COURSE GUIDE

CHM 391
PRACTICAL CHEMISTRY V-INORGANIC AND ANALYTICAL

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INTRODUCTION

CHM 391 (practical chemistry v-inorganic and analytical) is a practical chemistry course that exposes the students to the theory of useful analytical procedures involving quantitative and qualitative techniques. You are familiar with the theoretical concepts of titrimetric (volumetric) analysis, analytical techniques involving spectroscopic methods as well as the concept of errors as it relates to analytical chemistry, and different statistical tools for data handling.

The 300- level inorganic chemistry syllabus comprises the periodic table and the compounds formed from their elements, with the exception of those formed between carbon and hydrogen.

CHM 391 provides you the opportunity to apply the theoretical knowledge acquired in CHM 202 to quantitatively and qualitatively **analyze** elements of the periodic table as well as their compounds. It will enable you acquire the sense of collecting and assimilating the clues to determine the composition of unknown substances.

COURSE DESCRIPTION

This is basically an analytical/inorganic practical course. The analytical chemistry aspect deals with some spectroscopic technique employed in qualitative and quantitative estimation. The inorganic part of the practical is based on the use of classical methods of analysis to obtain quantitative and qualitative data/information of **analytes** of interest.

In both parts; analytical and inorganic practical, mainly inorganic elements and their compounds will be determined.

WHAT YOU WILL LEARN IN THIS COURSE

In this course you will learn about the principle of some spectroscopic methods as well as classical methods of analysis. You will be able to follow the experimental procedure outlined for each spectroscopic and classical method mentioned in this course to obtain the quantitative and qualitative information/data you are asked to determine. This will help you develop analytical skills required in analyzing an analyte.

COURSE AIMS

The course aims to give you the opportunity to explore different analytical techniques **viz–a-vis** spectroscopic and classical techniques available for quantitative and qualitative elucidation of the Composition of an unknown sample. In **doing so**, you learn to transfer your theoretical knowledge to solving practical problems. This course also aims to help you develop analytical skills.

COURSE OBJECTIVES

At the end of this course, you should be able to

- Describe the principle of UV visible spectroscopy
- Use UV visible spectroscopy to estimate the concentration of an analyte
- Explain the principle of **colorimetric** analysis
- Determine the concentration of a coloured substance by **colorimetric** method
- Explain the principle of Infrared (IR) spectroscopy
- Determine the functional groups present in a given sample
- Determine the concentration of an analyte by Infrared spectroscopic technique
- Explain the principle of Atomic Absorption Spectroscopy (AAS)
- Use Atomic Absorption Spectroscopic technique to determine the concentrations of metal ions in solution
- Explain the principle of precipitation gravimetry
- Use precipitation gravimetric technique to separate an analyte from a sample solution and determine the quantity of analyte present in a sample
- Explain the principle of qualitative inorganic analysis
- Separate cations of a group from another group and identify the cations in a group
- Explain the principle of potentiometric titration
- Determine the end point of a redox titration by potentiometry
- Explain acidity in water, sources and significance of acidity in water
- Determine acidity in water
- Explain alkalinity in water, sources and significance of alkalinity in water
- Determine alkalinity in water
- Explain hardness in water, sources and significance of hardness in water
- Determine hardness in water

WORKING THROUGH THIS COURSE

The course is divided into two modules which are subdivided into 10 units. It is required that you study the units in details and carry out the experiments contained herein. An instructor will guide you through the practical class.

COURSE MATERIALS

You will be provided with the following materials:

1. Course Guide
2. Study Units

STUDY UNITS

The following are the two modules and ten units contained in this course:

Module 1

Unit 1 UV- Visible Spectroscopy
Unit 2 Colorimetry
Unit 3 Infrared Spectroscopy
Unit 4 Atomic Absorption Spectroscopy

Module 2

Unit 1 Precipitation Gravimetry

Unit 2 Qualitative Analysis of Cations
Unit 3 Potentiometric Titration
Unit 4 Determination of Acidity in Water and Waste Water
Unit 5 Determination of Alkalinity in Water
Unit 6 Determination of Hardness in Water

Carrying out practical is very essential for understanding the theoretical concepts learned. This helps to move your cognitive level from knowledge to comprehension, application and synthesis.

