reading the same absorbance scales many times

(b) Variation associated with the three or four different analyst reading the same measuring scale or reading the lower measurement of a volumetric flask.

Obviously they would report varying values reflecting subjective interpolations between markings.

It has been observed that these types of errors always follow random distribution; hence mathematical laws of probability can help in arriving at conclusions regarding the most probable results in a series of measurements.

On a general note, errors affect the precision and accuracy of a measured quantity thereby raising questions on the integrity of the reported values.

3.1.3 Expressing Accuracy of a measurement

There are various ways by which accuracy of a measurement can be expressed, these include:

(a) Absolute Error or Absolute Uncertainty

This is variation or difference shown between the true value and the measured value. It is reported in the same units as the measurement

Example If a 4.97mg of an analyte is analysed as 4.91mg, the absolute error is 0.06

It becomes mean error if the measured value is the average of several measurements

(b) Relative Error or Relative Uncertainty

It is an expression comparing the absolute uncertainty to the size of its associated measurement or absolute error expressed as percentage of the true value.

Example. From. (a) Above, the relative error in the analysis is

$$\frac{0.06}{4.97} \times \frac{100}{1}\% = 1.21$$

The relative accuracy can then be deduced as follow.

$$\frac{4.91}{4.97} \times \frac{100}{1}\% = 98.79$$

Note that

(i) the relative accuracy and relative error always give 100% if summed together.

(ii) relative errors can be expressed (as shown above) as parts per hundred (i.e in%) or parts per thousand (ppt)

Example. (a) If the result of an analysis, is 29.74µg is compared to the true value of 30.15 µg. Calculate the relative error in part per hundred and part per thousand.

Solution

Absolute Error = 29.74 - 30.15 = -0.41

Relative Error in pph = $\frac{0.41}{30.15}$ x 100 % =

Relative error in ppt = $\frac{0.41}{30.15}$ x 1000 % = 0.45 ppt

Self Assessment Exercise

a) Define the following terms (i) Error (ii) Blank sample (iii) Part per thousands

b) Briefly describe the major types of error known.

c) Differentiate between qualitative and quantitative analysis.

4.0 Conclusion

Treatment of errors constitute a very important concept that helps in ascertaining the integrity of the values reported in an experiment reported

5.0 Summary

In this unit we have learnt that:

i) Analytical chemistry deals with both quantitative and qualitative analysis.

ii) Errors are variations that naturally accompanied the experiment performed.

iii) Two major types of errors are known namely: determinate and indeterminate errors.

iv) Determinate errors can be predicted and accounted for, as well as corrected while indeterminate errors are accidental and inherent in the experiment itself and hence can not be corrected.

v) Absolute and relative errors or uncertainty are two ways of expressing the accuracy of the measured values.

vi) Relative error can be expressed in terms of part per hundred (pph) , that is % or parts per thousand (ppt).

6.0 Tutor Marked Assignment

1 Differentiate between quantitative and qualitative analysis

2 Explain the meaning of the following terms

(i) Analyte (ii) Blank (iii) operational error.

3 Differentiate between random and systematic errors.

4 Briefly explain way by which systematic error can be predicted and corrected.

5 A standard serum containing 400 mg/L of chloride was analysed mg/L were obtained. Calculate (a) the mean value (b) absolute error and relative error in percent.

7.0 Further reading and Other resources.

1 Christian, G.D. (1980). Analytical Chemistry.3rd ed, John wiley and son, New York.

2 Harris, D.C. (1995). Quantitative Chemical Analysis. 4th ed. Freeman and Company, New York.

3 Khan, I.A. and Khanum K. (1994).Fundamentals of Biostatistics. Ukaaz Publications, Nagar.

4 Nwachukwu, V.O.(2006).Principle of Statistical Inference. Peace Publishers, Port-Harcourt.

Module 1 FUNDAMENTALS OF PRE ANALYSES

Unit 2 Statistical Treatment of Data

1.0 Introduction

In the past, great chemist had faced various challenges, which include the necessity to analyse a reasonable large number of samples in so many monitoring effort so as to ensure representative coverage, selection of appropriate method out of many known suitable analytical techniques, the problem of variations in reported values from different methodologies employed in analysing the same samples, coping with different measured values reported by the same operation in replicate and un thinkable interrelationship that could exist among the data generated. These problems and many others had forced scientist to just collecting ‘’base line’’ data for referral use, against which the future can be assessed.

However, it is now being realise that, with the statistical analytical tools various problems could be solved. Statistics enables analytical chemist to accept conclusions that have high probability of being correct and to reject conclusions that are doubtful. Hence statistical treatment of data helps in ascertaining the significance and integrity of values reported.

2.0 Objectives

At the end of this unit, students should be able to:

i. list appropriate statistical tools available for data handling;

ii. define various statistical terms and state their importance; and

iii. use various statistical tools in interpreting data and arrive at a safe conclusion.

3.0 Definitions of various Statistical Terms

3.1 Significant figures

It can be defined as the minimum number of digit required to express a given value in a scientific way with a measured precision.

This concept is very important in conveying the actual meaning and status of each digit. However many individual are not properly schooled in the use of significant figures and hence make figures in experimental reports appear confused.

The digit zero [0] can be a significant part of a measurement depending on where it occurs.

Generally, zeros are significant if:

i. They occur in the middle of a number

ii. They occur at the end of a number on the right-hand side of a decimal point.

Note that the number of significant figures in a measurement is independent of the placement of decimal point

Example: The significant zeros are underlined. 7**0**4, 0.07**0**4, 0.7**0**4, 7**0**4**0**, 0.7**0**4**0**. Ambiguity arises when a figure like 92500 is written in respect of the significant figures. However it could be written in any of the following ways.

9.25×10^4 - 3 significant figures

9.250×10^4 - 4 significant figures

9.2500×10^4 - 5 significant figures

Note that the first uncertain figure is the last significant figure.

3.1.1 Rounding Off

The problem often encountered in significant figures is when an arithmetical operation takes place and when the answer is to be rounded off. The operation is either addition/subtraction, multiplication/division.

The general rule is: Rounding should only be done on the final answer (not intermediate results) to avoid build-up of round-off errors.

3.1.2 Addition and Subtraction

Rule: Express all numbers with the same exponent and align all numbers with respect to the decimal point.

Round-off the answer according to the number of decimal places in the number with the fewest decimal places.

Example (a)
$$\begin{array}{r} 14.344137 \\ +\ 17.347799 \\ +\ 44.313 \\ \hline 76.504936 \end{array}$$
not significant

The final answer is 76.505

When adding or subtracting numbers expressed in scientific notation, all numbers should first be converted to the same exponent.

Example (b)
$$\begin{array}{r} 1.373 \times 10^5 \\ +\ 5.314 \times 10^3 \\ +\ 0.798 \times 10^6 \end{array}$$

Convert to the same exponent

1.373×10^5 $\quad 1.373 \times 10^5$

$5.314 \times 10^3 \Longrightarrow 0.05314 \times 10^5$

$0.798 \times 10^6 \quad 7.98 \times 10^5$

9.40614×10^5

Round off to fewest decimal point.

So the final answer is 9.41×10^{5}.

3.1.2 Multiplication and Division

The operation should be limited to the number digit contained in the number with the fewest significant figures.

Example (a)

$$\begin{array}{r} 3.26 \times 10^{-5} \\ \times\ 1.78 \\ \hline 5.80 \times 10^{-5} \end{array}$$

(b)

$$\begin{array}{r} 4.3179 \times 10^{12} \\ \times\quad 3.6 \times 10^{-19} \\ \hline 1.6 \times 10^{-6} \end{array}$$

(c)

$$\begin{array}{r} 34.60 \\ \times\ 2.46287 \\ \hline 14.05 \end{array}$$

Note that the power of 10 has no influence on the number of figures that should be retained.

3.1.3 Rounding Off Rule

Note that the rounding off should be done on the final answer, when the arithmetic operation must have been carried out.

The following rules validate rounding off operation.

1. If the digit following the last significant figure is greater than 5, the number is rounded up to the next higher digit.
2. If the number is less than 5, the number is rounded to the present value of the last significant figure

   Example: 9.47 = 9.5 } in two significant figures.

   9.43 = 9.4 }
3. If the last digit is a 5, the number is rounded off to the nearest even digit.

   Example: 4.65 = 4.6 not 4.7

   4.75 = 4.8

   4.55 = 4.6

3.2 Ways of Expressing Precision

Statistics has enabled scientist to accept or reject conclusions on figures depending on the degree of precision carried or attached by the numerical report.

Precision is defined as the degree of agreement between replicate measurements of the same quantity. There are various tools that are uses in expressing the precision. These include: average deviation, variance, standard deviation etc.

3.2.1 Average Deviation (A.D)

It is one of the methods of showing dispersion or way of ascertaining the deviation from the central values. It is otherwise called Mean Deviation. It helps further in measuring distribution that is based upon all the items in a distribution.

Mean deviation or average deviation =

$$\text{A.D} \qquad \frac{\sum|x - \bar{x}|}{n} \qquad \text{or} \qquad \frac{\sum|d\bar{x}|}{n}$$

dx = deviation from mean

n = number of observation

x = observation

$\bar{x}$ = sample mean

Coefficient of mean deviation = $\frac{\text{Mean deviation}}{\text{Mean}}$

As with accuracy, precision measurement such as average deviation can be expressed as an absolute figure or as a relative figure (%, pph, ppt etc)

3.2.2 Variance

This is simply called mean square deviation. Variance is an important measure in the quantitative analysis of data. It helps in isolating the effect of various factors. It also helps in developing some statistical theories.

$$\text{Variance } S^2 = \frac{\sum(x - \bar{x})^2}{n-1} \qquad \text{or} \qquad \frac{\sum(d\bar{x})^2}{n-1}$$

x = arithmetic mean

n = number of observation

3.2.3 Standard Deviation (SD)

It is the most commonly used absolute measure of dispersion. It measures how closely the data clustered about the mean.

Note: The smaller the standard deviation the more closely the data are clustered about the mean i.e homogeneity is observed when standard deviation is small.

Therefore, standard deviation measures the spread in a set of observation. Standard deviation (S) is simply the square root of the variance.

$$S = \sqrt{\frac{\sum (x - \bar{x})^2}{n - 1}} = \sqrt{\frac{\sum (dx)^2}{n - 1}}$$

Coefficient of Variation: The standard deviation is an absolute measure of dispersion. It is expressed in terms of unit in which the original data is collected. For instance the standard deviation of length of fish is different from standard deviation of weight of fish. To enable Comparism of the two, there is the need for conversion into relative measure. This relative measure of dispersion is known as coefficient of variation.

$$C.V = \frac{S}{\bar{x}} \times 100$$

Where S = Standard deviation

$\bar{x}$ = Mean

3.2.4 Standard Deviation of Mean

This is otherwise known as standard error of mean (SEM).

$$SEM = \frac{S}{\sqrt{N}}$$

Where S = Standard deviation

N = number of observation.

Note that when the sample given during the measurement of dispersion is less than 10 ,we use n – 1 but if it is more than10, we use n.

3.2.5 Student's t Test

This is a statistical tool used most frequently to compare the mean values from experimental procedure. It also helps in expressing confidence interval. This is the range within which the true value might fall within a given probability. The limit of this range is called confidence limit. The likelihood that the true value falls within the range is called the probability or confidence level, usually expressed as a percentage.

A statistical t-value is calculated (t_{cal}) and compared with the tabulated t-value (t_{tab}). If the calculated t-value exceeds the tabulated t- value, then there is a significant difference between the results of the two methods at that confidence level. If it does not exceed the tabulated t-value, then we can predict that there is no significant difference between the methods.

There are three ways by which t-test can be used.

(a) T-test when a standard or true value is known

$$\pm t = (\bar{x} - \mu)\sqrt{\frac{N}{S}}$$

Where x = mean value

μ = true value

N = number of observations

S = standard deviation

(b) T-test when comparing replicate measurements

$$\pm t = \frac{\bar{x}_1 - \bar{x}_2}{Sp}\sqrt{\frac{n_1 n_2}{n_1 + n_2}}$$

$$Sp = \sqrt{\frac{\sum x_1 i \; \square \; \bar{x}_1)^2 + \sum x_2 i \; \square \; \bar{x}_2)^2 + \ldots \sum x_k i \; \square \; x_k)^2}{n_1 + n_2 \; \square \; K}}$$

Where $\bar{x}_1, \bar{x}_2, \ldots\ldots \bar{x}_n$, are mean values of each of the set.

S_P = Pooled standard deviation

$x_{i1}, x_{i2}, \ldots, x_{ik}$ = Individual value in each set.

K = sets of analyses

(c) T-test when comparing individual difference.

This case applies when we use two different methods to make single measurement on several different samples. No measurement has been duplicated.

$$t = \frac{\bar{d}}{Sd}\sqrt{n}$$

$$Sd = \sqrt{\frac{\sum (di \; \square \; \bar{d})^2}{n \square 1}}$$

d_1 = The individual difference between two methods for each samples with regards to sign

$\bar{d}$ = The mean of all the individual difference.

3.2.6 F-test

This is a test designed to investigate whether there is a significant difference between two method based on their standard deviation commonly. It is defined in terms of variance.

$$F_1 = \frac{S_1^{\,2}}{S_2^{\,2}}$$

Where $S_1^{\,2} > S_2^{\,2}$. If the calculated F value exceeds tabulated F value at a given confidence level, there is a significant difference between the variance.

3.2.7 Correlation

This is a statistical tool with the help of which the relationship between two variables is studied. Indeed, Correlation studies also help to show degree of any association (quantitatively) between two sets of variables.

With this knowledge, one can predict if the existence of trend in one variable will affect the other. There are three major ways by which correlation is carried out.

i. Scatter diagram method

ii. Graphic method

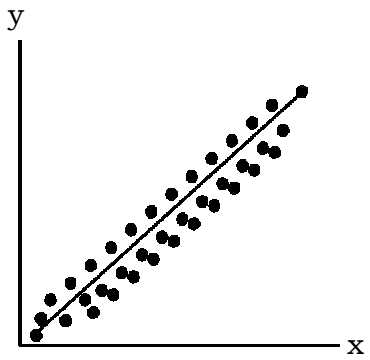
iii. Coefficient of correlation.

(i) Scatter Diagram Method

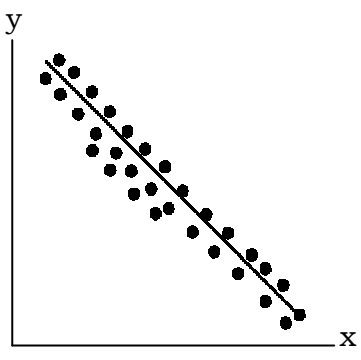
It is the simplest method for ascertaining correlation between two variables by plotting the values on a chart known as scatter diagram.

In plotting this diagram, note that the X variable is the independent variable while on y-axis you plot dependable variable.

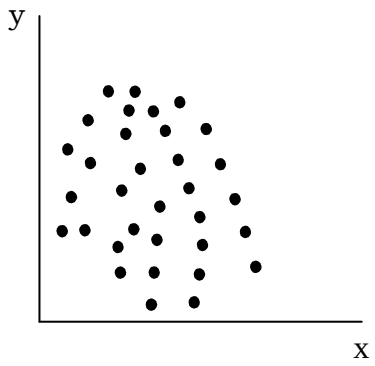
Example: The height of plant is on x axis while the number of flower is on y-axis. The following types + scatter graph are commonly obtained



(a) positive correlation



(b) Negative Correlation

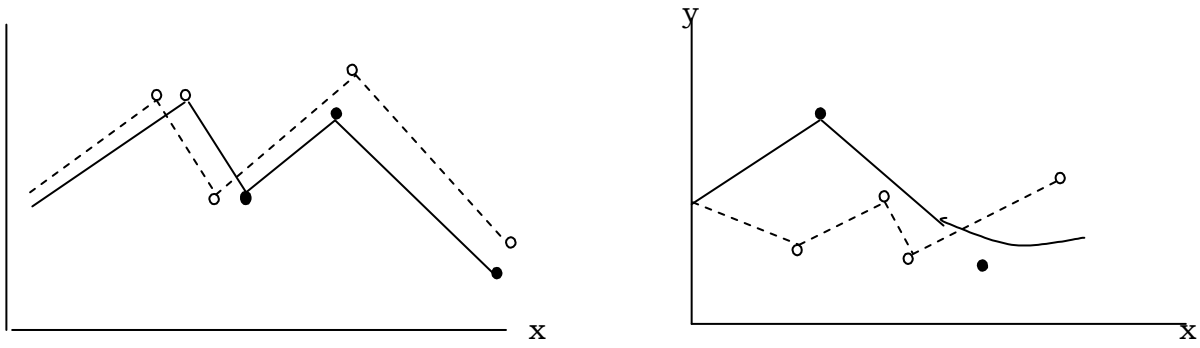


(c) No correlation

Figure 1.0mScatter Diagram Patterns of Correlation.

