

**MODULE 3      SELECTED ANALYTICAL TECHNIQUES**

- Unit 1      Physico-Chemical Analysis
- Unit 2      Gravimetric Analysis
- Unit 3      pH Notations and Buffer Solution

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**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 the 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 spectrum. This unit also reviews the instrumentation involved in the absorption spectrometric procedures.

## 2.0 OBJECTIVES

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

- explain the general working principle of spectrometry;
- define the technical terms associated with spectrometry;
- list the quantitative and qualitative applications of spectrometry in the analytical methods; and
- describe the instrumentation of the techniques.

## 3.0 HOW TO STUDY THE UNIT

1. You are expected to read carefully through this unit at least twice before attempting to answer the self-assessment questions or tutor- marked assignment.
2. Do not look at the solution given at the end of the unit until you are satisfied that you have done your best to get all answers.
3. Share your difficulties with your course mates, facilitators and by consulting other related material, particularly the internet.
4. Note that if you follow the instructions you will feel self fulfilled that you have achieved the aim of studying this unit. This should stimulate you to do more.

## 4.0 WORD STUDY

**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.

**Spectrometry:** is the measurement of the wavelength of electromagnetic radiation.

**Electromagnetic radiation:** is a type of energy that is transmitted through space at enormous velocities.

## 5.0 MAIN CONTENT

### 5.1 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.

### 5.2 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  $\lambda$  = Wavelength  
V = Wave number or frequency  
C = velocity of light =  $3 \times 10^{23}$  m/s

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

$$E = h\nu = \frac{hc}{\lambda}$$

where E = energy (photon)  
h = Plank's constant

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

### 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 0.78 $\mu$ m (780nm) to about 300 $\mu$ m but the range frequently used in analysis is from 2.5 $\mu$ m to 25 $\mu$ m.

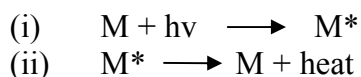
### 5.3 Absorption of Radiation

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 are:

- rotational transition
- vibration transition and
- electronic transition.

The molecule at ordinary room temperature is considered to be at lowest electronic energy state ( $E_0$ ). 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:



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.

### 5.3.1 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.

### 5.3.2 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.

$$\log \frac{P_0}{P} = ebc = A$$

where

$P_0$  = Incident ray

$P$  = Transmitted ray

$e$  = Molar absorptivity or extinction coefficient.

$c$  = Concentration

$b$  = Path length

$A$  = Absorbance

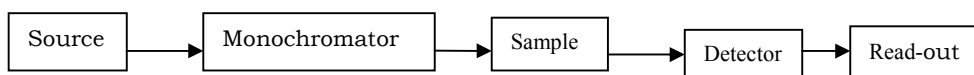
### 5.4 Limitations of Beer's Law

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

- (i) The Beer's describes successfully **only diluted solution**. So at high concentration (above 0.01M), 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 as a result of associated dissociation or reaction of absorbing species with the solvent.
- (iii) **Instrumental deviation**: Beer's 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.

## 5.5 General Principle of Instrumentation

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



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.

### 5.5.1 Sources

The source must have a readily detectable output 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.

### 5.5.2 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 desired 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-degree 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.

### 5.5.3 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 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.

### 5.5.4 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 detector

$K^1$  = sensitivity of detector

$K^n$  = Current constant (Dark current)

Various detectors 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 manufacturer.

Types of spectrophotometer known include:

1. Single-beam spectrometer
2. Double beam spectrometer
3. Gilford spectrometer

## 6.0 ACTIVITY

- i. A sample in a 1.0 cell is determined with a spectrometer 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?
- ii. Calculate the frequency, wave number as energy of visible light with wavelength of 10nm.
- iii. Mention and describe instrumentation of spectrometer.

## 7.0 SUMMARY

In this unit, you have learnt that:

- A. The definition and general principle of spectrometry or Spectrophotometry
- B. Basic concept of electromagnetic spectrum and radiation
- C. Absorption of Radiation
- D. Quantitative and qualitative applications of spectrometry
- E. General concept of instrumentation in spectrometry.

## 8.0 ASSIGNMENT

- i. 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.
- ii. Explain what is meant by limitations of Beer's law.
- iii
  - a. Describe radiation sources and detector for ultraviolet, visible and infrared regions of the spectrum.
  - b. Distinguish between the three types of monochromator.
- iv. Write briefly on types of spectrophotometer known.