Module 1 deals with some different spectroscopic techniques employed in analytical chemistry. These techniques include UV visible, colorimetric, infrared (IR) and atomic absorption spectroscopic techniques. Here the principles of the analytical techniques mentioned are explained. A practical session precedes each principle.

Module 2 deals with classical methods of analysis. The classical methods dealt with here are; precipitation gravimetry, qualitative inorganic analysis of cations, determination of acidity in

water, alkalinity as well as hardness in water using titrimetric method .The principle of precipitation gravimetry, qualitative inorganic analysis of **cations**, as well as acidity, alkalinity and hardness in water is explained briefly. This is preceded by a practical session.

TEXTBOOKS AND REFERENCES

Below are some recommended textbooks you may wish to consult to enhance your **learning?**

Also you may also need to exploit other e- reading facilities such as the internet.

Mendham, J., Denney, R.C., Barnes, J.D., and Thomas, M.J.K., (2008), Vogel's Textbook of Quantitative Chemical Analysis, 6th Edition, Pearson Education.

Gary, D.C., (1980), Analytical Chemistry, 3rd Edition, John Wiley & Sons, New York.

Braun, R.D., (1983), Introduction to Chemical Analysis, McGraw Hill, Auckland.

Harvey, D., (2000), Modern Analytical Chemistry, Mcgraw Hill Higher Education Companies, Boston.

ASSESSMENT

There are two aspects of assessment for this course: the tutor-marked assignment (TMA) and the end of course examination.

The TMAs shall constitute the continuous assessment component of the course. They will be marked by the tutor and equally account for 30% of the total course score. Each learner shall be examined in four TMAs before the end of course examination.

The end of course examination shall constitute 70% of the total course score.

SUMMARY

CHM 391 analytical and inorganic practical course is based on theoretical inorganic and analytical courses. Students are expected to make use of the theoretical knowledge acquired from these courses to determine the quantitative and qualitative composition of elements of the periodic table and their elements exception of those formed between carbon and hydrogen.

MAIN COURSE

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MODULE ONE (ANALYTICAL)

UNIT 1 UV- VISIBLE SPECTROSCOPY

3.8 EXPERIMENTAL

In-text Question
4.0 Self-Assessment Exercise (s)

5.0 CONCLUSION

6.0 SUMMARY

7.0 REFERENCES/ FURTHER READING

Unit 1: UV- Visible Spectroscopy

3.1 Principle for UV- Visible Spectroscopy
https://www.youtube.com/watch?v=raUbBpqf74Q

3.3 Applications of Uv-Visible Spectroscopy
https://www.youtube.com/watch?v=d3p6bjMjW0g

3.4 DETERMINATION OF THE CONCENTRATION OF AN ANALYTE USING UV VISIBLE SPECTROSCOPY
https://www.youtube.com/watch?v=rllHziqWlgU

3.4. 1 Using UV- Visible absorption spectra to find concentrations
https://www.youtube.com/watch?v=0aL_A5tfYHI

3.4.1.2 Determination of wavelength of absorption for the preparation of calibration curve
https://www.youtube.com/watch?v=Il9hlMT0aUQ

3.4.1.3 Finding concentration by plotting a calibration curve
https://www.youtube.com/watch?v=P_XyUykj10I

3.5 IDENTIFICATION OF AN ANALTYTE USING UV-VISIBLE SPECTROSCOPY
https://www.youtube.com/watch?v=sfxEj_MxBcs

3.6 Brief Introduction to A Spectrophotometer
https://www.youtube.com/watch?v=qbCZbP6_j48

3.7 Brief description of how to use a UV–Visible spectrophotometer
https://www.youtube.com/watch?v=s5uIVQGFDE4

1.0 INTRODUCTION

Spectroscopy 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 **to** at it. Spectroscopy is also defined as a method of analysis, which involves the measurements of the intensity and wavelength of radiation that is either absorbed or transmitted. **Specifically spectroscopy is the study of the interaction between matter and electromagnetic radiation**. What you need to understand from **these** definitions is that, when electromagnetic radiation passes through a solution of a compound (sample), a certain amount of light radiation is absorbed by the molecules. According to Beer's law, the amount of radiation absorbed by the molecule in solution is proportional to the number of absorbing molecules in the solution (concentration). The absorbed radiation brings about a decrease in the intensity of the transmitted (unabsorbed) radiation. The more the number of absorbing molecules (concentration), the greater is the intensity of absorption. Spectroscopic techniques can be used in the determination of the concentration (quantitative analysis) of an analyte and in the identification (qualitative analysis) of an analyte. The instruments used to study or measure the absorption or emissions of electromagnetic radiation as a function of wavelength are spectrometers and spectrophotometers.