(ii) Graphic method

This is a mutual mathematical graph in which graphs of two variables in question are plotted and are related to one another. The graphs would either show positive or negative correlation.



(a) Positive Correlation (b) Negative Correlation

Figure 2.0 Graphical Pattern of Correlation

(iii) Coefficient of Correlation

This is when the degree of relationship can be established by calculating a coefficient which always gives a quantitative measure of the degree of closeness between two variables. This postulate is the basis for ranking numerical measure of degree of correlation. One of such numerical measured is Pearson Correlation coefficiency, r.

$$r = \frac{\sum (x - \bar{x})\ (y - \bar{y})}{\sqrt{\sum (x - \bar{x})^2\ \sum y - y)^2}}$$

x = the independent variable

y = dependent variables

r = correlation coefficient

x and y are the mean values of independent and dependent variables respectively

However for simplification purposes, the r can be rewritten as:

$$r = \frac{\sum xy - \frac{\sum x \sum y}{n}}{\left[\sqrt{\sum n^2 - \frac{(\sum x)^2}{n}}\right]\left[\sum y^2 - \frac{(\sum y)^2}{n}\right]}$$

The r calculated would show the degree of the interrelationship goingas indicated in Table 1 below.

Table 1.0 Interpretation of Degree of Correlation

Degree of Correlation	Positive	Negative
Perfect correlation	+1	-1
Very high correlation	+ 0.9 or more	-0.9 or more
Sufficient correlation	+0.75 to 0.9	-0.75 to - 0.9
Moderate correlation	+0.6 to 0.75	-0.6 to -0.75
Possible correlation	+0.3 to 0.6	-0.3 to -0.6
Possibly No correlation	Less than 0.3	Less than -0.3
Absent of correlation	0	0

SELF ASSESSMENT EXCERCISE

1. Briefly describe various ways by which precision can be expressed.
2. Explain the meaning and importance of the following terms:

   (i) Precision and Accuracy (ii) Standard Error Mean (iii) Significant figures

4.0 Conclusion

Statistical treatment of data helps scientist to correctly present and interpret data. It also reveals the inherent possible inter relationship with other variables and the population.

5.0 Summary

In this unit we have learnt that :

i. Statistical handling of data is very important.

ii. Significant figures help to reveal the status of all digits in the measurement as well as indicating the degree of its uncertainty

iii. Rounding off of figures generally implies tha the degree of uncertainty in a figure he to be propagated.

iv. Various ways by which precision in a figure can be expressed include average deviation, standard deviation, variance, etc

v. Both T and F tests are capable of revealing the significance of the difference between mean values from different experiment

vi. Various ways of showing correlation between two variables and their merits are possible.

6.0 Tutor Marked Assignment

1. Differentiate between F and T test
2. Calculate the average deviation and the average relative deviation of the following set of analytical results: 18.40g, 18.37g, 18.43g and 18.39g.
3. How many significant figures does each of the following number have? (a) 2000.06 (b) 6.030×10^{-4} (c) 7.30×10^{10}
4. Distinguish between accuracy and precision
5. Replicate samples of silver alloys are analysed and determined to contain 95.67, 95.61, 95.71 and 95.60% of silver metal. Calculate (a) average deviation in ppt, (b) the standard deviation and (c) the relative standard deviation of mean

7.0 Further reading and Other resources.

1 Christian, G.D. (1980). Analytical Chemistry.3rd ed, John wiley and son, NewYork.

2 Harris, D.C. (1995). Quantitative Chemical Analysis. 4th ed. Freeman and Company, New York.

3 Khan, I.A. and Khanum K. (1994).Fundamentals of Biostatistics. Ukaaz Publications, Nagar.

4 Nwachukwu, V.O.(2006).Principle of Statistical Inference. Peace Publishers, Port-Harcourt.

Module 1 FUNDAMENTALS OF RELIABLE ANALYSES

Unit 3 **Theory of Sampling**

1.0 Introduction

There are certain important steps that naturally precede chemical analysis if the result or data generated is to have any significance. These steps include:

(i) Sampling (ii) Production of a homogenous mixture for analysis and (iii) Drying the collected sample.

Sampling wrongly done will not yield any meaningful result no matter how painstaking or laborious the analysis is. Materials to be analysed more often than not, exist not only in a large size but also in complex non homogeneous forms. Hence, attention, commitment and expertise are required to obtain a true representative sample. The number or size of the sample is all geared towards desired result, achievable only when the problem of analytical exercise is well defined.

This unit covers the scope and as principle employed in getting true sample, preparation of sample and Statistics of sampling.

2.0 Objectives

At the end of this unit, students should be able to:

(i) explain the basic principle of sampling;

(ii) state types of sampling; and

(iii) list and explain the various methods of sampling

3.0 Basic principles of sampling.

Sampling can be described as the operations involved in procuring a laboratory size that is a true representative of "a whole lot" for a particular analytical exercise.

Sampling is indeed the most difficult step in the entire analytical process; however, it remains the only key to the success of the whole analytical programme.

Good sample irrespective of the type or method of sampling should possess the following properties:

(i) A good sample must have the same characteristic or features with that of the original population from where it is selected.

(ii) The nature of the sample must be the same with that of the population and must remain so throughout the analytical exercise.

(iii) The number of samples should be large enough to make the result reliable.

Indeed, the methods used in collecting a true representative sample depends on various factors which include:

(i) The knowledge and experience of the analyst or sampler

(ii) The result of survey on the nature, size and configuration of the site of materials to be sampled.

(iii) The level of sensitivity of the desired result.

It is important to note that, there is virtually no single technique that can satisfy all requirements in any sampling case. Modifications and combination of some techniques may be necessary in some sampling cases.

3.1 Sampling techniques.

Basically there are two main sampling techniques.

(i) **Random Sampling**: This is a method of sampling in which each item of the population has equal chance of being included in the samples. Random sampling can be from either finite samples or infinite samples.

(ii) **Stratified Sampling**: It is a technique employed when population is heterogeneous with respect to the variables (parameters) under study. The population is divided into varying homogeneous groups or strata and random sample is drawn from each stratum and pooled together.

3.2 Types of Samples.

The following are various types of sample that can be collected.

(i) **Grab Samples**: These are single samples collected at specific spot at a site over a short period of time. These types samples represent a "snap shot" in both space and time of the sampling area.

Grab Sampling can be (a) discrete grab samples (ie) samples taken at a selected location depth and time, (b) depth- integrated sample which are collected over a predetermined part or to entire depth of an area with respect to location and time.

Grab Sample is suitable either when the source is known to vary with time or when source composition varies in space.

(ii) **Composite Samples**: These types of sample provide more representative sampling of heterogeneous matrices in which the composition of the analyte of interest may vary over a period of time and or space. Composite samples can be (i) sequential (time) composites are collected using continuous and constant equipment (like pumping machine or by mixing equal volume of water collected at a regular time interval, (ii) Flow-Proportional Composite Samples are collected at a rate proportional to flow rate.

(iii) **Integrated Samples**: At times, information or result desired may be best provided by analysing mixture of grab samples collected from different points simultaneously or as nearly so as possible using discharge- weighted methods such as equal width increment (EWI) or equal discloses increment (EDI).

Generally sampling can be done manually or with the aid of instrument depending on various factors such as cost of the analysis, size of the sampling site and the numbers of samples to be procured.

3.3 Gross and Laboratory size Samples.

Irrespective of the state of materials to be sampled, the level of heterogeneity, the size , nature and volume of the sample and configuration of the site , the interest of the analyst is to generate gross sample from which laboratory size sample is obtained for analysis.

3.3.1 Gross sample

Ideally, gross sample is a miniature replica of the bulk of materials to be analysed. It corresponds to the "whole lot" both in chemical composition and in particle size distribution. A certain portion of the whole must be removed through any of the sampling methods earlier discussed. The sample may be grab or composite depending on the judgement of the analyst. The competence and expertise required for obtaining the gross sample vary and depend on the situation at hand. This range from sampling homogeneous situation of liquid and gases, to sampling particulate solids, to sampling of metal and alloys.

The size of the gross sample needs not to be larger than necessary. The size is determined by the following factors

i. the uncertainty that can be tolerated between the composition of the samples as a whole;
ii. the degree of heterogeneity of materials being sampled; and
iii. the level of particle size at which heterogeneity begins.

3.3.2 Laboratory size sample

This is the ultimate sample on which analysis is carried out from non homogeneous material. The gross sample may weigh several hundreds of kg or more. A laboratory size that is almost one over thousands or less is obtained. Diminutions in particles size is essential as the weight of the sample is decreased to ensure that the sample composition continue to be representative of the original materials.

The sample obtained upon arrival at the laboratory received further treatment before it is eventually analysed. The integrity of sample to maintain chain-of-custody procedure must be ensured.

3.3.2.1 Coning and Quartering method of sample selection

It is a method sampling selection which aim at reducing the samples without creating a systematic bias. The technique involves pouring the sample so that it takes on a conical shape, and then flattening it out into a cake. The cake is then divided into

quarters and two quarters which face opposite one another are discarded, whilst the other two are combined and constitute the reduced sample. The same process is continued until a reasonable amount of material is obtained. Analyses are made with respect to the sample obtained.

3.3 The chain of custody procedure is the following:

1 Sample label (including bar code label)

2 Sample seals

3 Fields log book

4 Chain of custody books

5 Sample analysis request sheet

6 Sample delivery to the laboratory

7 Receipt and logging of sample

8 Assignment of sample for analysis

9 Disposal

The chain of custody procedure helps in identifying the source of contamination (if any) and help the analyst in planning.

3.4 Treatment or Preparation of Sample

Samples brought to the laboratory require further treatment before analysis commences. This is due to the need to convert the sample from the nature in which it exist at the site of sampling to the form in which it can be analysed. The treatments also help in eliminating the possible sources of contamination and sample degradation that could lead to sample destruction. The treatment of samples also ensure the homogeneity of samples, so that any small portion removed for the analysis will be identical to any other fraction.

Major activities during the preparation of samples include.

I Concentration: - this implies reducing the water content of a sample material (drying)

Ii Dissolution: - this involves converting sample material in solid form to solution

Iii Grinding and Crushing:- This involves reducing the size of particles of sample materials. It helps increasing the surface area thereby allowing effective attack of reagents during reaction.

1v Mixing solids laboratory samples:- It is essential that solid materials be thoroughly mixed in order to ensure random distribution of the components in the analytical sample.

The figure below shows sample treatment chart

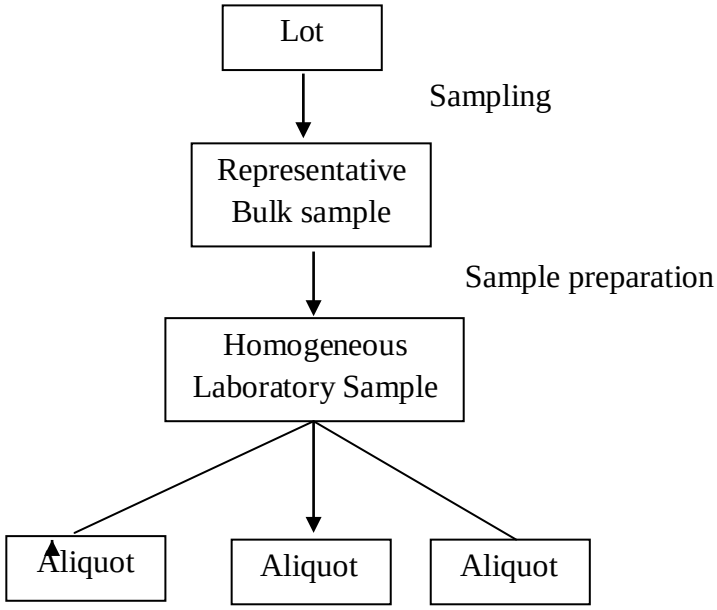


Fig. 1.0 Sample treatment flow chart

3.5 Statistics of Sampling

The use of statistics has gone a long way in helping to unravel some of what could be a difficult decision to make at the sampling site. Such decisions as what should be the sample size or what number of samples to collect could be statistically handled.

(i) **What should be the size of sample?**

When n particles are drawn from mixture of two kinds (such as liver tissue particle and droplet of water), the sampling standard deviation will be

$$\sigma_n = \sqrt{npq}$$

Where p and q are the fractions of each kind of particles present

The relative standard deviation is $\sigma n/n = \sqrt{pq}/n$

The relative variance $(\sigma n/n)^2$ is therefore

$$R^2 = \left(\frac{\sigma n}{n}\right) = \frac{PE}{n} = nR^2 = pq$$

Where mass of the sample drawn (m) is proportional to the number of the particles drawn

$MR^2 = K_S$

K_S = Sampling Constant

$$m = \frac{Ks}{R^2}$$

(ii) **What number of samples to collect ?**

The sampling contribution to the overall uncertainty can be minimised by analysing more samples

Rearranging student's t-test will allow us to know the number of sample required to meet a desired confidence levels

$$\mu - \bar{x} = \frac{ts_s}{\sqrt{n}}$$

$$n = \frac{t^2 s^2}{(\mu - x)}$$

Let $\mu - \bar{x}$ be $= e$

$$n = \frac{t^2 s^2}{e^2}$$

where μ = true population mean

$\bar{x}$ = measured mean

n = number of sample needed

S^2 = variance

3.6 Sample Decomposition.

This is converting the accessible sample matrices to the form which is accessible to instrument. There are various methods employed in decomposition. This varies depending on the chemical nature of the sample.

3.6.1 For Inorganic Solids

(a) Strong mineral acids are good solvent for many organics. Acids such as hydrochloric acid, nitric acid, hydrofluoric acid, perchloric and sulphuric acids are commonly used to this regard.

(b) Fusion of Inorganic Materials with acid or basic flux in a molten state, is the only way through which some materials are digested. The sample is mixed with flux in a ratio of about 1 to 10, or 20, sample to flux, the combination is heated in an appropriate crucible until the flux becomes molten, the cooled solid is then afterward dissolved dilute acid or water.

3.6.2 **Organic material** such as plant or animal tissue or biological fluid are usually decomposed by

i. Wet Digestion: This is achieved by boiling sample materials with oxidizing mineral acid or mixture of acids.

ii. Dry Ashing: This involves heating the materials at high temperature (400-700^{0}C) in a muffle furnace until it is turned to ashes. This is later dissolved in mineral acid or water

Self Assessment Exercise

1. What is the chain of custody procedure**?**

2. Explain the meaning of the following terms (a) Coning (b) Quartering (c) Wet digestion**?**

3. Write brief note on (a) Random Sampling (b) Stratified Sampling (c) Grab Sampling

(d) Composite Sampling

4.0 Conclusion

Sampling remains a key to a successful analytical exercise, if the result generated must be valid. No matter how meticulous an analyst may be or how sensitive the instrument may respond, once the sampling stage is badly handled, the entire result obtained is fraught with errors

5.0 Summary

In this unit ,we have learnt about

(i) The definition of basic principle of sampling.

(ii) The methods of sampling as well as the types of samples.

(iii) Detail of chain of custody proceeding.

(iv) Preparation of samples.

(v) Decomposition of sample.

(vi) Statistics of sampling.

6.0 Tutor Marked Assignment

1 What are the two principal means of dissolves inorganic material?

2 Describe the principle of ashing and wet digestion

3 What are the procedures of chain- of- custody?

4 Justify this statement: “sampling is the key to a successful analysis

5 Explain in detail, sample preparation

7.0 Further reading and Other resources.

1 Christian, G.D. (1980). Analytical Chemistry.3rd ed, John wiley and son, New York.

2 Harris, D.C. (1995). Quantitative Chemical Analysis. 4th Ed. Freeman and Company, New York.

3 Khan, I.A. and Khanum K. (1994).Fundamentals of Biostatistics .Ukaaz Publications, Nagar .

4 Laitimen, H.A . and Hesiscs, W.E. (1995). Acid-Base Equilibria in Water. 2nd Ed. McGraw Hill Inc., New York

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Module 2 BASIC CONCEPT OF TITRMETRIC ANALYSIS

UNIT 1: GENERAL PRINCIPLES OF VOLUMETRIC ANALYSES

1.0 Introduction

Titrimetric analysis (Titration) is one of the core and the most useful analytical procedures that make up quantitative techniques in analytical chemistry. It is fairly rapid with good degree of accuracy. It involves measuring the volume of the reagent (titrant) needed to react with the analyte (test substance or titrand).