## 9.0 REFERENCES/FURTHER READING

- Christian, G. D. (1980). *Analytical Chemistry*. (3<sup>rd</sup> ed). New York: John Wiley and son.
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## UNIT 2 GRAVIMETRIC ANALYSIS

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### 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, you should be able to:

- define related terms in gravimetry;
- explain the general principle of gravimetry;
- list the types of gravimetric analysis commonly used; and
- explain the various steps involved in gravimetric analysis.

### 3.0 HOW TO STUDY THE UNIT

1. You are expected to read carefully through this unit at least twice before attempting to answer the self-assessment questions or tutor- marked assignment.
2. Do not look at the solution given at the end of the unit until you are satisfied that you have done your best to get all answers.
3. Share your difficulties with your course mates, facilitators and by consulting other related material, particularly the internet.
4. Note that if you follow the instructions you will feel self fulfilled that you have achieved the aim of studying this unit. This should stimulate you to do more.

### 4.0 WORD STUDY

**Coprecipitation:** is the process by which precipitates tend to carry down from the solution other constituent that are normally soluble, causing contamination of precipitate.

**Peptization:** is the process whereby particles revert to the colloidal state when coagulated particles are filtered and washed with water.

### 5.0 MAIN CONTENT

#### 5.1 Definition

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

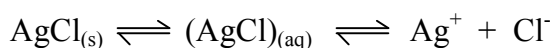
#### 5.2 Major Types of Gravimetric Analysis

- (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 exists in equilibrium with the solid materials, that is they are slightly soluble.



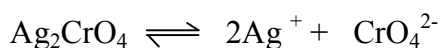
The general rule is that for precipitation to be formed the product of  $(Ag^+)$  and  $[Cl^-]$  must be greater than  $K_{sp}$ .

If the product is just equal to  $K_{sp}$ , all the  $Ag^+$  and  $Cl^-$  would remain in the solution.

$$K_{sp} = [Ag^+][Cl^-]$$

The concentration of any solid such as  $AgCl$  which is proportional to its density, is constant and is combined in equilibrium constant to give  $K_{sp}$ .

$K_{sp}$  for  $Ag_2CrO_4$  is as follow:



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

$$NB : K_{sp} = S^2$$

*Example 1: The  $K_{sp}$  of  $AgCl$  at  $25^\circ C$  is  $1.0 \times 10^{-10}$ . Calculate the concentration of  $Ag^+$  and  $Cl^-$  in a saturated solution of  $AgCl$ , and the molar solubility of  $AgCl$*



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

$$\text{then, } [Ag^+] = [Cl^-] = s$$

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

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

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

From relationship, 
$$K_{sp} = \frac{K_{sp}^0}{f_{Ag^+} \cdot f_{Cl^-}}$$

NB:  $K_{sp}^0 = \text{thermodynamic solubility product} = 1.0 \times 10^{-10}$

$f_{Ag} = \text{activity coefficient for silver} = 0.75$

$f_{Cl^-} = \text{activity coefficient for chloride} = 0.76$

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

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

## Steps of a Gravimetric 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

### 5.2.1 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 reagents 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.

### 5.2.2 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

### 5.2.3 Digestion of Precipitation

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  $\text{AgCl}$ ,  $\text{Ag}^+$  are alternated with  $\text{Cl}^-$ , 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

### 5.2.4 Washing and Filtration of the Precipitates

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 e.g.  $\text{HNO}_3$ , or  $\text{NH}_4\text{NO}_3$  for  $\text{AgCl}$ .

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.

### 5.2.5 Drying and 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<sup>0</sup>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.).

### 5.2.6 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.

$$\text{Gravimetric Factor} = \frac{F.W \text{ Substance Sought}}{F.W \text{ Substance Weighted}} \times \frac{a}{b}$$

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<sub>2</sub>O<sub>3</sub> and weighing it. If a 1.52 g sample yields Mn<sub>3</sub>O<sub>4</sub> weighing 0.126g, what would be the percent Mn<sub>2</sub>O<sub>3</sub> in the sample? The percent Mn?

$$\% \text{ Mn}_2\text{O}_3 = \frac{0.126 \text{ Mn}_3\text{O}_4 \times (3 \text{ Mn}_2\text{O}_3 / 2 \text{ Mn}_3\text{O}_4) (\text{g Mn}_2\text{O}_3 / \text{Mn}_3\text{O}_4) \times 100\%}{1.52 \text{ g sample}}$$

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

$$= 8.58\%$$

$$\% \text{ Mn} = \frac{0.126 \text{ Mn}_3\text{O}_4 \times (3 \text{ Mn} / \text{Mn}_3\text{O}_4) (\text{gMn} / \text{Mn}_3\text{O}_4) \times 100\%}{1.52 \text{ g sample}}$$

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

$$= 5.97\%$$

### 5.3 Volatilization of Gravimetric Analysis

In this form of gravimetric analysis, the substance to be determined is separated in a gas form from the remainder 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<sub>2</sub> or MnO<sub>2</sub> at elevated temperatures to complete the oxidation to be CO<sub>2</sub> and H<sub>2</sub>O.