2.0 Intended Learning Outcomes (ILOs)

After studying this unit, you should be able to:

- Explain the fundamental principle behind spectroscopy
- Discuss/ explain UV- Visible spectroscopy
- State and explain the principle of UV- Visible spectroscopy
- State the uses of UV-Visible spectroscopy toPrepare standard solution
- Construct calibration curve based on Beer's law
- Explain how UV-Visible spectroscopy can be used to determine the concentration of an analyte and identification of an analyte
- Carry out experiments which involve the use of UV- Visible spectroscopy to analyse a sample

3.0 MAIN CONTENT

3.1 PRINCIPLE OF UV- VISIBLE SPECTROSCOPY

Principle: it involves the absorption of electromagnetic radiation by the substance in the ultraviolet and visible regions of the spectrum. This will result in changes in the electronic structure of ions and molecules through the excitations of bonded and non-bonded electrons.

The electromagnetic radiation covers a long range of radiations which are broken down into different regions according to wavelength. **The ultraviolet (UV) and visible region of the electromagnetic spectrum covers the wavelength range from 100 nm to about 800 nm. The vacuum ultraviolet region, which has the shortest wavelengths and highest energies (100-**

200 nm), is difficult to make measurements in and is little used in analytical procedures. Most analytical measurements in the UV region are made between 200 and 400 nm. The region occurs between 400 and 800 nm. Below 200 nm, the air absorbs appreciably and so the instruments are operated under a vacuum; hence, this wavelength region is called the vacuum ultraviolet region. The visible region is the region of wavelengths that can be seen by the eye, that is, the light appears as a colour. It extends from the near ultraviolet region (**400** nm) to about **800** nm. **The energy levels involved in transitions in the UV- visible region are the electronic levels of atoms and molecules**. **Example, although light atoms have widely spaced energy levels, some heavy atoms have their outer orbitals close enough together to give transition in the visible region.** When an organic molecule absorbs UV- Visible radiation, the energy from UV or visible light causes the outer electrons from a lower energy to be raised to a higher energy level, corresponding to an electronic transition. This transition of electrons is from molecular bonding orbital to the higher energy anti-bonding molecular orbital. According to the molecular orbital theory, the shared electron pair of a covalently bonded atoms may be thought of as occupying molecular orbitals (MO) which is of a lower energy and has a corresponding unoccupied orbitals called **anti-bonding** molecular orbitals, these correspond to excited state energy levels (higher energy level). When the molecule is in the ground state, both electrons are paired in the lower-energy bonding orbital – this is the Highest Occupied Molecular Orbital (HOMO). The **anti-bonding,** in turn, is the Lowest Unoccupied Molecular Orbital (LUMO).

When organic molecules that are capable of absorbing UV- Visible radiation are exposed to the radiation at a wavelength with energy equal to the difference between the energy of the HOMO and LUMO (with energy equal to ΔE, the HOMO-LUMO energy gap) this wavelength will be absorbed and the energy used to bump one of the electrons from the HOMO to the LUMO. The energy absorbed appears as absorption peaks at the wavelength it corresponds to on the UV – Visible spectrum. The extent of absorption of electromagnetic radiation corresponds to the concentration of the analyte through the application of Beer – Lambert law.

Molecules containing pi electrons or non-bonding electrons can absorb the energy in the form of ultraviolet or visible light to excite these electrons to higher anti- bonding molecular orbitals. The more easily excited the electrons (i.e. lower energy gap between the HOMO and the LUMO) the longer the wavelength of light it can absorb.