This unit examines the general principle of volumetric analyses which include technical terms used in describing the analytical procedure, various types of volumetric titrations and calculation in volumetric analysis.

2.0 Objectives

At the end of this unit students should be able to:

a. explain what volumetric analysis is;

b. list and explain the various technical terms surrounding volumetric analysis;

c. list the general requirements for volumetric titration;

d. name the forms of volumetric analysis available; and

e. Solve fundamental calculations involved in volumetric analysis

3.0 Definition of Volumetric Analysis

Volumetric analysis is an analytical technique that deals with reactions between measured volumes of a regent known as titrant against the test substance called analyte in a stochiometric manner. It is a quantitative study.

3.1 Principles and technical terms involved in Volumetric Analysis

In a titration the addition of the reagent solution (titrant) of known concentration to analyte continues until their reaction is complete. Titrant is usually added from burette to the titrand or the analyte in a conical flask.

If the concentration of H^+ titrant is known, the reaction between the analyte and titrant is also known, and then the amount of the analyte can easily be calculated.

3.2 General (Basic) Requirements for Titration.

i. The titration reaction should have large equilibrium constant i.e each addition of titrant must be completely used up by the analyte.

ii. The reaction must be rapid.

iii. There should be known reaction pattern between the analyte and titrant

iv. There should be no side or parallel reaction i.e the reaction should be specific with no interference.

v. The reaction should be quantitative

vi. There should be distinct features in some property of the solution when the reaction is complete

vii. The end point should coincide with the equivalence point and be reproducible

3.3 Various Methods of Detecting Completion of a Titration Reaction

i. Observing sudden colour change in the indicator.

ii. Monitoring spectrophotometric absorbance change.

iii. Detecting a sudden change in the voltage or current between a pair of electrodes.

iv. Observation of marked change of pH in the titration tof an acid with a base.

3.4 Various Technical Terms in Volumetric Analysis

These are some of the various terms used in the volumetric techniques under analytical chemistry

i. ***Indicator***: is a compound with a physical property (colour) which changes abruptly near the equivalence end point. The change is colour is due complete consumption of analyse near the equivalence point whose concentration is known.

iii. ***Standardisation***: is a process by which the precise concentration of a solution is determined

iv. ***Primary Standard***: is the purest form of reagent which is used to prepare a standard solution. The purity is above 99.9%

v. ***Equivalence point***: This is the point in which the quantity of titrant added is the exact amount necessary for stochiometric reaction with the analyte or the titrand.

vi. ***End point:*** This is the actual point when a reaction is observed to be complete

vii. ***Titration Error***: The difference between the equivalence point and end point. It is sometimes called indicator error, if indicator is used as a means of detecting end point.

viii. ***Blank titration***: It is the type of titration in which the solution does not contain the analyte of interest. It is always carried out to estimate the amount of titration error

ix. ***Direct titration***: Is the most common form of titration in which titrant is added to the analyte until reaction is complete

x. ***Back titration***: It is the type of titration necessary when direct titration does not give clear or sharp end point. It involves adding a known excess of the standard reagent to the analyte. Then a second standard reagent is used to titrate the excess of the first reagent so as known the amount of first standard reagent that is consumed by analyte.

3.5 Characteristics of standard solution

An ideal standard solution for volumetric analysis must have the following properties.

i. Its concentration should remain constant for months or years after preparation so as to avoid the need to re -standardise

ii. Its reaction with analyte should be rapid.

iii. The reaction with the analyte must be describable by equation.

iv. A method must exist for detecting the equivalence point between the reagent and analyte.

3.6 Forms (Types) of Volumetric Procedures.

i. Acid-Basic titration: This is determination of the concentration of an acid or base by exactly neutralising the acid or base with acid or base of known solution. It allows for quantitative analyses of the concentration of an unknown solution.

The most obvious application of acid base (neutralisation) titration includes determination of innumerable inorganic, organic and biological species that possess inherent acidic or basic properties. Elemental and kjeldahl analysis are some of the other application and they are of research and industrial importance

Ii Oxidation- reduction (redox) titration: This is a type of titration characterised by the transfer of electron from one substance to another (from reductant to the oxidant) with the end – point determined calorimetrically or potentiometrically. The principle is based upon reacting the analyte of interest with a standard solution of oxidizing or reducing agent.

Various applications are known. These include determination of iron in ore and calcium in oxalate

Iii Precipitation titration: is a titration in which, as it proceeds toward the end point, the substance of interest is precipitates out soultion as an insoluble salt: ie. Ag+(aq,unknown) + Cl-(aq,titrant) --> AgCl(s). This usually makes it difficult to determine the endpoint precisely. As a result, precipitation titrations often have to be done as "back" titrations.

Iv Complexometric titration. Complexometric titration (sometimes chelatometry) is a form of volumetric analysis in which the formation of a colored complex is used to indicate the end point of a titration. Complexometric titrations are particularly useful for the determination of a mixture of different metal ions in solution. An indicator capable of producing an unambiguous color change is usually used to detect the end-point of the titration.

3.7 Volumetric calculation

The key step is to relate the moles of titrant to the mole of analyte. In this section, a general framework would only be provided, due to space and time constraints. However any situation (calculation) can be adapted.

Molarity is a major concept required for volumetric calculation. However, chemist also use the equivalent weight (or the milli equivalent weight) as the basis of volumetric calculation.

Equivalent and equivalent weight are used instead of moles and formula weight.

Normal concentration depends on the particular reaction and reaction should be specified.

$$\text{Mole} = \frac{\text{gramme (g)}}{\text{Molecular mass (F.w)}}, \qquad \text{millimole} = \frac{\text{mg}}{\text{Fw (molecular mass)}}$$

$$\text{Molar Concentration (M)} = \frac{\text{moles}}{\text{Litres}} \text{ or } M = \frac{\text{millimole}}{\text{mL}}$$

Normality

$$N = \frac{\text{equivalent}}{\text{Litre}} = \frac{\text{Meq}}{\text{mL}}$$

Equivalent = mole x (no of reacting unit per molecule)

Meq = mole x (no of reacting unit per molecule)

3.7.1 Molarity

The volumetric calculation often assume that the reaction between analyte and titrant is on 1:1 basis, hence these are valid.

millimole = mL x M

mg = m mole x FW (molecule mass)

So based on 1:1

$$\%\ A = \frac{\text{mg analyte}}{\text{mg sample}} \times 100\%$$

That is,

$$\% A = \frac{M\ (mole/mL)\ x\ ml\ x\ F.W_{analyte}\ (mg/mmole)\ x\ 100\%}{mg\ sample}$$

Example 1: How many millilitres of 0.25M of H_2SO_4 will react with 10ml of a 0.25M solution of NaOH ?

The equation of the reaction is $H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$

Twice as many millimole of NaOH as of H_2SO_4 will react or

M_{H2SO4} x ml $_{H2SO4}$ $= M_{NaOH}$ x ml $_{NaOH}$ x ½(mmoles H_2SO_4 /mmoles NaOH)

Therefore ml H_2SO_4 =

$$\frac{0.25mmoles/ml \times 10ml \times 1/2\ ½(\text{ mmoles } H_2SO_4 \text{ /mmoles NaOH})}{0.25mmoles/ml}$$

ml H_2SO_4 = 5.0ml

Example 2: A sample of pure salicylic acid is analysed by titration. What size of sample should beused so that percent purity is equal to five times the millilitre of 0.0500M NaOH used to titrate it?

Let y = ml NaOH; % Salicylic acid (HA) 5y

$$\% HA = \frac{M_{NaOH} \times ml_{NaOH} \times 1\ (mmole\ HA/mmole\ NaOH) \times f.W_{HA}\ (mg/mmole)}{mg\ of\ sample} \times 100\%$$

$$5y\ \% = \frac{0.0500M \times yml \times 1 \times 138mg/mmole}{mg\ of\ sample} \times 100\%$$

mg of sample =138mg.

However, it is now realised that not all substance react on 1:1 mole basis and so the need for a generalised formula for calculation.

Assuming $xA + yT \dashrightarrow P$

where A is the analyte, T is the titrant and P is the product.

Then,

$$M\ mole_A = formula\ \frac{mmole}{1} \times \frac{x}{y}\left(\frac{A\ mmole}{mmole}T\right)$$

$$M\ mole_A = \frac{M\ mole}{1} \times \frac{x}{y}\left({}^{Mmole\ A}/_{mmole\ T}\right)$$

$$\text{M mole}_A = M_T \left(\text{mmole}/\text{ml}\right) \text{x Ml}_T \text{ x } \frac{x}{y} (\text{mmole A}/\text{mmole T})$$

$$Mg_A = \text{mmole}_A \text{ x fw}_A \ (\text{mg}/\text{mmole})$$

$$Mg_A = M_T \left(\text{mmole}/\text{ml}\right) \text{x Ml}_T \text{ x } \frac{x}{y} (\text{mmole}_T) \text{x Fe}_A \ \text{mg}/\text{mm}$$

Therefore,

$$\% A = \frac{M \left(\text{Mmole}/\text{ml}\right) \text{x Ml}_T \ x \ \frac{x}{y} \left(mmole\ A/mmole_T\right) \ x \ Fw \ x \ 100\% \ \ Mg/mmole}{\text{Mg sample}}$$

or

$$\left(\text{MT moles}/\text{Ml}\right) \text{ x Ml}_T = \text{Mmole}_A \text{ x } \frac{y}{x} (\text{mmole}_T/\text{mmole}_A) =$$

$$\frac{Mg_A}{Fw \ (\text{mg}/\text{mole})} \text{ x } \frac{y}{x} \ (\text{Mmole T}/\text{Mmole A})$$

$$\frac{M_T = Mg_A (Fw_A) \text{ x } \frac{y}{x} \ (\text{Mmole T}/\text{Mmole A})}{Ml_T}$$

3.7.2 Normality

$$\text{ef wt Acid} = \frac{F.W_{Acid} \ (g/Mole)}{1 \text{ equivalence}/\text{mole}} = \frac{F.W_{Acid}}{\text{No of reacting unit}}$$

$$\text{eq wt HCl} = \frac{F.W_{HCl} \ (g/mole)}{1 \ \text{equivalence}/\text{ml}}$$

$$\text{eq wt } H_2SO_4 = \frac{F.W_{H_2SO_4} \ (\text{mg}/\text{mole})}{2 \ \text{equivalence}/\text{ml}}$$

$$\text{eq wt } H_3PO_4 = \frac{\text{F.W}_{H_3PO_4}\ (^{mg}/_{mole})}{3\ \text{equivalence}/_{ml}}$$

So equivalent weight is the weight of a substance in grams that will furnish one mole for the reacting unit.

$$\text{equivalence} = \frac{g}{\text{eq wt } (^{g}/_{eqn})} \qquad \text{meg} = \frac{mg}{\text{equit } (^{mg}/_{eq})}$$

$$N = \frac{equiv}{Liter} = \frac{^{g}/_{eg}\ wt(^{g}/_{eg})}{Litre}$$

$$N = \frac{Meq}{Ml} = \frac{^{mg}/_{g}\ wt(^{mg}/_{meq})}{Ml}$$

Note that the major advantage of this concept of normality is that one equivalent of substance will **ALWAYS** react with one equivalent of substance.

$$\text{Meq}_A = \frac{\text{Mg}_A}{\text{equt}_A\ (^{mg}/_{meq})} = N_T\ (^{meq}/_{ml})\ x\ Ml_T$$

$$\text{Mg}_A = \text{Meq}_T\ x\ \text{eq wt}_A\ (^{mg}/_{meq})$$

$$\text{Mg}_A = N_T\ \left(^{Meq}/_{ml}\right)\ x\ Ml_T\ x\ \text{eq wt}_A\ (^{mg}/_{meq})$$

$$\%\quad A = \frac{N_T\ (^{Meq}/_{ml})\ x\ Ml_T\ x\ \text{eq wt}_A\ (^{mg}/_{meq})}{\text{mg Sample}} x\ 100\%$$

A + B ---→ product

$$Meq_A = meq_B$$

Therefore one can calculate the volume of the two substances that react

$$N_A\ (^{meq}/_{ml})\ x\ ML_A = N_t\ (^{meq}/_{ml})\ x\ Ml_T$$

Reacting units in s

Equiv weight = $\frac{F.w}{No\ of\ reacting\ unit}$

Since there are various specific reaction, the major task is to evolve the reaction unit in each specific reactions, so as to calculate the equivalent weight from the relationship.

i. Acid-base reaction, the reaction unit for acid and bases is the proton H^+

$$eq\ wt = \frac{F.w}{No\ of\ H^+}$$

ii. Reduction – oxidation: The reacting unit of this type of reaction is electron. A reducing agent liberates e- thereby got oxidized, while oxidizing agent takes on electron thereby got reduced.

$$eq\ wt = \frac{F.w}{No\ of\ Mole\ of\ e^-\ gaines\ or\ lost}$$

iii. Precipitation and complexometric Reaction: In this case, though there is no reacting unit exchanged but reactant merely combine, the change on cations (metal ions) is assumed to be the reacting unit.

$$eq\ wt_{m+} = \frac{Atomic\ weight}{change\ (+n)}$$

Example: A solution of sodium carbonate is prepared by dissolving 0.212g of Na_2CO_3 and diluting to 100ml. Calculate the normality of the solution (a) if it is used as monobasic acid, and (b)if t is used as dibasic acid

(a) $N = \frac{mg_{Na2CO3}/(Na_2CO_3/1)}{ml} = \frac{212mg/(106.0/1mg/meq)}{100ml} = 0.0200eq/ml$

(b) $N = \frac{mg_{Na2CO3}/(Na_2CO_3/2)}{ml} = \frac{212mg/(106.0/2mg/meq)}{100ml} = 0.0400eq/ml$

SELF ASSESSEMTN EXERCISE

1 Highlight the general requirements for titrimetric analyses.

2. Explain the following terms: (a) Blank titration (b) Basic titration (c) primary standards (d) indicator error

3. Briefly explain the various classes of volumetric analysis.

4.0 Conclusion

Volumetric analysis is a common analytical method for carrying out quantitative investigation. It covers various specific known titration which include acid-base, oxidation- reduction, precipitation and complexometric titrations.

5.0 Summary

In this unit we have learnt that

1 Volumetric titration is a very rapid and precise analytical quantitative method.

2 For titrimetric analysis to be valid, it must satisfy some requirements such as rapidity, quantitative in nature and must be presentable in equation.

3 There are various ways by which equivalence point can be detected

4 That there are four basic types of volumetric analyses. These are acid-base, redox (oxidation-reduction), and precipitation and complexometric titrations.

5 Various technical terms that are involved in the volumetric analysis

6 Volumetric calculations are usually done based on Molarity and normality

6.0 Tutor Marked Assignment

1 Give concise meaning of the following terms :(a) back titration, (b) standard solution, (c) titration error, (d) equivalence point.

2 Differentiate between end point and equivalence point.

3 Write briefly on four known classes of volumetric analysis.

4 Differentiate between Molarity and normality

5 A solution of sodium carbonate is prepared by dissolving 0.420g of Na_2CO_3 and diluting to 100mL. Calculate the normality of the solution

(a) If it is used as a monoacidic base,

(b) If it is used as an acidic base.

6 How many millitre of 0.25 M solution of H_2So_4 will react with 10ml of a 0.25M solution of NaOH?

7 Calculate the number of milliequivalent of chlordane $C_{10}H_6Cl_6$ (gfw – 410) in 0.500g of the pure insectside. Assuming that all of the chlordane present is ultimately titrated with Ag^+.

7.0 Further reading and Other resources.

1 Christian, G.D. (1980). Analytical Chemistry.3rd ed, John wiley and son, New York.

2 Harris, D.C. (1995). Quantitative Chemical Analysis. 4th Ed. Freeman and Company, New York.

3 Khan, I.A. and Khanum K. (1994).Fundamentals of Biostatistics .Ukaaz Publications, Nagar .

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5 Nwachukwu, V.O.(2006).Principle of Statistical Inference. Peace Publishers, Port-Harcourt.