The product is then passed through chamber containing P<sub>4</sub>O<sub>10</sub> which absorb H<sub>2</sub>O and another chamber of NaOH on asbestos which absorbs CO<sub>2</sub>. The increase in mass of each chamber tells how much of H<sub>2</sub> 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.

### 5.4 Application of Gravimetric in Separating Metals

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

Here are some factors that influence solubility of precipitate. They 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 has been developed to enhance the precipitation.

- (i) Inorganic Precipitating Agent

<b>Precipitating Agent</b>	<b>→</b>	<b>Element Separated</b>
a. NH <sub>3(aq)</sub>	→	Be, Al, Fe, Sc
b. H <sub>2</sub> S	→	Cu, Zn, As
c. (NH <sub>4</sub> ) <sub>2</sub> MoO <sub>4</sub>	→	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:

<b>Reducing Agent</b>		<b>Analyte</b>
SO <sub>2</sub>	→	Se, An
SnCl <sub>2</sub>	→	Ag
HCOOH	→	Pt
H <sub>2</sub>	→	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.

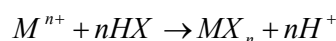
Organic precipitating agents have advantages of giving precipitate that are of very low solubility in water and with a favourable gravimetric factors.

Two types of organic precipitating agents are in use.

- (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



Some common examples of organic precipitating agents

<b>Organic reagent</b>		<b>Metal precipitated</b>
Dimethylglyoxime	→	Pb
8-hydroxyquinoline (oxine)	→	Al, Mg
Sodium diethyldithiocarbonate	→	K, Pb, Cs, Tl, Ag, Cu, Hg

## 6.0 ACTIVITY

- i. A compound weight 4.0mg produced 13.25mg of CO<sub>2</sub> and 2.41mg of H<sub>2</sub>O upon combustion. Find the percent age weight of C and H in the sample.
- ii. Highlight various necessary steps for successful precipitation gravimetric analysis.



## 7.0 SUMMARY

In this unit, you have learnt that:

- A. Definition and principle of gravimetric analysis
- B. Major types of gravimetric analysis
- C. Various steps involved in precipitation gravimetric analysis
- D. Basic concept of volatilization gravimetric analysis
- E. Technical terms involved in the gravimetric analysis.

## 8.0 ASSIGNMENT

- 1a. Describe in detail various steps involved in precipitation gravimetric analysis.
- b. Critically assess the need of gravimetric analysis to the modern analytical exercise.
- ii. What do you understand by the following terms: (a) Occlusion (b) Hydrophobic precipitation (c) Supersaturation (d) Post precipitation.
- iii. Differentiate between the two major types of gravimetric analysis known.
- iv. The  $K_{sp}$  of AgCl at 25<sup>0</sup>C is  $1.0 \times 10^{-10}$ . Calculate the concentration of Ag<sup>+</sup> and Cl<sup>-</sup> in a saturated solution of AgCl and the molar solubility of AgCl.

## 9.0 REFERENCES/FURTHER READING

Christian, G. D. (1980). *Analytical Chemistry*. (3<sup>rd</sup> ed), New York: John Wiley and Son.

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## UNIT 3 PH NOTATIONS AND BUFFER SOLUTION

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### 1.0 INTRODUCTION

This unit looks at the potential of hydrogen of a system and ways of measuring it in various media. It 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. This unit also covers 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, you should be able to:

- define pH and state its mathematical relationship to  $[H^+]$ ;
- define a buffer solution and explain how it works;
- construct and interprets the pH scale; and
- enumerate the various factors that influence the action of buffer solution.

### 3.0 HOW TO STUDY THE UNIT

1. You are expected to read carefully through this unit at least twice before attempting to answer the self-assessment questions or tutor- marked assignment.
2. Do not look at the solution given at the end of the unit until you are satisfied that you have done your best to get all answers.

3. Share your difficulties with your course mates, facilitators and by consulting other related material, particularly the internet.
4. Note that if you follow the instructions you will feel self fulfilled that you have achieved the aim of studying this unit. This should stimulate you to do more.