In-text Questions

The greater intensity of absorption is defined by ——

Answer

The more the number of absorbing molecules (concentration),

3.2 KINDS OF MOLECULES THAT CAN ABSORB UV-VISIBLE RADIATION

Not all molecules absorb UV – Visible radiation. When the energy gap between the HOMO and LUMO is large**,** absorption will not take place, but when this energy gap is small absorption will take place. The electronic transitions that take place in the visible and ultraviolet regions of the

electromagnetic radiation are due to absorption of radiation by specific types or groups, bonds, and functional groups within the molecule, known as chromophores **[such as azo (–N=N-) ; carbonyl(-C=O), methine (-CH=), nitro (-NO_2) and quinoid groups]**. These contain valence electrons of low excitation energy.

3.2.1 The kinds of possible transitions an organic molecule can undergo are:

$\sigma \rightarrow \sigma^*$ Transitions

An electron of a saturated compound in a bonding σ orbital is excited to the corresponding **anti-bonding** orbital σ^*. The energy required is large. The high excitation energy makes it unable to contribute to absorption in the visible or uv regions. For example, methane (which has only C-H bonds, and can only undergo $\sigma \rightarrow \sigma^*$ transitions) shows an absorbance maximum at 125 nm. Absorption maxima due to $\sigma \rightarrow \sigma^*$ transitions are not seen in typical UV-Vis. spectra (200 - 700 nm).

n **$\rightarrow \sigma^*$ Transitions**

Saturated compounds containing atoms with lone pairs (non-bonding electrons) are capable of $n \rightarrow \sigma^*$ transitions. These transitions usually need less energy than $\sigma \rightarrow \sigma^*$ transitions because the **non-bonding** electrons are less tightly held than sigma electrons, however, the energy gap between the HOMO 63and LUMO is large. $n \rightarrow \sigma^*$ transitions occur at wavelengths less than 200nm.The number of organic functional groups with $n \rightarrow \sigma^*$ peaks in the UV region is small.
n **$\rightarrow \sigma^*$ and $\sigma \rightarrow \sigma^*$ Transitions**

Unsaturated compounds containing atoms with lone pairs (non-bonding electrons) **which** are capable of $n \rightarrow \pi^*$transition. The **non-bonding** electrons are less tightly held, they can be excited by visible or uv radiation to unoccupied pi **anti-bonding** orbital `. Electrons in pi orbitals of an unsaturated compound are responsible for $\pi \rightarrow \pi^*$Transitions. They are the most readily excited and responsible for a majority of electronic spectra in the visible and uv regions.

It is important to mention at this point that, most absorption spectroscopy of organic compounds are based on transitions of *n* or π electrons to the excited state π^*. This is because the absorption peaks for these transitions fall in an experimentally convenient region of the spectrum (200 - 700 nm). The energy gap between the HOMO and LUMO is small.

Generally the compounds that absorb strongly UV-visible radiation are molecules with conjugated pi systems (compounds having more than one double bond, alternating a single bond). In these group, the energy gap for $\pi \rightarrow \pi^*$ transitions is smaller than for isolated double bonds, and thus the wavelength absorbed is longer.

Molar absorptivities from $n \rightarrow \pi^*$ transitions are relatively low, and range from 10 to100 L mol^{-1} cm^{-1}. $\pi \rightarrow \pi^*$ transitions normally give molar absorptivity between 1000 and 10,000 L mol^{-1} cm^{-1}.

3.2.2 Electronic transition involving inorganic compounds

Charge - Transfer Absorption: Many inorganic species show charge-transfer absorption and are called *charge-transfer complexes*. For a complex to demonstrate charge-transfer behaviour, one of its components must have electron donating properties and another component must be able to accept electrons. Absorption of radiation then involves the transfer of an electron from the donor to an orbital associated with the acceptor.

The intense colour of metal chelates is frequently due to charge transfer transitions. This is simply the movement of electrons from the ligand to metal ion or vice versa. Such transitions include promotion of electrons from d-d levels in the ligand or from π bonding orbitals to the unoccupied orbitals of the metal ion or promotion of d-d bonded electrons to unoccupied π orbitals of the ligand. When such transitions occur, a redox reaction actually occurs between the metal ion and the ligand. Usually, the metal ion is reduced and the ligand is oxidized, and the wavelength (energy) of maximum absorption is related to the ease with which the exchange occurs.