Module 2 BASIC CONCEPT OF TITRMETRIC ANALYSIS

Unit 2 **Acid-Base Titration**

1.0 Introduction

Acid-base titration is one of the types of volumetric analyses. It is the most commonly used throughout the realm of chemical analysis. Through the use of titration curve, both acidic and basic component of a material (sample) can be determined. In this unit, how to select a suitable indicator for detecting completion of titration reaction, preparation of standard acid or base solution (medium) are part of the areas covered.

2.0 Objectives

At the end of this unit, students should be able to

i. explain correctly acid-base titration;

ii. define some basic technical terms in acid- base titration;

iii. Outline the basic concepts and principles involved in acid - base titration;

iv. use acid-base titration curve to determine components of a given sample;

v. explain the principle of selecting a suitable indicator; and

vi. prepare standard acid and base solution.

3.0 Acid-base Titration

It is a volumetric analytical method which relates acid and base stochiometrically till reaction is completed. It is a very simple, reproducible and accurate analytical technique.

Acids and bases have been described by various theories notably which are:

i. Arrhenius theory which describes an acid as any substance that ionises partially or completely in water to give hydrogen ion, while base is any substance which ionises partially or completely in water to give hydroxyl ions.

ii. Bronsted -lowry theory describes an acid as a substance that can donate a proton and a base as any substance that can accept a proton.

There is a medium (solvent) necessary for the titration reacting to occur which can be aqueous or non aqueous.

3.1 Solvents Classification

The solvents may be classified into three groups based on certain principles.

(i) Amphiprotic-those solvents that have both basic and acidic properties e.g water, ethanol. These solvents can ionise.

(ii) Aprotic- those solvents that are neither appreciably acidic or basic. They are weakly polar in nature e.g. benzene tetrachloride.

(ii) Basic but not acidic- these solvents are extremely weak bases. They are non-ionisable e.g. ether and ketone.

.3.2 Monitoring pH changes

For the study of various acid-base titration, to be comprehensive and goal oriented, the study would monitor trends of change in pH as titrant is added to the analyte. These stages to cover:

(i) Before equivalence point;

(ii) At equivalence point; and

(iii) After equivalence point

3.2.1 Titration of Strong Acid against Strong Bases.

The reaction is a neutralisation. This type of acid-base titration is always a strong acid on a strong base.

The first step- is to write a comprehensive ionic equation of the reaction.

Example: Titrating HCl against NaOH.

The exercise in the system is $H^+ + Cl^- + Na^+ + OH \dashrightarrow H_2O + Na^+ + Cl^-$

The ionic equation is $H^+ + OH^+ \dashrightarrow H_2O$. This is otherwise known as titration reaction. The equation can also help in determining/calculating the composition and pH after each addition of titrant.

V_x (ml) (Molarity of x) = V_y (ml) (Molarity of y)

$$V_x = \frac{V_y M_y}{m_x}$$

Where x is for the acid and y is for the base

At V_x the equivalence point is reached. Prior to this V_x point, there will be excess of OH and after the V_x point, there will be excess of H^+. Therefore, in plotting titration curve pH versus the volume y of the titrant (x), there are three variable regions, Viz:

i. Before reaching equivalence point, the pH is determined by the excess of OH in the solution.

ii. At equivalence point, the H^+ is just sufficient to completely react with all OH. So the pH is determined by dissociation of water, while $K_W = 10^{-14}$

So the reaction goes to completion.

iii. After reaching equivalence point, pH is determined by the excess H^+ in the solution.

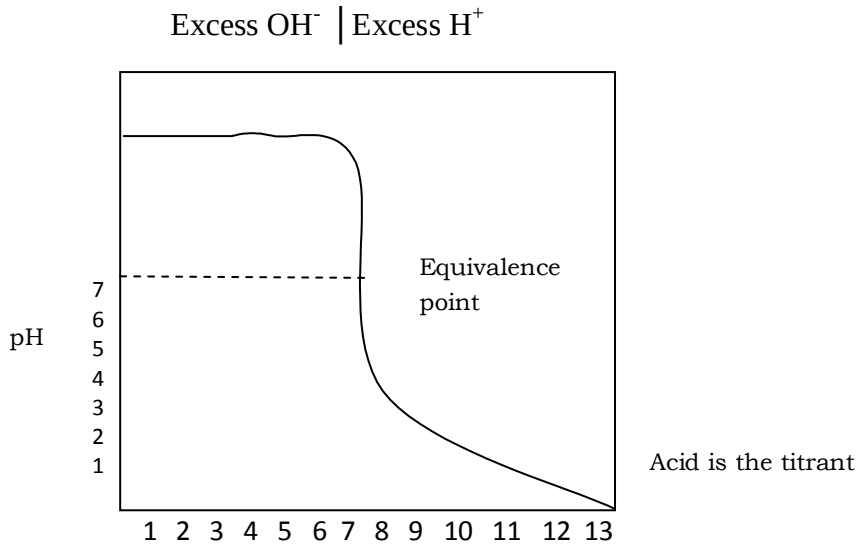


Fig. 1.0 The titration curve of H^+ being added to OH^-

(mL) acid

The magnitude of the break (end point) depends on the concentration of both titrant and analyte.

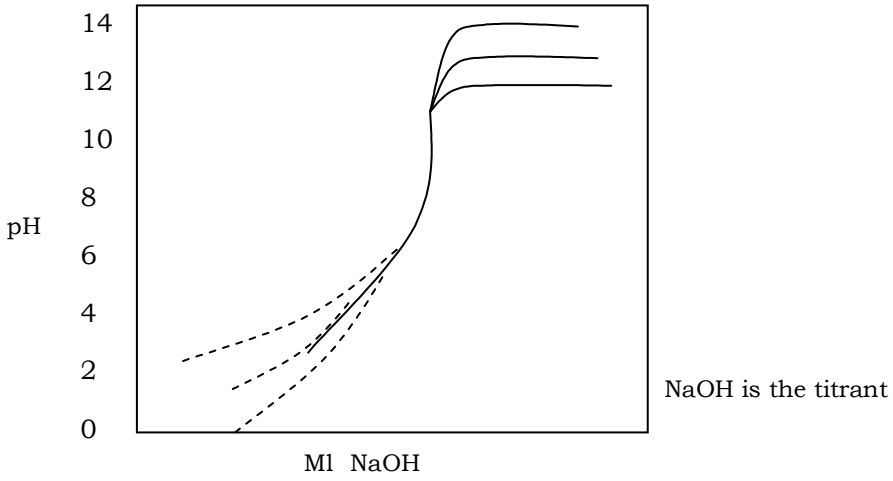


Fig. 2.0 The titration curve of

Curve 1 0.1m HCl against 0.1 m NaOH

Curve 2 0.01 HCl against 0.01m NaOH

Curve 3 0.001 HCl against 0.01m NaOH

3.2.2 Titration of weak Acids Against Strong Bases

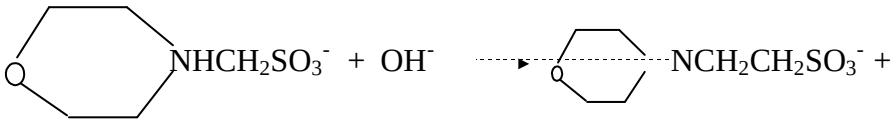
The titration reaction is neutralisation. Strong base is the titrant while the weak acid is the analyte.

1st step – write the ionic equation

If we are titrating MES against NaOH

MES ⟹ 2 - (N-morphline) ethanesulfonic acid. It is a weak acid with pKa =6.15

Titration Equation



H_2O

From the reaction

V_m (ml) (molarity M_m) = V_n (ml) (Molarity M_n) =

$$V_m = \frac{V_n M_n}{M_m}$$

It is helpful to calculate Vm needed to reach equivalence.

where m = strong base (titrant)

n = weak acid (analyte)

The titration calculation is then divided into four stages which is also reflected in the titration curve.

1. Before any base is added, the solution contains just HA in water. It is a weak acid problem in which pH is determined by the equilibrium

   $$HA \rightleftharpoons H^+ + A^-$$ (Ka)

2. From the first addition of NaOH until before the equivalence point, there exist a mixture of unreacted HA and the A^- produced by the reaction. Henderson – Hasselbalch equation can be used to find the pH.

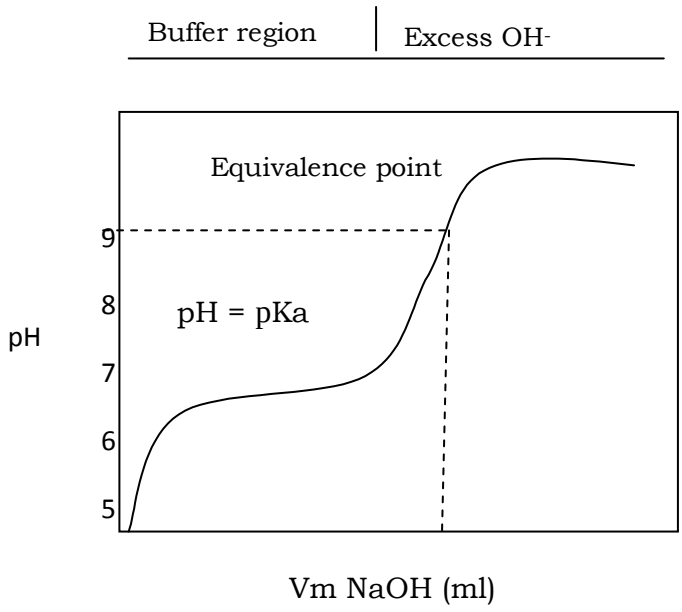
   Hasselbalch equation is an equation which express pH of a buffer solution as a function of the concentration of the weak acid or base and the salt component of the buffer system.

   Hasselbalch equation : $pH = pK_a + \log \frac{[A^-]}{[HA]}$

3. At equivalence point 'all' of the HA has been converted to A^-. The problem is the same as if the solution had been made by merely dissolving A^- in water. pH can be determined by the reaction.

$$A^- + H_2O \rightleftharpoons HA + OH^-$$

4. Beyond the equivalence point, excess NaOH is being added to a solution of A^- to a good approximation the pH is determined by strong base. We calculate the pH as if we simply add excess NaOH to water the



Before the reaction titration started at all, we have only weak acid in the medium acid and so pH is calculated as for weak acid. At the commencement of titration, some HA is converted to A^- and so buffer system is set up. As the titration continues, the pH slowly increase as the ratio of A^- : HA changes.

At the mid point of the titration [OAc]=[HOAc] and pH is equal to pKa. The pH of equivalence point will be alkaline.

The weaker the acid (the smaller Ka),the longer the positive K_b of the salt and the more alkaline the equivalence point.

3.2.3. Titration of Weak Base Against Strong Acids

It is also a neutralisation reaction. It is just the opposite of the case of weak acid against strong Base.

The titration reaction is $B + H^+ \rightarrow BH^+$.

The reaction goes to completion after each addition of acid. There are also four stages shown in titration curve.

1. Before acid is added, the solution contains just the weak base in water.

   The pH is determine by the K_b reaction

   $B+H_2O \rightleftharpoons BH + OH^-$

(2) After the commencement of titration up to equivalence point there is a mixture of **B** and BH^+. That is Buffer system is set up. K_b can easily be determined from the titration curve.

3. At the equivalence point. B has been converted into BH^+, a weak acid. The pH is calculated by the consideration of dissociation of acid BH^+

   $BH^+ \overset{kb}{\rightleftharpoons} B + H^+$ $\qquad Ka = \frac{Kw}{Kb}$

The formal concentration of BH^+, F' is not the same as the original formal concentration of B, because of the some dilution that has occurred. Because the solution contains BH^+ at the equivalence point, it is acidic. The pH at the equivalence point must be below 7

4 After the equivalence point, there is excess of H^+ in the solution.

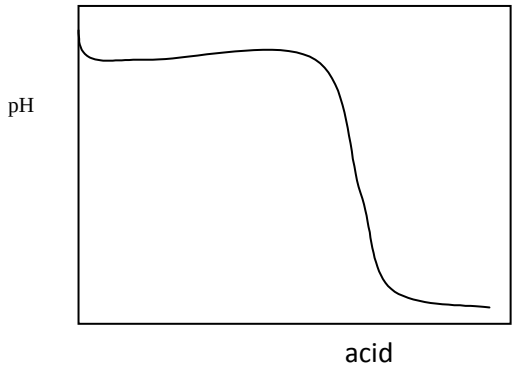


Fig .4.0 Titration curve after

3.2.4 Titration of Polyprotic Systems

There are some bases that hydrolyse in more than one step, thereby having more than one dissociation constant. Generally, the principle developed for the titration of monoprotic systems readily applies to them.

For example, consider titration of base (B) against Acid (H) in which the base is dibasic.

The titration equation

$B + H \longrightarrow BH^+$ …… a

$BH^+ + H^+ \quad BH_2^{2+}$ …….. b

The titration curve shows reasonable sharp breaks at both equivalence points.

From equation (a)

Vb x nb - Va x na

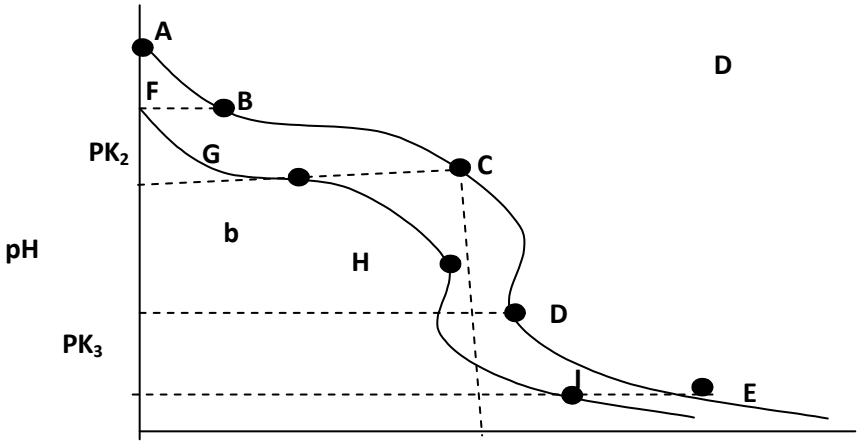
Where "b" is for the base and "a" is for the acid

$$Va = \frac{Vb \times na}{Ma}$$

The volume of the acid required to reach 1st equivalence point is Va_1

Going by equation (b), the volume of acid to reach 2nd equivalence point is 2 x Vai

So , $Va_2 = 2\ Va_1$



Point C and E are the two equivalence points while point B and D are the half-neutralization points whose values equal pKa_2 as pK_1 respectively. The titration curve is in the following Phases

(i) Point A. Before any acid is added, the solution contains just B, a weak base whose pH can be found as follows.

$$\underset{y-x}{B} + H_2O \xrightarrow{kb} \underset{x}{B^+} + \underset{x}{OH^-}$$

y = Original volume of B in the system

$$[H^+] = \frac{Kw}{x} = pH$$

Point B. Between point A and C, we have buffer system established containing B and BH^+. B is half way to equivalence point. So $[B] = [BH^+]$, pH is calculated using Henderson- Hasselbalch for weak acid whose dissociation constant is Ka_2 for BH_2^{2+}

$$Ka_2 = \frac{Kw}{Kb_1}$$

To calculate pH at B

$$pH = pKa + \log \frac{[B]}{[BH^+]}$$

Point C. This is the first equivalence point .B has been converted to BH^+, the intermediate form of diprotic acid BH_2^{2+}.

$$[H+] = \sqrt{\frac{K_1K_2F + K_1K_w}{K_1 + F}}$$

where F is the formal concentration of BH^+

$$pH = \tfrac{1}{2} [PK_1 + PK_2]$$

Point D_1. At any point between C and E, we can consider the solution to be buffer containing BH^+ and BH_2^{2+}

$$pH = pKa_1 + \log \frac{[BH^+]}{BH_2^{2+}}$$

Point E: Point E is the second equivalence point at which solution is formerly the same. The pH is determined by the acid dissociation reaction of BH_2^{2+}.

$$BH_2^{2+} \rightleftharpoons BH^+ + H^+$$

F-x x x

3.3 Detecting the End Point with Indicator

The use of an acid-base indicator to find end point is a more convenient method. It involves adding small amount of acid-base indicator, itself an acid or base, whose various protonated species have different colours.