#### 4.0 WORD STUDY

**pH:** is a measurement of acidity or alkalinity of a solution. **Buffer:** is a substance that resists changes of pH in a system provided the amount of acid/base added is small. **Buffer capacity:** is 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

#### 5.0 MAIN CONTENT

##### 5.1 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.

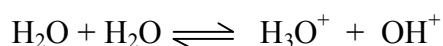
Mathematically, pH is defined by Sir SØrensen as the negative logarithm to base 10 of  $[H^+]$ .

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.



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



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

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

This is always equal to  $1.0 \times 10^{-14}$  at  $25^\circ C$

Taking log of both side, gives

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

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

$$-\log K_w = \text{pH} + \text{pOH}$$

$$\text{p}K_w = \text{pH} + \text{pOH}$$

But at 25°C, pH = 7 and pOH = 7

Hence,  $-\log K_w = 14.00$

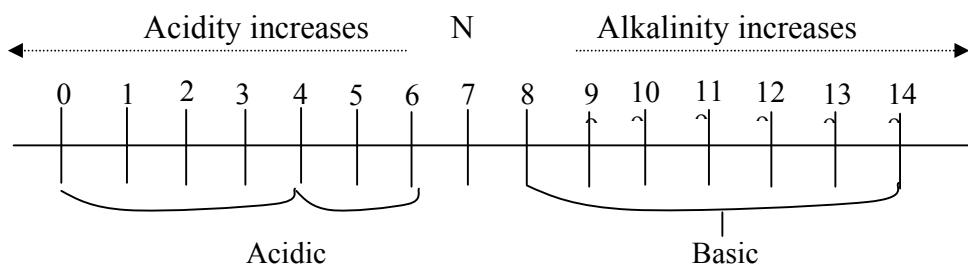
i.e.  $\log K_w = -14$  or  $K_w = 10^{-14}$

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

$$\text{p}K_w = \text{pH} + \text{pOH} = 14.00$$

## 5.2 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 of hydrogen ion is greater than 1M. It is attainable in concentrated solution of strong acid such as HCl and H<sub>2</sub>SO<sub>4</sub>.



where N= Neutrality

### 5.2.1 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<sup>+</sup> in the solution in ion- exchange equilibrium. The more the H<sup>+</sup> in solution, the more the H<sup>+</sup> ions that are bound to the glass surface. The operation of glass electrode is represented as:

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

where  $\beta$  is the electromotive efficiency = 1.00/or 0.98 and constant is known as Asymmetry Potential.

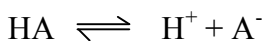
### 5.2.2 pH at Elevated Temperature

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 ionisation constant of the acid and bases from which the buffer system is derived.

### 5.3 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 consists 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:



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

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

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

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

$$\text{pH} = \text{p}K_a + \log \frac{[\text{salt}]}{[\text{Acid}]} \quad \text{This is the Henderson- Hasselbalch equation}$$

### 5.4 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.

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

If a solution is deionised, the ratio of pH remains constant. When a small amount of strong acid is added, it will combine with an equal amount of  $\text{A}^-$  to convert it to HA. The ratio of  $[\text{A}^-]$   $[\text{HA}]$  is small, so the change in pH is small, while if a strong base that is added it combines with  $[\text{HA}]$  to form an equivalent amount of  $\text{A}^-$ . Again, the change in pH is small.

## 6.0 ACTIVITY

- i. Define the term “Buffering capacity” of a buffer system.
- ii. What is the hydroxyl ion concentration when (a)  $1.0 \times 10^{-3}\text{M}$  solution of HCl acid is prepared and (b) 50mL of 2.0 M  $\text{H}_2\text{SO}_4$  is diluted to 250mL with a solution of 0.1 M NaOH
- iii. Calculate the pH of a 0.500M solution of  $\text{Na}_3\text{PO}_4$
- iv. Calculate the pH of solution by mixing 20ml of 0.10M NaOH solution and 50ml of 0.1M acetic acid.

## 7.0 SUMMARY

In this unit, you have learnt that:

- (a) A buffer capacity is the maximum amount of acid or base that can be added to a buffer system without causing any change or appreciable change in the pH of a system.
- (b) A buffer solution is defined as a solution that resist change in pH of a system

## 8.0 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  $\text{Na}_3\text{PO}_4$
- iv.
  - a. Calculate the pH and POH of  $2.00 \times 10^{-3}\text{M}$  solution of acetic acid
  - b. Calculate the  $[\text{H}^+]$  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.

## 9.0 REFERENCES/FURTHER READING

Christian, G. D. (1980). *Analytical Chemistry*. (3<sup>rd</sup> ed), New York: John Wiley and Son.

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