Molar **absorptivity** from charge-transfer absorption are large (greater **than**10, 000 L mol^{-1} cm^{-1}).

3.3 APPLICATIONS OF UV-VISIBLE SPECTROSCOPY

A. Quantitative analysis: Measurement of the relation between concentration and absorbance allows quantitative analysis using the Beer-Lambert law. Many organic compounds and inorganic complexes may be determined by direct absorptiometry using the Beer-Lambert Law.

Three criteria that must be observed include

i. The absorptivity of the species to be determined must be reasonably large.
ii. The species must be stable in solution. It must not oxidize or precipitate or change during the analysis (unless the analysis intends to study that change).
iii. Calibration must be carried out over the range of concentration to be determined (Agreement with the Beer-Lambert law must be established). In simplification

- UV-Vis spectroscopy is routinely used in analytical chemistry for the quantitative determination of different analytes, such as highly conjugated organic compounds, transition metal ions and biological macromolecules.
- UV-Vis spectroscopy can be used to determine the concentration of an analyte in a solution. This is based on Beer – Lambert law. The law is simply an application of the observation that, within certain ranges, the absorbance of a chromophore at a given wavelength varies in a linear fashion with its concentration: the higher the concentration of the molecule, the greater its absorbance. If we divide the observed value of A at λ_{max} by the concentration of the sample (c, in mol/L), we obtain the molar absorptivity, or extinction coefficient ε which is a characteristic value for a given compound
- The wavelengths of absorption peaks can be correlated with the types of bonds in a given molecule and are valuable in determining the functional groups within a molecule.

B. Structure effects: The structure of a molecule determines the nature of its UV or visible spectrum and facilitates qualitative analysis of a sample. The structures of organic

molecules may be classified in terms of the functional groups, which they contain. If they absorb UV or visible radiation in a particular regionthey are called chromophores[such as azo (–N=N-); carbonyl (-C=O), methine (-CH=), nitro ($-NO_2$) and quinoid groups], i.e (absorbing group in molecules). A molecule containing a chromophore is called a chromogen

Ultraviolet and Visible Spectroscopy provide information about compounds that have conjugated double bonds. An important property of conjugated systems is that they absorb energy in the ultraviolet-visible region of the spectrum as a result of electronic transitions. The region of the electromagnetic spectrum covered by most ultraviolet spectrophotometers is from 200 to 400 nm, a region commonly referred to as the near ultraviolet. Wavelengths shorter than 200 nm require special instrumentation and are not used routinely. The region covered by most visible spectrophotometers runs from 400 nm (violet) to 800 nm (red). Recall that wavelength (λ) is inversely related to the energy of radiation: the shorter the wavelength, the greater the energy. Ultraviolet light therefore, has greater energy than visible light.$E = hv = \frac{hc}{\lambda} = h\bar{v}c$

In the ground state, electronic configuration of a molecule, all the electrons are in the lowest-energy molecular orbitals. When a molecule absorbs light with the energy required to promote an electron to higher energy molecular orbital – when it undergoes an electronic transition – the molecule is then in an excited state. The relative energies of the bonding, nonbonding and anti-bonding molecular orbitals are shown below;