The colour o the ionized form is different from the unionized form. One form may be coloured, the other form may be colourless.

$$HIn \rightleftharpoons H^+ + In^-$$

(Red) Blue

The unionized form is red while the ionized form is blue. Then the Henderson-Hasselbalch equation gives

$$pH = pKIn + \log \frac{[In^-]}{[HIn]}$$

Note that since the indicator is a weak acid or base, the amount added should be kept minimal so that it does not contribute appreciably to the pH. Moreover, the smaller the quantity of the indicator added, the sharper the colour changes.

There are other methods though not as simple as the use of indicator, through which end point can be detected. These include:

(i) the use of pH electrode;
(ii) the use of derivatives; and
(iii) the use of gram plot.

Self assessment exercise

1 Define the following terms
   (a) Monoprotic acid-base system
   (b) Polyprotic acid-base system
   (c) Indicator
2 Highlight various stages of acid-base titration curve.
3 Brifly explain how an indicator works.

4.0 Conclusion

Acid-base titration remains one of the most commonly used volumetric analytical techniques. It is very simple, precise and fairly accurate. Various types of acid base systems exist. The use of indicator makes it easier and convenient for the end point to be detected.

5.0 Summary

In this unit, we have learnt about:

(i) Definition and fundamental principle of acids-base trimetric method
(ii) Classification of solvent need as to act as a medium for the titration
(iii) Various phases of titration survey of (a) strong acid versus strong base (b) Strong acid versus weak base, (c) weak acid verses strong acid, (d) Polyprotic system
(iv) The use of indicator to defect end point.
(v) Other methods of detecting end point

6.0 Tutor marked assignment

1 Highlight various phases of acid-base titration curve
2 Consider the titration of 40.0ml of 0.20M malonic acid with 0.100M NaOH. Calculate the pH at each point listed and sketch the titration curve when Vb = 0.0, 8.0, 12.5, 19.3, 25.0, 37.5, 50.0 and 56.3ml
3 Make a short note on the classification of solvents in acid-base system
4 Write short note on pH :
   (a) before equivalent point;
   (b) at equivalence point; and
   (c) after equivalence point of strong acid versus strong base system

7.0 Further reading and Other resources.

1 Christian, G.D. (1980). Analytical Chemistry.3rd ed, John wiley and son, New York.

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MODULE 2 BASIC CONCEPT OF TITRMETRIC ANALYSIS

Unit 3: Oxidation Reduction Titration

1.0 Introduction

Oxidation – Reduction titration (redox) is one of the main types of volumetric analytical techniques. It is based on oxidation – reduction reaction in which electrons are transferred from one substance to another. It helps in determining the component of many substances qualitatively. This unit covers balancing redox reaction equations as well as principles of electrochemical cell and how electrode potential can be used to predict which oxidizing and reducing agent might get involve in the reaction. It also includes construction and use of Redox titration curve.

2.0 Objectives

By the end of two unit, students should be able to :

i. Explain the mechanism of redox titrations;
ii. Explain the technical terms and principles involved in the titration of redox components;
iii. Illustrate the principle of Electrochemical cells; and
iv. use of redox titration curves to predict component of given substance.

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3.0 Definition.

Oxidation – Reduction reaction is a reaction which involves the movement of electrons from one point to another, in a reaction between analyte and titrant. The general principle of Redox reaction lies in the fact that reaction occurs between a reducing and an oxidizing agent

3.1 Review of some known technical terms in redox reaction.

1. ***Oxidation*** –simply defined as loss of electrode to give higher oxidation state. The electrode is always more positive

2. ***Reduction*** - Is gain of electron to give lower oxidation state. The reduction electrode is always more negative (more negative).

3. ***Oxidizing agent*** is the substance (s) that tend to take up an electron(s and get reduced to lower oxidation state.

4. ***Reducing agent*** is the substance(s) that tend to give up electron(s) and get oxidized to higher oxidation state.

$$Ox_1 + Red_2 \rightleftharpoons Red_1 + Ox_2$$

(Oxidizing agent) (Reducing agent)

The tendency to oxidise or reduce depends on the reduction potential of a substance. The course of monitoring redox titration by potentiometry requires the need to review and understand very well the fundamental of electrochemical cells and electrode potential.

3.2 Electrochemical cell

It is a device in which electrolysis of solution takes place. It is a compartment where electrochemical reaction occurs. There are basically two types of cells.

3.2.1 **Galvanic cell**: This is the type of electrochemical cell in which a chemical reaction spontaneously occurs to produce electrical energy.

3.2.2 **Electrolytic cell**: It is the type of chemical cell in which electrical energy under the influence of an external source of power produces chemical energy. A typical cell is made up of electrolyte, electrodes and salt bridge.

3.2.3 **Electrodes** are strip of metals that are conducting in nature. There are two types; [i] Anode, where oxidation takes place [ii] Cathode where reduction takes place.

(ii) Electrolyte: is a liquid or molten subtance (solution) that can allow passage of electrical current. They are conducting in nature.

(iii) Salt bridge: This is often made up of KCl crystals. They connect two reacting systems (beaker) together, thus allowing movement of electron from one beaker to another thereby preventing overconcentration of electron in beaker. However it disallows any other substance from passing.

E cell = E right – E left = E cathode – E anode = $E^+ - E^-$

Nearnst Equation: This is the equation that relates the standard potential of a system with the concentration of both oxidized and reduced form when they are expressed in unit activity.

$$aOx + ne^- \rightleftharpoons b\,Red$$

By Nearnst **equation** $\mathbf{E = E^o} - \frac{2.2320^{RT}}{nf} \log \frac{(\mathrm{Re}d)^b}{(Ox)^a}$

Each electrode has the tendency to loose or gain electron when in reaction, the tendency of each electrode is referred to as electrode potential. The electrode potential is more often the function of its make up which has great impact on the cell reaction.

Note that

i. The more positive the electrode potential, the greater the tendency of the oxidized form to be reduced e.g $Ce^{4+} + e^- \rightarrow Ce^{3+}$ $E^o = + 1.70v$ .Therefore, Ce^{+4} is a strong oxidizing agent while Ce^{3+} is a very weak reducing agent.

the The more positive the electrode potential, the stronger the oxidizing power of oxidized form is and the weaker the reducing power of the reducing form is.

ii. The more negative the reduction potential, the weaker the oxidizing power of the oxidized form is and the stronger the reducing power of the reduced forms is.

e.g $Zn^{2+} + 2e^- \rightarrow Zn$, $E^o = -0.76$ is very negative. So, Zn^{2+} is a weak oxidizing agent while Zn is a strong reducing agent.

3.3 Redox Titration Curve

The course of redox titration is monitored potentiometrically. Potentiometer measures in voltage, the concentration of species in solution.

Titration reaction is

$$Ce^{4+} + Fe^{2+} \rightarrow Ce^{3+} + Fe^{3+}$$

Titrant analyte

However note that at each electrode, the following half reaction occur. Ka

$Fe^{3+} + e \rightleftharpoons Fe^{2+}$ $E^o = + 0.77V$

$Ce^{4+} + e^- \rightleftharpoons Ce^{3+}$ $E^o = + 1.61V.$

At the calomel reference electrode, the half reaction is $2Hg^{+} + 2Cl^{-} \rightarrow HgCl_2 + 2e^{-}$

Therefore the cell reaction can be in other ways.

(i) $2Fe^{3+} + 2Hg + 2Cl^{-} \rightleftharpoons 2Fe^{2+} + Hg_2Cl_2^{-}$

[i] $2Ce^{4+} + 2Hg + 2Cl \rightleftharpoons 2Ce^{3+} + Hg_2Cl_2$

The titration curve is divided into three phases (stages).

(1) Before equivalence point: Each aliquot of Ce^{4+} added is consumed and create equal mole of Ce^{3+} as Fe^{3+}. Prior to the equivalence point excess Fe^{2+} remain in the solution, Therefore, calculating the E of the cell is ensure through the activity of Fe^{2+}.

$$E = E^{+} + E^{-}$$

E = the potential of the cell

E^{+} = potential for reduction

E^{+} = Potential for Ref Electrode calomel

NB: $E^{+} = E^{o} - 2.3026RT \log \frac{[Red]}{[ox]}$ Nearnst equation

$$E = \left[0.767 - 0.05916 \log \frac{[Fe^{2+}]}{[Fe^{3+}]} \right] \rightarrow 0.241$$ Potential for Calomel Electrode

Potential for Fe^{3+} reduction in 1M $HClO_4$

$$E = 0.5266 - 0.059.6 \log \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

(2) At equivalence point, enough Ce^{4+} has been added to react with all Fe^{2+}.

So $[Ce^{4+}] = [Fe^{2+}]$

all Ce^{4+} are converted to $Ce^{3,+}$ while Fe^{2+} are converted to Fe^{3+}

$[Ce^{3+}] = [Fe^{3+}]$

$$E_f = 0.707 - 0.05916 \log \frac{[Fe^{2+}]}{[Fe^{3+}]} \quad .....(1)$$

$$E^+ = 1.70 - 0.05916 \log \frac{[Ce^{3+}]}{[Ce^{4+}]} \quad .....(2)$$

Neither the equation 1 or 2 alone is enough to calculate E^o of the cell, but combination of the two equations

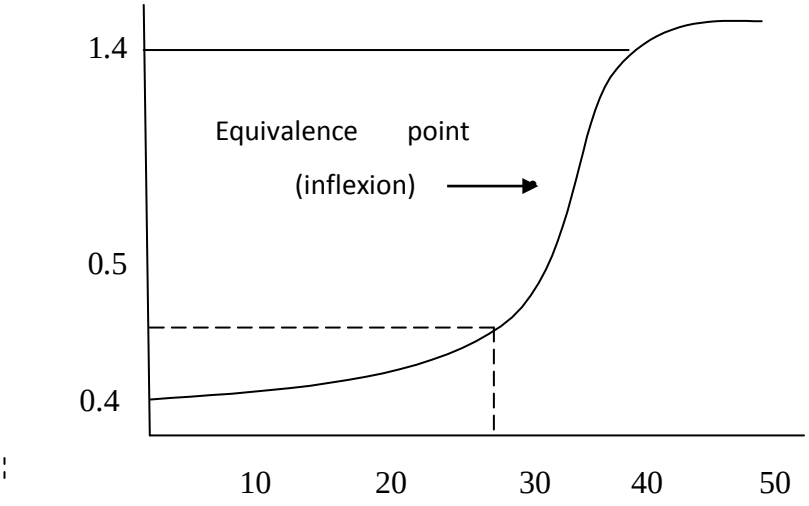
$$2E^+ = 0.767 + 1.70 - 0.05916 \log \frac{[Fe^{2+}]}{[Fe^{3+}]} - 0.05916 \frac{[Ce^{3+}]}{[Ce^{4+}]}$$

$$2E^+ = 2.46V$$

$E_+ = 2.46/2 = 1.23V$

$E = E^+ - E$ calomel

$E = 1.23 - 0.241 = 0.99V.$



Redox Titration curve

3. After Equivalence Point

Almost all Fe^{2+} are now in form of Fe^{3+} while the excess Ce^{4+} remained in the system. So the E of cell is formed from the activity of Ce^{4+}.

$$E = E_+ - E \text{ calomel} = 1.70 - 0.05916 \log \frac{[Ce^{3+}]}{[Ce^{4+}]} - 0.24$$

$E_+ = 1.70$

$$E_t = E^o \frac{Ce^{4+}}{Ce^{3+-}} - 0.241$$

$E = 1.216V$

3.4 Detecting Redox End Point

The end point of the redox titration can be determined by the use of electrode to measure potential and is plotted against the volume of titrant. Three visual indicators are commonly used.

(i) ***Self indicator***

This is when the titrant is highly coloured .The colour change may be used to detect the end point.

Example: Titration of acidified $KMnO_4$ against freshly prepared $FeSO_4$ solution. $KMnO_4$ which is deep blue/pink converts to colourless at end point.

(ii) ***Starch indicator***

Starch indicator is often used when the titration involves iodine /starch complex, which is blue colour but at the end point turns colourless but addition of drops of starch turns it back to blue.

(iii) ***Redox Indicators***

These are highly coloured dyes. They are weak reducing or oxidizing agent. They are potential dependent. Example is Ferroin whose colour changes from pale blue to red and is potential dependent.

3.5 Iodimetry and Iodometry

Both are analytical techniques that involves the use of iodine [I^-] but of different status

(i) Iodine is a moderately strong oxidizing agent and can be used to titrate reducing agent. Titration with I_2 as oxidizing agent is called iodimetric analysis. It is performed in neutral or mildly alkaline (pH = 8) medium.

(ii) Iodine is also a weak reducing agent and will reduce oxidizing agent so when an excess iodine is added to a solution of an oxidizing agent, I_2 is produced in an amount equivalent to the oxidizing agent present. Such analytical method is known as iodometric method

Self Assessment Exercise

1 What is an (a) oxidizing agent, (b) a reducing agent? Give two examples in each case.

2 Differentiate between Iodimetry and Iodometry.

3 Explain the following terms: (a) Galvanic cell, (b) Electrolyte, (c) Salt bridge.

4.0 Conclusion

Redox titration is a fairly accurate and precise analytical method, if a proper indicator is selected.

5.0 Summary

In this unit, we must have learnt about :

(i) Definition of redox titration and various technical terms.

(ii) Electrochemical cell and cell potential

(iii) How to use Nearnst equations to monitor potenmetrically, the activity of species at, before and after equivalence point.

(iv) Redox indicator

6.0 Tutor marked Assignment

1 Differentiate between the two major types of electrochemical cells known

2 Explain the following terms:

(i) Reducing agent (ii) Oxidizing agent (iii) Electrode potential (iv) Salt bridge

3 Calculate the potential of half reaction of solution of 10^{-3} M in $Cr_2O_7^{2-}$ and 10^{-2} M in Cr^{3+} of pH 2.0

4 Differentiate between Iodometry and Iodimetry

5 Name the various types of indicators often used in Redox titration. Write briefly about each of the named indicators.

7.0 Further reading and Other resources.

1 Christian, G.D. (1980). Analytical Chemistry.3rd ed, John wiley and son, New York.

2 Harris, D.C. (1995). Quantitative Chemical Analysis. 4th Ed. Freeman and Company, New York.

3 Khan, I.A. and Khanum K. (1994).Fundamentals of Biostatistics .Ukaaz Publications, Nagar .

4 Laitimen, H.A . and Hesiscs, W.E. (1995). Acid-Base Equilibria in Water. 2nd Ed. McGraw Hill Inc., New York

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Module 2 BASIC CONCEPT OF TITRMETRIC ANALYSIS

Unit 4 Complexometric and Precipitation Titrations

1.0 Introduction

Some metal ions form slightly soluble salts or slightly dissociated complexes. The formation of these complexes can be the basis for accurate, more precise and convenient titrimetric determination for such metal ions. Titration based on these complexes is known as complexometric titrimetric method.

This unit reviews some fundamentals of the complexing agents called chellate, their effects and their equilibrium. Titration curves of complexometric and precipitation titrations are also discussed.

2.0 Objectives

By the end of this unit, students should be able to :

i. explain the principle of complex ion formation;

ii. explain the working principle of EDTA in complexometric titrations using appropriate indicators;

iii. use titration curves to illustrate both the complexometric titration and precipitation titrations; and

iv. list the applications of complexometric titration and precipitation titrations.

3.0 Definition

Complexometric titration is an analytical method which is used to determine larger number of metals that form soluble salt or slightly dissociated complexes.

Almost all metals on the periodic table form complex with electron donating agent (ligand) (e.g. O, N, and S atoms) which are capable of satisfying the coordination number of such metal. The metals are lewis acids, (electron accepting species), while the ligands are lewis bases (election pair donors).

3.1 Ligands

Ligands are complexing agents that bind with the metals to form complexes. The number of ligand that complexes metals depends on the coordination number of the metal. Hence there are majorly two types of ligands.

i. **Monodentate Ligands**: are those ligands that bind the metal ion through only one atom (the carbon atom) e.g CN^-, NH_3

ii. **Multidentate Ligands**: These are the types of ligands that attach to metal ion through more than one ligand atom. *Example* is EDTA (ethylenediaminetetreacetic acid) called Chelating Ligand. ATP (adenosine triphosphate) is another important tetra dentate ligand.

3.2 Formation Constant

Most of the ligands except, perhaps, nitrilotriacetic acid (NTA), form complexes with metal ions in the stochiometric 1:1 (ligand: metal ion) ratio regardless of the charge on the ion.