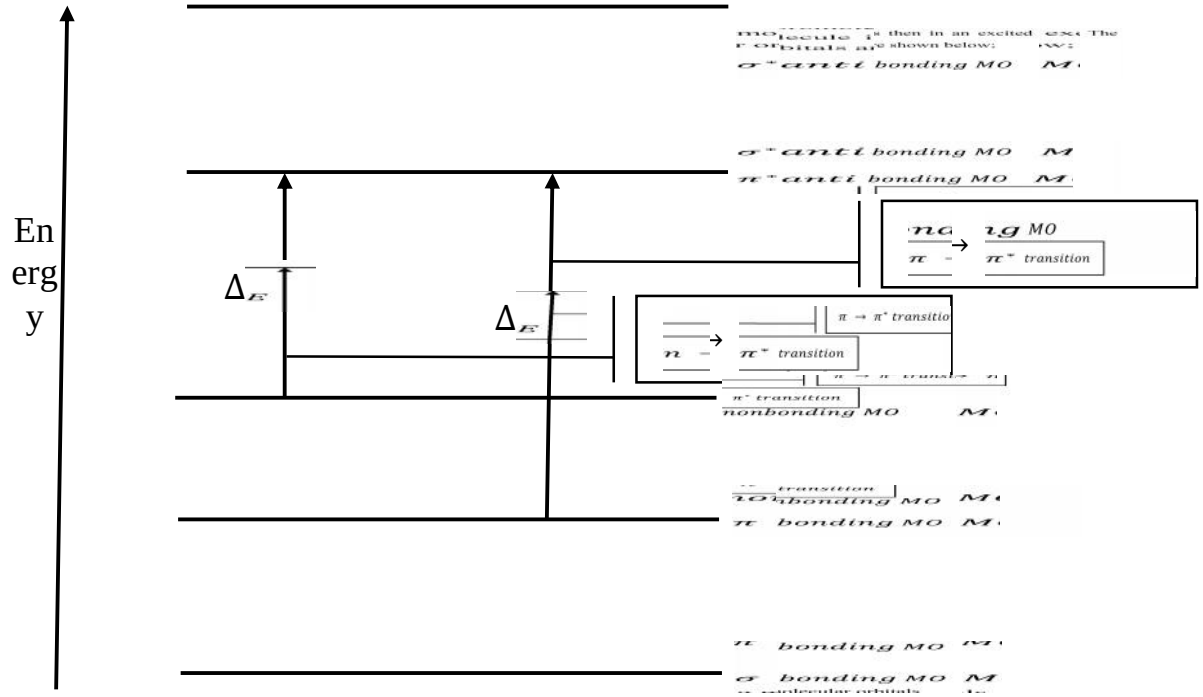


Fig 1: The relative energies of the bonding, nonbonding and anti-bonding molecular orbitals

TERMINOLOGIES

- Auxochrome: A saturated group with non-bonded electrons which, when attached to a chromohore, alters both the wavelength and the intensity of the absorption (e.g., -OH, $-NH_2$, $-NR_2$ -SH etc.)
- Chromophore: A covalently unsaturated group responsible for electronic absorption (e.g., C=C, C=O, esters, amides, $-NO_2$ etc.).
- Bathochromic Shift: The shift of absorption to a longer wavelength (also known as "red shift").
- Hypsochromic Shift: The shift of absorption to a shorter wavelength (also known as "blue shift").
- Hyperchromic Effect: An increase in absorption intensity.
- Hypochromic Effect: A decrease in absorption intensity.

THE BEER LAMBERT LAW

Ultraviolet and visible spectral data are recorded as plots of absorbance (A) on the vertical axis versus wavelength on the horizontal axis.

$$Absorbance\ (A) = log\frac{I_o}{I} = \frac{1}{T}$$

Where, I_0 is the intensity of radiation incident on the sample, I is the intensity of the radiation transmitted, T is transmittance through the sample.

The extent of absorption of ultraviolet-visible radiation is proportional to the number of molecules capable of undergoing the observed electronic transition; therefore, ultraviolet-visible spectroscopy can be used for quantitative analysis of samples. The relationship between absorbance, concentration, and length of the sample cell (cuvette) is known as the Beer-Lambert law.

The proportionality constant in this equation is given the name molar absorptivity (e) or extinction coefficient.

$$Beer - Lambert\ Law: (A) = \ \varepsilon\, c\, l$$

Where, A is the absorbance (unit-less), ε is the molar absorptivity (in per moles per litre per centimetre, $M^{-1}cm^{-1}$), c is the concentration of solute (in moles per litre, M), and l is the length of the sample cell, or cuvette (in

centimeters, cm). The molar absorptivity is a characteristic property of a compound and is not affected by its concentration or the length of the light path

Deviation from Beer Lambert Law

This occurs if:

- The concentration of the absorbing species is not dilute i.e., when it's greater than 10^{-2}M.
- When the absorbing species are involved in dissociation, association or interacts with the solvent molecules,
- When the absorbance measurements are not made at the points in the spectrum where the wavelength is broad maximum
- When unabsorbed stray light passess the optical system

Limitation Beer Lambert Law

1. Instrumental Deviation due to monochromatic interferences
2. Chemical Deviation: due to degree of dissociation, ionization, hydration and complex formation in absorbing species.
3. The law is successful for absorption behaviour of dilute solutions. In high concentrated solutions, the average distance between molecules of absorbing solute diminishes to such an extent that they affect charge distribution of neighbouring molecules which affect the wavelength maximum and molar absorptivity of the sample.