The equilibrium constant for the reaction of a metal ion with a ligand is called the formation constant K_f – It is also called stability constant K_s or K_{stab}

$$K_f = \frac{[\text{Product}]}{[\text{Reaction}]}$$

eg $Ag^+ + 2NH_3 \rightleftharpoons Ag(NH_3)_2^+$

$$K_f = \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2}$$

However equilibria could also be written in reverse direction as dissociation. The constant is then called instability constant K_i , or dissociation constant, K_d

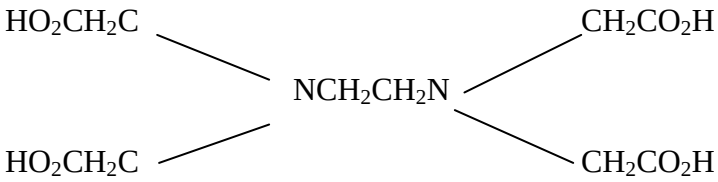
$Ag(NH_3)_2^+ \longrightarrow Ag^+ + 2(HN_3)$

$$K_d = \frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2]}$$

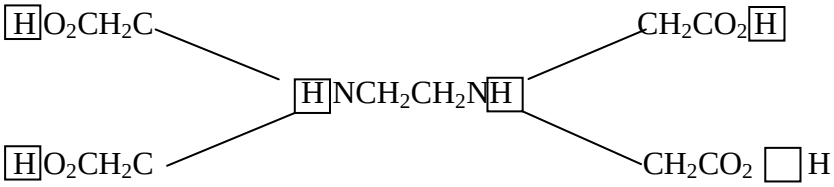
Hence, $\boxed{K_d = \frac{1}{K_f}}$

3.3 EDTA TITRATIONS

EDTA is the most widely used chelator in the field of analytical chemistry, through direct titration or indirect sequence of reactions. It has a sharp end point corresponding to the stochiometric complex formed. The ligand is called chelating agent, while the complex formed with metal ion is called chelate. EDTA is a hexaprotic system designated as H_6Y^{2+} with the exact structure



EDTA is a hexaprotic H_6Y^{2+}, because the number of acidic hydrogen atom lost upon complete metal complex formation is six. The first four that are lost apply to carboxyl protons while the last two are of ammonium protons.



However, the neutral acid is tetraprotic which is designates by H_4Y, not all H_4 referring to proton from carboxyl proton, with different PKa values.

EDTA has four PKa values corresponding to the step wise dissociation of the four protons

$$H_4Y \rightleftharpoons H^+ + H_3Y^- \qquad Ka_1 = 1.0 \times 10^{-2} = \frac{[H^+]\,[H_3Y^-]}{H_4Y}$$

$$H_3Y^- \rightleftharpoons H^+ + H_2Y^{2-} \qquad Ka_2 = 2.2 \times 10^{-3} = \frac{[H^+]\,[H_2Y^{2-}]}{[H_2Y^-]}$$

$$H_2Y^{2-} \rightleftharpoons H^+ + HY^{-3} \qquad Ka_3 = 6.9 \times 10^{-7} = \frac{[H^+]\,[HY^{-3}]}{[H_2Y^{2-}]}$$

$$HY^{3-} \rightleftharpoons H^+ + Y^{4-} \qquad Ka_4 = 5.59 \times 10^{-11} = \frac{[H^+]\,[Y^{4-}]}{[HY^{3-}]}$$

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Anion is the ligand species in complex formation, the complex formed are markedly affected by the pH. H_4Y has low solubility in water, hence the commonly used reagent is disodium salt, ($Na_2H_2Y_2.2H_2O$).

The fraction [α] for each species is the fraction of EDTA in that form.

Example $\alpha\, Y^{4-}$ is the fraction of EDTA in the form of

$$\alpha\, Y^{4-} = \frac{[Y^{4-}]}{[H_4Y] + [H_3Y^-] + [H_2Y^{2-}] + [HY^{3-}] + [Y^{4-}]}$$

$$\alpha\, Y^{4-} = \frac{[Y^{4-}]}{[EDTA]}$$

Where EDTA is the total concentration of all free EDTA species in the solution

Free EDTA means EDTA not complexed to metal. Formation constant, K_f, of metal - EDTA complex is the equilibrium constant for the reaction

Example $M^{n+} + Y^{4-} \rightleftharpoons MY^{n-4}$

$$K_f = \frac{[MY^{n-4}]}{[M^{n+}]\,[Y^{4-}]}$$

$$Ca^{2} + Y^{4-} \rightleftharpoons CaY^{2-}$$

$$K_f = \frac{[CaY^{2-}]}{[Ca^{2+}]\,[Y^{4-}]}$$

3.3.1 Conditional Formation Constant

Due to the fucntionability of pH on the equilibrium, the fraction of EDTA is not all Y^{4-} at pH below 10.24. Species such as HY^{3-}, HY^{2-} predominate at lower pH.

Therefore to conveniently express the fraction of free EDTA, there is the need used for substitution and rearrangement as follows:

Substitute $\alpha\, Y^{4-}\ [Y^1]$ or $\alpha\, Y^{4-}\ [EDTA]$ as $[Y^4]$

$$K_f = \frac{[MY^{n-4}]}{[M^{n+}]\,\alpha\, Y^{4-}\ [Y^-]} \quad \text{or} \quad \frac{[MY^{A-4}]}{[M^{n+}]\ \alpha\, Y^{4-}\ [EDTA]}$$

K^1 = conditional formation constant

Rearranging gives

$$K_f \alpha Y^{4-} = K^1 \quad \frac{[MY^{n-4}]}{[M^{n+}]\ [Y^-]} \quad \text{or} \quad \frac{[MY^{A-4}]}{[M^{n+}]\ [EDTA]}$$

This equation can be used to calculate the equilibrium concentration of the different species at a given pH. It is also called effective formation constant.

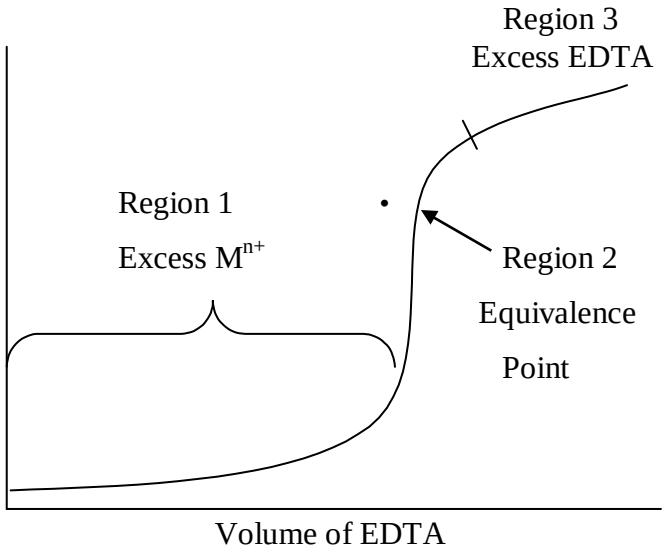
3.3.2 EDTA TITRATION CURVE

The concentration of the metal ion can be calculated easily during the course of complexometric titration of metal ion and EDTA in which chelating agent (titrant) is added to the sample containing metal in (analyte). The titration is analogous to that of a strong acid metal ion and weak base (EDTA).

The titration reaction is

$$M^{n+} + EDTA \rightleftharpoons MY^{N-4}$$

$$K_f^1 = \alpha Y^{4-}\ K_F$$



If K_f^1 is large, then the reaction is considered to be complete at each point of titration. The titration curve is usually divided into three phases.

(1) Before equivalence point: Each addition of EDTA is consumed completely at this stage, so there is excess of M^{n+} left. The concentration of free metal ion is equal to the concentration of excess, unreacted M^{n+}. The dissociation of MY^{n-4} is negligible

(2) At equivalence point: The concentration of EDTA is exactly as that of metal ion in the solution. The solution is treated as if it is dissolving pure MY^{n-4}

$MY^{n-4} \rightarrow M^{n+} + EDTA$

So at equivalence point M^{n+} = EDTA

(3) After equivalence point,

Now there is excess of EDTA while the entire metal ion has been virtually consumed and all metal ions in form of MY^{n-4}. The concentration of free EDTA can be equated to the concentration of excess EDTA added after the equivalence point.

3.3.3 Detecting the End Point

There are methods involved when trying to detect the end point in complexometric titrations. These methods include:

(i) the use of metal ion indictor.

(ii) use of mercury electrode.

(iii) Glass (pH) electrode

(iv) Ion -selective electrode

However, the use of metal ion indicator appears the most convenient and efficient

3.3.4 METAL ION INDICATOR

A metal-ion indicator is a compound which changes when it binds to a metal ion. It is important to note that.

> "For a metal-ion indicator to be useful, it must bind metal less strongly that EDTA does .

There are so many different types of metal - ion indicators, which include Erichrome Black T, Calmagite, murexide, xylenol, pyridylazonephthol, etc. A typical example is the using of Erichrome Black T in the titration of Mg^{2+} with EDTA

$$Mg\ In + EDTA \longrightarrow Mg\ EDTA + In$$

(red) colourless colourless (blue)

Most metal ion indicators are acid-base indicator. If the metal-indicator does not dissociate easily to release metal to EDTA to form metal-EDTA complex, the metal is said to be blocked.

However, the blocked EDTA can be titrated through back titration. Example, excess EDTA (standard) can be added to Cu^{2+}. The indicator is added and excess EDTA is back-titrated with Mg^{2+}.

3.3.5 EDTA Titration Techniques

There are many types of titration methods involved with EDTA. This is probably due to large number of elements that can be titrated through EDTA. The techniques include:

(i) ***Direct titration***: In this type of titration, analyte is titrated with standard EDTA. The analyte is buffered to an appropriate pH at which conditional formation constant is larger and free indicator has a distinct colour. Addition of auxiliary complexing agent such as ammonia, tartarate, and citrate is added to prevent metal ion from, precipitating in the absence of EDTA.

(ii) ***Back-Titration***: a known excess of EDTA is added to the analyte. The excess EDTA is then titrated with standard solution of a second metal ion.

Back titration is useful if the metal ion precipitate in the absence of EDTA. The metal ion used in the back titration must not displace the analyte metal ion from its EDTA sample.

(iii) ***Displacement Titration:*** It is a type of titration in which analyte is usually treated with excess $Mg(EDTA)^2$ to displace Mg^{2+}, which is later titrated with standard EDTA. Displacement titration is often used when metal ions do not have satisfactory indicator.

$$M^{n+} + MgY^{2-} \rightarrow MY^{n-4} + Mg^{2+}$$

(iv) ***Indirect Titration*****:** Anions that form precipitate with certain metal ion can be analysed with EDTA by indirect titration.

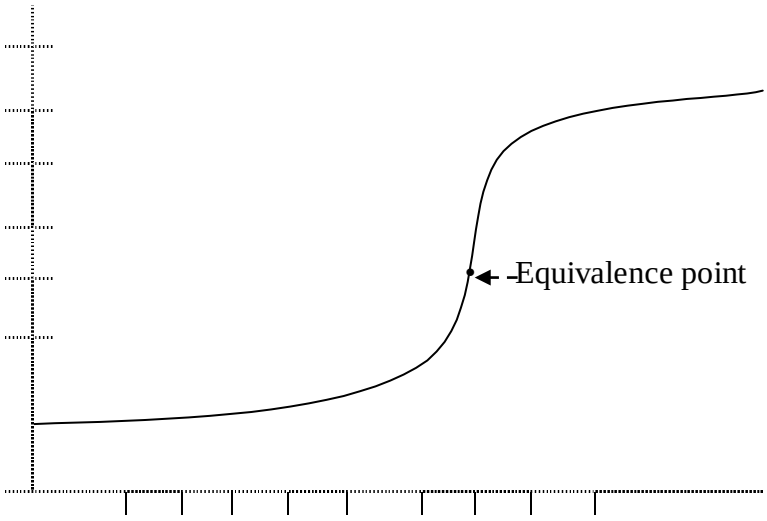
Example $SO_4^{=}$ precipitate with excess Ba^{2+} at pH 1.0 .$BaSO_4$ is filtered, washed and boiled with excess EDTA at pH 10, to bring back Ba^{2+} into solution as Ba $[EDTA]^{2-}$. The excess EDTA is back titrated with Mg^{2+}.

(v) ***The Use of Masking Agent*****:** This is used to prevent the element from interfering in the analysis of another element. Masked element can however be damasked after the analysis of element of interest by reacting with anion that has stronger affinity with the element masked, after which it is then titrated.

3.4 Precipitation Titration

This type of titration is very useful in determining the concentration of analyte which precipitates with the anion or titrant. It is useful, provided that equilibrium are rapid and a suitable means of detecting the end point is available.

Titration curve



Consider Cl^- being titrated with $AgNO_3$ which is similar to acid-base titration. Prior to the equivalence point, part of the Cl^- is consumed by $AgNO_3$ to precipitate AgCl. The pH is determined by the remaining Cl^- in the system.

At equivalence point, there is saturated solution with AgCl. The Cl^- is almost exactly the same with $AgNO_3$ added, while at points beyond the equivalence point, this is determined from the concentration of Ag^+ and K_{sp} values.

The smaller to the K_{sp}, the larger the break at equivalence point.

3.4.1 Detecting End Point

End point can be detected by either with the use of potentiometer with an appropriate electrode. Indicator can also conveniently be used. There are two major types of indicators.

(i) ***First type*** forms a coloured compound with the titrant when it is in excess.

Example (i) In Mohr method for determining Cl^- which is titrated with $AgNO_3$, chromate (CrO_4^{2-}), soluble salt is the indicator. This produces yellow solutions. When Cl^- precipitate is complete, the first excess Ag^+ reacts with indicator to precipitate red Ag_2ClO_4.

(ii) In Volhard Titration, F^{2+} (Ferrion) is added as indicator which forms soluble complex with the first excess of titrant.

$$Fe^{2+} + SCN \rightarrow Fe(SCN)^{2+}$$

(iii) ***The second type*** of indicator is adsorption indicator. The indicator becomes adsorbed on the precipitate at the equivalence point. The colour of the indicator changes when it is adsorbed.

Example Fajans method. Fluorescien is used as an indicator for halides at pH 7.

Self assessment Exercise

1 Explain the following terms: (a) Ligand, (b) Formation constant and(c) Conditional formation constant.

2 Give the mathematical expressions for the various formation constant in the complete dissociation of EDTA.

3 Write briefly about the types of complexometric titrations known

4.0 Conclusion

Complexometric titrations are useful tools in determining concentration of metals that form complex with some anions (ligand) under varying pH system which would not have been feasible in an ordinary acid-base titration. Precipitation titration is particularly useful in handling halides while complexometric titrations are much broader in applications.

5.0 Summary

In this unit, we have learnt about:

(i) The definition and basic principle in complexometric titration.

(ii) The underlying principle in precipitation titration.

(iii) Ligands and their formation.

(iv) Detailed structure and properties of EDTA.

(v) Different phases and application of titration curve for complexometric and precipitation titrations.

(vi) Various types of complexometric titrations.

(vii) Types of indicators in both titrations.

6.0 Tutor Marked Assignment

1 Differentiate between monodentate and multidentate ligands.

2 Explain briefly types of complexometric titrations you know.

3 Calculate the concentration of Mg^{2+} and show shape of titration curve for reaction of 50.0mL of 0.020 M Mg^{2+} (buffered to pH 10) with 0.020M EDTA.

4 Suppose that 0.01M Fe^{2+} is titrated with 0.002M EDTA at pH 2,what is the concentration of free Fe^{3+} at the equivalence point and beyond equivalence point.

(iv) What is a masking agent ? Give three examples.

7.0 Further reading and Other resources.

1 Christian, G.D. (1980). Analytical Chemistry.3rd ed, John wiley and son, New York.

2 Harris, D.C. (1995). Quantitative Chemical Analysis. 4th Ed. Freeman and Company, New York.

3 Khan, I.A. and Khanum K. (1994).Fundamentals of Biostatistics .Ukaaz Publications, Nagar .

4 Laitimen, H.A . and Hesiscs, W.E. (1995). Acid-Base Equilibria in Water. 2nd Ed. McGraw Hill Inc., New York

5 Nwachukwu, V.O.(2006).Principle of Statistical Inference. Peace Publishers, Port-Harcourt.

MODULE 3 SELECTED ANALYTICAL TECHNIQUES

UNIT 1 **PHYSICOCHEMICAL ANALYSIS (UV)**

1.0 Introduction

Spectroscopy or spectrometry is a major branch of analytical chemistry that deals with the study of concentration of analyte as a function of amount of radiation absorbed when electromagnetic radiation from appropriate source is directed at it.

All chemical species interact with electromagnetic radiation, and in the course, diminishing the intensity or the power of the radiated beam. Measurement can be brought about by the infrared, visible and ultraviolet regions of the spectrometer. This unit also reviews the instrumentation involved in the absorptiometric procedures.

2.0 Objective

At the end of this unit, students should be able to:

(i) Explain the general working principle of spectrometry;
(ii) define the technical terms associated with spectrometry;
(iii) list the quantitative and qualitative applications of spectrometry in the analytical methods ; and
(iv) describe the instrumentation of the techniques

3.0 Definition and general principle of spectrometry

Spectroscopy is that branch of chemistry which is based upon the measurement of decrease in the power of the radiation (attenuation) brought about by the analyte when electromagnetic radiation is made to pass through the analyte.

3.1 Electromagnetic spectrum

Electromagnetic radiation is a type of energy that is transmitted through space at enormous velocities. It is a form of energy that is propagated as a transverse waves which vibrate perpendicularly to the direction of propagation and this imparts a wave motion to the radiation. Wave parameters used to further describe the propagation include velocity, frequency, wave length and amplitude. Wave number is a reciprocal of wavelength which is the number of waves in a unit. The mathematical relationship is $\lambda = C/v$

Where λ = Wavelength

V = Wave number or frequency

C= velocity of light

Electromagnetic radiation process is a certain amount of energy, the unit of which is called photon. It is related to frequency by

$$E = hv = \underline{hc} / \lambda$$

where E =energy (photon)

h = Plank's constant

The electromagnetic spectrum can be arbitrarily broken down into different region according to wave length.

3.1.1 Regions of Electromagnetic Spectrum:

(i) ***Ultraviolet region*** which extends from about 10 to 380nm, though the most analytical useful region is from 200-300nm, known as near ultraviolet region.

(ii) ***Below the 200nm***. Here, air plays appreciable roles and so the instrument operates under vacuum. Hence the region is called vacuum ultraviolet.

(iii) **Visible region**. It is a very small wavelength region that can be seen by human eyes. The region starts from 380nm to about 780nm. The light therein appears in colours.

(iv) ***Infrared region.*** This extends from about 0.78µm (780nm) to about 300nm but the range frequently used in analysis is from 2.5nm to 25nm.

3.2 Absorption of Radiation

When radiation passes through a transparent layer of materials (solids, liquid or gas), some of the radiation is absorbed by the atom or molecule in the materials. There are three basic processes by which molecules can absorb radiations. All involves bringing molecules to higher internal energy level. These re (i) rotational transition, (ii) vibration transition and (iii) electronic transition.

The molecule at ordinary room temperature is considered to be at lowest electronic energy state (E_o).Upon absorbing a photon of energy, it moves to higher energy state called excited state.

The absorption of electromagnetic radiation by some species M is considered to undergo a two-step process:

(i) $M + hv \longrightarrow M^*$

(ii) $M^* \longrightarrow M + heat$

The first step involves absorbing radiation and the species is converted to an excited species (M*) the life time of M* is very short, after which it undergoes the second step called relaxation which results in products of heat and the original metal M.

The absorption of radiation can be used either for qualitative or quantitative analysis.

3.2.1 Qualitative techniques

When the absorption of light takes place in the visible region, object transmits or reflects only a portion of the light. When polychromatic light (white light), which contains the whole spectrum of wavelength in the visible region is passed through an object, it absorbs certain wavelengths, and leaving the unabsorbed wavelength to be transmitted. The transmitted (unabsorbed) wavelengths are seen as colours. Table 1.0 shows the absorbed and unabsorbed colour of different wavelength

Table 1.0 Absorption of light in the visible region.

Wavelength (nm)	Absorbed colour	Transmitted colour
380-450	Violet	Yellow-green
450-495	Blue	Yellow
495-570	Green	Violet
570-590	Yellow	Blue
590-610	Orange	Green-blue
610-750	Red	Blue-green

Absorption spectroscopy also provides useful tools for qualitative analysis. The radiation whose wavelengths are within the ultra-violet and infrared regions is particularly useful in this regard.

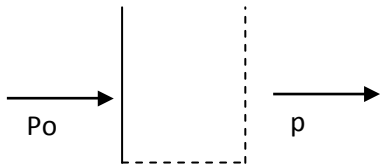
Identification of pure compounds involves comparing the spectral characteristics of unknown sample with those of pure compounds. A close match is accepted to be a good evidence of chemical identity, particularly if the spectrum of the unknown contains a number of sharp and well-defined peaks.

Absorption in the infrared region is more useful for qualitative purposes because of wealth of fine structure that exist in the spectral of many compound .The detail of this is beyond the scope of this unit.

3.2.2 Quantitative techniques

The absorption measurement involves reduction of power (attenuation) experienced by the beam of radiation as it passes through the solution. This can be related quantitatively to the concentration of analyte in the solution.

The amount of radiation absorbed by the sample is determined by what is known as Beer's law which says when a monochromatic radiation passes through absorbing specie, the power of the beam is progressively decreased as more energy is absorbed by the particle. The decrease in power depends upon the concentration of the absorber and the length of the path transverse by the beam.



$$\log \frac{Po}{P} = \epsilon bc = A$$

where

Po = Incident ray

P = Transmitted ray

ϵ = Molar absorptivity or extinction coefficient.

c = Concentration

b = Path length

A = Absorbance

3.3 Limitations of Beers law

There are some observed factors that limit the application of Beeŕs law. These include, linear relationship between absorptive and concentration. The linear relationship does not always occur as are result of the following observations:

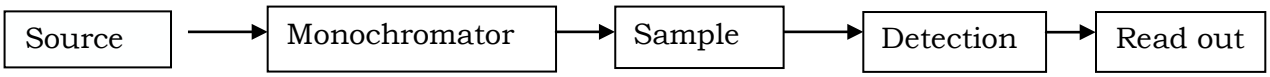
(i) The Beeŕs describes successfully ***only diluted solution***. So at high concentration (above 0.01F), there is a deviation from the linearity nature of the relationship.

(ii) ***Chemical deviation***: chemical causes non linearity to occur when non-symmetrical chemical equilibrium is operational. This is brought about a result of associated dissociation or reaction of absorbing species with the solvent.

(iii) ***Instrumental deviation***: Beeŕs law is only obeyed when monochromatic light is used. But the use of truly monochromatic light is seldom practical, the alternative polychromatic light will cause deviation from the law.

3.4 General Principle of instrumentation

Spectrometer, the name of the instrument employed in spectrometry is built on 4



1. A source of continuous radiation over the wavelength from the source spectrum
2. A Monochromator for selecting a narrow band of wavelength from the source spectrum
3. A detector for converting radiant energy to electrical energy
4. Read out device to read the response of the detector.

3.4.1 Source

The source must have a readily detectable out put of radiation over the wavelength for which the instrument is designed.

(i) ***For visible region***- the commonly used source is tungsten filament incandescent lamps whose behaviour is similar to that of black-body radiator.

Sources of this kind emit continuously radiation that is more characteristic of the temperature of the emitting surface than that of materials of which it is composed.

(ii) ***For ultraviolet region***, a low pressure hydrogen or deuterium discharge tube is generally used as a source. Ultraviolet sources must have a quartz window because glass is not transparent to UV radiation.

(iii) ***For infrared region***, a Nernst glower is used as a source. This consists of a rod made of mixture of rare earth oxides.

3.4.2 Monochromator

This is a device which disperses radiation into its component wavelength. It consists of system of lenses, mirrors and slits that direct radiation of the deserved wavelength from the Monochromator towards the detectors of the instrument.

There are three types of Monochromator- Prism, grating and double Monochromator

(i) Prism Monochromator: It employs a 60-deg prism for dispersion.

(ii) Grating Monochromator: Dispersion of UV, visible and infrared radiation is brought about by the passage of a beam through a transmission grating or by reflection from a reflection grating.

(iii)Double Monochromator: Many of modern monochromators contain two disperses element; two prisms, two gratings or a prism and a grating for effective performance.

3.4.3 Sample Container

The sample container otherwise known as cell must be transparent in the wavelength region being measured. There are various materials that can be used for cell construction. These include NaCl, KBr, Ti and Br. The cell for use in visible and as ultraviolet spectrometers is usually square curvet of 0.1m thickness. However for infrared, short path length is required, though it is often difficult to produce.

3.4.4 Detector

Detectors will also vary with the wavelength region to be measured. To be useful, a radiation detector must respond over a broad wavelength range. It should in addition, be sensitive to low levels of radiation power, respond rapidly to the radiation, produce an electrical signal that can be amplified, and have a relatively low noise level. The signal produced must be directly proportional to the power of beam striking it.

$$G = K^1P + K^n$$

where G = electrical response of the detection

K^1 = sensitivity of detector

K^n = Current constant (Dark current).

Various detectors include commonly used are:

1. Phototube commonly used for uv and visible region
2. Photomultiplier tube is more sensitive than phototube; used for visible and UV region. Others include photocell, photo conductive cell, thermocouple or Bolometer, as well as pneumatic cell.

Generally the design of various spectrometers is the same but there are some variations depending on the maker.

Types of spectrophotometer known include:

1. Single-beam spectrometer

2. Double beam spectrometer

3. Gilford spectrometer

Self Assessment Exercise

1 A sample in a 1.0 cell is determined with a spectrometre to transmit 80% of light at a certain wavelength. If the absorptivity of this substance at this wavelength is 2.0, what is the concentration of the substance?

2 Calculate the frequency, wave number as energy of visible light with wavelength of 10nm.

3 Mention and describe instrumentation of spectrometer

4.0 Conclusion

Spectrometry or spectrophotometer is therefore an instrumental analytical technique that is elaborately used to determine quantitatively and qualitatively, components of a material. It is precise and accurate. The instrumentation is fairly convenient to operate if the basic understanding is available.

5.0 Summary

In end of this unit, we have learnt about:

(i) The definition and general principle of spectrometry or Spectrophotometry.

(ii) Basic concept of electromagnetic spectrum and radiation.

(iii) Absorption of Radiation.

(iv) Quantitative and qualitative applications of spectrometry.

(v) General concept of instrumentation is spectrometry

6.0 Tutor marked assignment

1 Describe in detail the instrumentation of spectrometry

2 A solution containing 3.75mg/100ml of A (wt, 210) has a transmittance of 39.6% in a 150cm cell at 480nm. Calculate the molar absorptivity of A.

3 Explain what is meant by limitations of Beers law

4 Describe radiation sources and detector for ultraviolet, visible and infrared regions of the spectrum

5 Distinguish between the three types of Monochromator.

6 Write briefly on types of spectrophotometer known.

7.0 Further reading and Other resources.

1 Christian, G.D. (1980). Analytical Chemistry.3rd ed, John wiley and son, New York.

2 Harris, D.C. (1995). Quantitative Chemical Analysis. 4th Ed. Freeman and Company, New York.

3 Khan, I.A. and Khanum K. (1994).Fundamentals of Biostatistics .Ukaaz Publications, Nagar .

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5 Nwachukwu, V.O.(2006).Principle of Statistical Inference. Peace Publishers, Port-Harcourt.

Module 3 SELECTED ANALYTICAL TECHNIQUES

Unit 2 Gravimetric Analysis

1.0 Introduction

Gravimetric analysis is an analytical method that is based upon the measurement of the weight of known composition. It is one of the most accurate and precise methods of macro quantitative techniques. In gravimetric analysis, the substance of known composition must be related chemically to the analyte.

This analytical technique (gravimetry) was one of the major analytical techniques employed in analysis of ores and industrial materials in the past. This unit will cover specific steps of gravimetric analysis.

2.0 Objectives

At the end of this unit, students should be able to

(i) definition related terms in gravimetry;
(ii) explain the general principle of gravimetry;
(iii) list the types of gravimetric analysis commonly used; and
(iv) explain the various steps involved in gravimetric analysis.

3.0 Definition

Gravimetric analysis is an analytical technique which involves measurement of weight of components of known sample. It is a quantitative technique.

3.1 Major Types of Gravimeter analysis

(i) ***Precipitation gravimetric*** analysis

(ii) ***Volatilization gravimetric*** analysis

1. Precipitation Gravimetric Analysis

It is the most commonly used type. It briefly involves making the specie to be determined to chemically react with a reagent to yield a product of limited solubility; after filtration and other suitable chemical treatment, the solid residue of known chemical composition is then weighed. One important concept that needs to be well understood is precipitation equilibria.

Precipitation Equilibria: when substance have limited solubility and their solubility is exceeded, the ions of dissolved portion exist in equilibrium with the solid (undissolved portion) .It does not mean they are completely insoluble but rather, some

dissolved portion exist in equilibrium with the solid materials, that is they are slightly soluble.

$AgCl_{(s)} \rightleftharpoons (AgCl)_{aq} \rightleftharpoons Ag^+ + Cl^-$

The general rule is that for precipitation to be formed the product of (Ag^+) and $[Cl^-]$ must be greater than Ksp .

If the product is just equal to Ksp, all the Ag^+ and Cl^- would remain in the solution

$Ksp = [Ag^+][Cl^-]$

The concentration of any solid such as AgCl which is proportional to its density, is constant and is combined in equilibrium constant to give Ksp.

Ksp for Ag_2CrO_4 is as follow

$Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}$

$Ksp = [Ag^+]^2 [CrO_4^{2-}]$

NB : $Ksp = S^2$

Example 1: The Ksp of AgCl at 25oC is 1.0 x10^{-10}. Calculate the concentration of Ag+ and Cl$^-$ in a saturated solution of AgCl, and the molar solubility of AgCl

The reaction equation is $AgCl_{(s)} \rightleftharpoons Ag^+ + Cl^-$

So when AgCl ionises, equal amounts of Ag^+ and Cl^- are formed

then, $[Ag^+] = [Cl^-] = s$

$s^2 = 1.0 \times 10^{-10}$

$s = 1.0 \times 10^{-5} M$

Example 2 : Calculate the solubility of silver chloride in 0.10M $NaNO_3$.

From relationship $K_{sp} = \dfrac{K^o_{sp}}{f_{Ag+} . f_{Cl-}}$

NB: K^o_{sp} = thermodynamic solubility product $= 1.0 \times 10^{-10}$

f_{Ag} = activity coefficient for silver = 0.75

f_{Cl-} = activity coefficient for chloride = 0.76

$$K_{sp} = 1.0 \times 10^{-10} = \frac{1.8 \times 10^{-10}}{(0.75)(0.76)} = s^2$$

$$s = \sqrt{1.8 \times 10^{-10}} = 1.3 \times 10^{-5} M$$

.

STEPS OF A GRAVITMETRIC ANALYSIS

The gravimetric analysis requires two major measurements namely the weight of the sample and the weight of the product of known composition derived from the sample (Analyte). To achieve this, the following steps are required.

i. Preparation of solution
ii. precipitation
iii. digestion
iv. filtration
v. washing
vi. drying
vii. weighting
viii calculation

3.1.1 Preparation of Solution

Solution whose condition enhances formation of precipitate is the first step. Various interfering substances that may obstruct this must be removed. The commonest way of removing interferences is by introducing reagent that selectively mask the interfering substances thereby, removing this from the chemical activity in the solution. The conditions of the solution that must be adjusted, so as to encourage precipitation are temperature, pH, volume of the solution and concentration of other constituents.

3.1.2 Precipitation

The precipitate should be sufficiently insoluble and should contain larger crystals so that they can be filtered.

Introducing precipitating agent always help in ensuring the formation of desirable precipitate. The ideal precipitating agent would react specifically with the analyte to produce solid that would (i) have a sufficiently low solubility to minimise loss (ii) be readily filtered and washed free of contaminants and (iii) be unreactive and of known composition after drying.

Precipitation occurs through Supersaturation and Nucleation. This is followed by crystal growth. The larger the supersaturation, the more rapid the growth of crystal.

$$\text{Relative Supersaturation} = \frac{Q - S}{S}$$

where Q = concentration

S = Solubility

Higher relative Supersaturation → Many small crystals (high surface area)

Low relative Supersaturation → Fewer larger crystals Low surface area)

Generally, to keep Q low and S high the following conditions must prevail.

i. Formation of Precipitate from dilute solution to keep Q low

ii. Add dilute precipitating reagent slowly with effective stirring

iii. Obtain Precipitate from unit solution

iv. Carrying out precipitation at low pH

3.1.3 Digestion of Precipitate

This is an important step in gravimetric analysis. The two types of crystals formed are small crystals and large crystals. However, when the precipitate is allowed to stand, the larger crystals grow at the expense of small crystals, thereby forcing the small crystal to dissolve and precipitate on the surface of the larger crystal. Individual then agglomerate to effectively have a common counter ion layer. Some insoluble crystalline precipitate known as colloidal are formed. Ions are arranged in a fixed pattern alternating the positive and negative charges. For example, in AgCl, Ag^+ are alternated with Cl^-, so that the net surface charge is zero. However surface tends to adsorb ion that is in excess. The adsorption creates a primary layer that is strongly adsorbed and is an integral part of the crystal. This attracts ion of opposite charge in a counter layer or secondary layer, so as to give overall neutral particle. Particles

coagulate when the counter layer neutralizes the primary layer. When coagulated particles are filtered and washed with water, the secondary layers become loosely bound and the particles revert to the colloidal state through a process called **peptization.**

Colloidal particles could be hydrophilic or hydrophobic. Precipitates tend to carry down from the solution other constituent that are normally soluble, causing contamination of precipitate through a process called **coprecipitation**. Coprecipitation can occur through the following known process:

(i) *Occlusion*

(ii) *Surface adsorption*

(iii) *Post Precipitation*

3.1.4 Washing and Filtration of the Precipitaties

Precipitates are washed after filtration, so as to remove any co precipitated impurities. The mother liquor which wet the precipitation is also removed. However, peptization does occur when water is used to wash the precipitation. This is often prevented by adding electrolyte to the wash liquid eg. HNO_3, or NH_4NO_3 for AgCl.

A test is often conducted to ensure the washing is completed and effective. This is done by testing the filtrate for the presence of ion of precipitation.

3.1.5 Drying nd Igniting of Precipitate

The wash liquid and the adsorbed electrolyte from the precipitate are further treated so as to have precipitation in a form suitable for weighing. This is done usually by heating (drying) at 110-120^{0}c for one or two hours. Ignition is required, when the precipitation is to be heated at much higher temperature so as to convert the precipitate to a more suitable form for weighing. The drying process continues until a constant weight is achieved (i.e. successive weighing differs by the factor of 0.3 or 0.4mg.)

3.1.6 Calculation

This is always on the percentage basis

If A is the analyte of interest, then

$$\% A = \frac{\text{Weight of A}}{\text{Weight of sample}} \times 100$$

More often, the weight of A is not measured directly. Instead, the species that is usually isolated and weighed either contain A or can be chemically related to A.

Gravimetric factor is needed to convert the weight corresponding to A.

$$\text{Gravimetric factor} = \frac{\text{F.w substance Sought}}{\text{Fw Substance weighed}} \times \frac{a}{b}$$

Where a and b are integers that make the numerator and denominator chemical equivalent.

Example 1. An ore is analysed for manganese content by converting the manganese to Mn_2O_3 and weighing it. If a 1.52 g sample yeildsMn_3O_4 weighing 0.126g, what would be the percent Mn_2O_3 in the sample? The percent Mn?

$$\%\ Mn_2O_3 = \frac{0.126\ Mn_3O_4 \times (3\ Mn_2O_3/2\ Mn_3O_4)\ (g\ Mn_2O_3\ /\ Mn_3O_4)\ x100\%}{1.52\ g\ sample}$$

$$= \frac{0.126 \times [3\ (157.9)/2(228.8)] \times 100\%}{1.52}$$

$$= 8.58\%$$

$$\%\ Mn = \frac{0.126\ Mn_3O_4 \times (3\ Mn/\ Mn_3O_4)\ (gMn\ /\ Mn_3O_4)\ x100\%}{1.52\ g\ sample}$$

$$= \frac{0.126 \times [3\ (54.94)/2(228.8)] \times 100\%}{1.52}$$

$$= 5.97\%$$

3.2 Volatilization gravimetric analysis

In this form of gravimetric analysis, the substance to be determined is separated in a gas form from the reminder of the sample. The weight of volatile component is then compared with the weight of non-volatilized portion. This method is otherwise called gravimetric combustion analysis.

In this form of quantitative analysis, partially combusted product is passed through catalyst such as Pt gauze, CuO, PbO_2 or MnO_2 at elevated temperatures to complete the oxidation to be CO_2 and H_2O.

The product is then passed through chamber containing P_4O_{10} which absorb H_2O and another chamber of NaOH on asbestos which absorbs CO_2. The increase in mass of each chamber tells how much of H_2 and C are generated respectively.

Combustion analysis has currently undergone rapid changes unlike in the past when changes are restricted to the weight of combustion product. Modern instrument use thermal conductivity, infrared absorption or coulometry (with electrochemical generated reagent) to measure the product.

3.3 Application of gravimetry as a separation method of metals

Gravimetric analysis are very precise and accurate, if it is carried out under the right experimental conditions.

These are some factors that influence solubility of precipitate. These include

(i) Temperature

(ii) Solvent

(iii) Rate of precipitation formation

Generally, in the application of gravimetric method to separate metals from a material, varying precipitating agent have been developed to enhance the precipitation.

(i) **Inorganic precipitating agent**.

	Precipitating Agent		**Element separated**
a.	$NH_{3(aq)}$	→	Be, Al, Fe, Sc
b.	H_2S	→	Cu, Zn, As
c.	$(NH_4)_2\ MoO_4$	→	Cd, Pb
d.	HCl	→	Ag, Na, Si

.

(ii) **Reducing Agent**

This is better because it converts the analyte to its elemental form for weighing.

Some of the commonly used reducing agents are listed below

Reducing Agent		**Analyte**
SO_2	→	Se, An
$SnCL_2$	→	Ag
HCOOH	→	Pt
H_2	→	Re, Ir

(iii) **Organic Precipitating agents**

There are large numbers of organic compounds that are very useful as precipitating agent for metals. Some are selective, while some are very broad in the number of elements they precipitate.

Organic precipitating agents have advantages of giving precipitate that are of very low solubility in water and with a favourable gravimetric factors.

Two types of organic precipitating agents are in use, a follows:

(i) One form slightly soluble non-ionic complexes called coordination compound

(ii) The other forms ion bonding between inorganic species and the reagent.

Organic precipitation agents are chelating agents which form slightly soluble uncharged chelate with metal ion.

pH adjustment regulates the selectivity and nature of chelating substances

$$M^{n+} + n\,HX \rightarrow MXn + n\,H^{+}.$$

Some common examples of organic precipitating agents

Organic reagent		Metal precipitated
Dimethyglyoxime	→	Pb
8-hydroxyquinoline (oxine)	→	Al, Mg
Sodium diethyldithiocarbonate	→	K,Pb, Cs,Tl, Ag, Cu, Hg

Self Assessment Exercise

(i) A compound weights 4.0 mg, produced 1 .25mg of CO_2 and 2.41mg of H_2O upon combustion. Find the weight percents of C and H in the sample.

(ii) Highlight various necessary steps for successful precipitation gravimetric analysis.

4.0 Conclusion

Gravimetric analysis, though a time consuming analytical technique, has much of its success hinged on the competence and commitment of the analyst. It remains a useful technique that is seldom, if ever, limited in sensitivity (or measurement).

Gravimetric method has been developed for most, if not all, inorganics and cation as well as mental species. A variety of organic substances can also be readily determined.

4.0 Summary

5.0 In the end of this unit, we have learn about

(i) Definition and principle of gravimetric analysis.

(ii) Major types of gravimetric analysis.

(iii) Various steps involved in precipitation gravimetric analysis.

(iv) Basic concept of volatilization gravimetric analysis.

(v) Technical terms involved in the gravimetric analysis.

6.0 Tutor marked assignment

1 Describe in detail various steps involved in precipitation gravimetric analysis

2 What do you understand by the following terms:(a) Occlusion (b) Hydrophobic precipitation (c) Supersaturation (d) Post precipitation

3 Differentiate between the two major types of gravimetric analysis known

4 The Ksp of AgCl at 25^0C is 1.0 x 10^{-10}. Calculate the concentration of Ag^+ and Cl^- in a saturated solution of AgCl and the molar solubility of AgCl.

5 Critically assess the need of gravimetric analysis to the modern analytical exercise.

7.0 Further reading and Other resources.

1 Christian, G.D. (1980). Analytical Chemistry.3rd ed, John wiley and son, New York.

2 Harris, D.C. (1995). Quantitative Chemical Analysis. 4th Ed. Freeman and Company, New York.

3 Khan, I.A. and Khanum K. (1994).Fundamentals of Biostatistics .Ukaaz Publications, Nagar .

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Module 3 SELECTED ANALYTICAL TECHNIQUES

Unit 3 **pH notation and Buffer solution**

1.0 Introduciton

This unit looks at the potential of hydrogen of a system and ways of measuring it in various media. The unit also discusses the construction of pH scale and its interpretation. Buffer is a term used for a substance that resists slight changes in pH of a system. The unit also cover the preparation of buffer as well as various factors that affect the effectiveness of buffer action.

2.0 Objectives

At the end of this unit, students should be able to

(i) define pH and state its mathematical relationship to [H^+];

(ii) define a buffer solution and explain how it works;

(iii) construct and interpretes the pH scale; and

(iv) enumerate the various factors that influence the action of buffer solution.

3.0 Definition of pH

pH can be simply defined as the potential of hydrogen in a system. It shows the extent of acidity and basicity of a system under investigation.

Mathematically, pH is defined by sir SØrensor as the negative logarithim to base 10 of $[H^+]$.

i e $pH = -\log [H^+]$.

The only source of H^+ is as a result of dissociation of water in which equal concentration of H^+ and OH^- are products.

$$H_2O \rightleftharpoons H^+ + OH^-$$

Water undergoes self ionization known as **autoprotolysis** in which, it acts as both and acid and base.

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^+$$

The autoprotolysis constant is equilibrium constant, K_W, called the ionic product of water.

$K_w = [H^+][OH^+]$

This is always equal to 1.0×10^{-4} at 25^oC

Taking log of both side, gives

$\log K_w = \log [H^+] + \log [OH^-]$

$-\log K_w = -\log [H^+] + -\log [OH^-]$

$-\log K_w = pH + pOH$

$pK_w = pH + pOH$

But at 25^oC, pH = 7 and pOH= 7

Hence, $-\log K_w = 14.00$

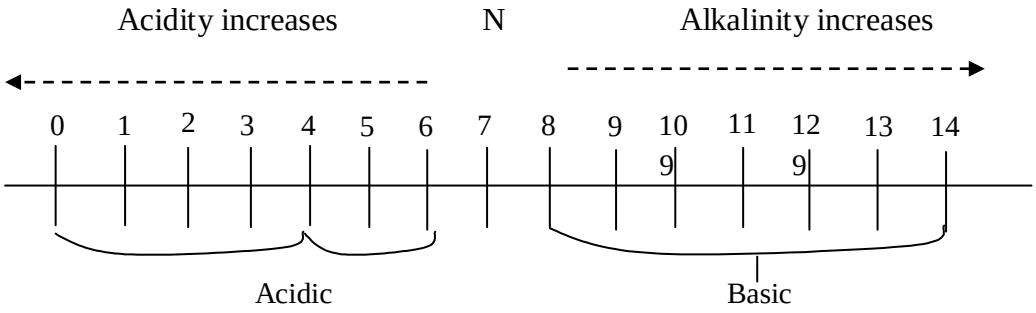
i.e. $\log_{10} = -14$ or $K_W = 10^{-14}$

NB: the (-) sign is an indication that, concentration encountered is less than 1.0M.

$pK_w = pH + pOH = 14.00$

3.1 pH Scale

A universal pH scale put the pH of most solution in the range 0.0 - 14.0. This should not give an illusion that it is impossible to have negative pH (-pH). It only means that the concentration hydrogen is greater than 1M. It is attainable in concentrated solution of trong acid such as HCl and H_2SO_4.



NB- N= Neutrality

3.1.1 Measurement of pH

pH is measured with a glass electrode. A glass electrode is an ion-selective electrode. It is very sensitive. The pH sensitive part of the electrode is the thin glass membrane that culminates in the slope of a bulb.

Most of the metal cation are located in the hydrated gels region of the metal membrane. These metals diffuse into the solution and are replaced by H^+ in the solution in ion- exchange equilibrium. The more the H^+ in solution, the more the H^+ ions that are bound to the glass surface. The operation of glass electrode is represented as

$$E = \text{Constant} + \beta (0.05915 \log \frac{A_{H^+} \text{ (outside)}}{A_{H^+} \text{ (inside)}} \quad \text{at } 25^0\text{c}$$

where β s the electromotive efficiency = 1 0 0ør 0 9 8 and constant is known as asymmetry potential.

3.1.2 pH at Elevated Temperature

The main factor that determines the real pH of a system is temperature. At high temperatures in a fluid system, the pH turns out to be high. Not only does pH affect the ionisation of water in the body system, it also changes the pH of a neutral solution to about 7.4, thereby affecting the ionization constant of the acid and bases from which the buffer system is derived.

3.2 Buffer Solution : A buffer solution can be defined as a solution that resists changes in pH when small amount of acid or base is added or when dilution occurs. Buffer solution consist of a mixture of a weak acid and its salt or a weak base and its salt.

Consider the acid HA undergoing dissociation under an equilibrium condition:

$$HA \rightleftharpoons H^+ + A^-$$

$$K_a = \frac{[H^-][A^-]}{[HA]}$$

$$\log Ka = \log \frac{[H^-][A^-]}{[HA]} = \log [H^+] + \log \frac{[A^+]}{[HA]}$$

$$- \log H^+ = \log K_a + \log \frac{[A^+]}{[HA]}$$

$$pH = Pk_a + \log \frac{[A^+]}{[HA]}$$

$$pH = Pk_a + \log \frac{[salt]}{[Acid]}$$

This is the Henderson- Hasselbalch equation

3.3 Buffer Capacity

This is simply defined as the maximum amount of an acid or base that can be added to a buffer system without causing a change or appreciable change in pH of a system.

Note that the buffering mechanism for a mixture of a weak acid and its salt can be explained as governed by log ratio of salt and acid.

$$pH = \text{constant} + \log \frac{[A^-]}{[HA]}$$

If a solution is deionised, the ratio of pH remains constant. When a small amount of strong acid s added, it will combine with an equal amount of A^- to convert it to HA.

The ratio of $[A^1]$ [HA] is small, so the change in pH is small, while if i is t strong base that is added it combines with [HA] to form an equivalent amount of A^-. Again the change of pH is small.

Self Assessment Exercise

i. Define the term "Buffering capacity" of a buffer system.

ii. What is the hydroxyl ion concentration when (a) 1.0 x 10^{-3}M solution of HCl acid is prepared and (b) 50mL of 2.0 M H_2SO_4 is diluted to 250mL with a solution of 0.1 M NaOH

iii. Calculate the pH of a 0.500M solution of Na_3PO_4

4.0 Conclusion

pH is a measurement of acidity or alkalinity of a solution. A buffer keeps resisting changes of pH in a system provided the amount of acid/base added is small.

Buffer solution, in principle, can be prepared by combining calculated quantities of a suitable conjugate acid-base pair.

5.0 Summary

In end of this unit, we have learn about

(i) Definition of pH and its concept.

(ii) Definition of buffer solution.

(iii) The source of H^+ is from autoprotolysis of water.

(iv) Effect of temperature on the pH and Henderson Hasselbalch equation.

6.0 Tutor Marked Assignment

(i) Explain the meaning of the following terms

(a) Buffering mechanism (b) buffer capacity (c) negative pH .

(ii) What is pH?

(iii) Calculate the pOH of 0.100M of Na_3PO_4

(iv) Calculate the pH and POH of 2.00 x 10^{-3}M solution of acetic acid

(v) Calculate the $[H^+]$ of a solution prepared by mixing 2.0ml of a strong acid solution of a pH 3.00 and 3.0ml of a strong base of pH10.

(vi) Calculate the pH of solution by mixing 20ml of 0.10M NaOH solution in and 50ml of 0.1M acetic acid.

7.0 Further reading and Other resources.

1 Christian, G.D. (1980). Analytical Chemistry.3rd ed, John wiley and son, New York.

2 Harris, D.C. (1995). Quantitative Chemical Analysis. 4th Ed. Freeman and Company, New York.

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