INSTRUMENTATION

Ultraviolet and Visible Spectrometer consist of the following components:

1. Radiation Source: usually a constant source of radiation energy where intensity or power can be changed. Example are Deuterium lamp for UV range; Tungsten/halogen for visible range
2. Monochromator: is a dispensing device used to select an appropriate wavelength to be used
3. Sample Compartment: is an arrangement which allow transmitting of radiation source to sample and the reference sample solution.
4. Detector: is used to measure the radiant energy which is transmitted as a measure of electric signals.

5. Readout Indicator: used to measure the signals for computation and final processing.

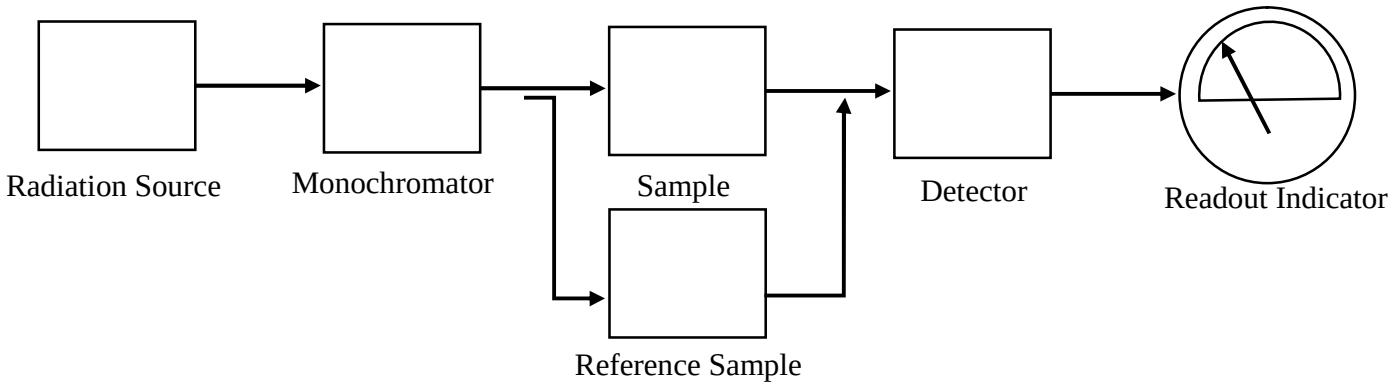


Fig 2: Schematic Diagram of Ultraviolet – Visible Spectrometer

WOODWARD-FIESER RULE FOR DETERMINATION OF CONJUGATED COMPOUNDS

Woodward (1941) predicted λ max values only for the lowest energy transition ($\pi \Rightarrow \pi^*$) from HOMO to LUMO.

1. Base values for Dienes

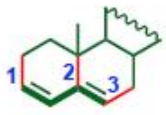
- Base value for an unsubstituted, conjugated, acyclic or heteroannular diene = 214 nm
- Base value for an unsubstituted, conjugated, homoannular diene = 253 nm

Increments for:

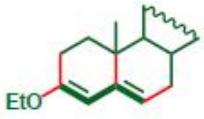
- Each extra double bonds in conjugation = + 30 nm
- Exocyclic double bond (effect is twofold if the bond is exocyclic to two rings) = + 5 nm

Substituent effect:

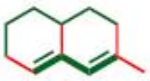
- -OCOR or –OCOAr = + 0 nm
- Simple alkyl substituents or ring residue = + 5 nm
- Halogen (-Cl, -Br) = + 5 nm
- OR (R=Alkyl) = + 6 nm
- SR (R=Alkyl) = + 30 nm
- NR2 (R=Alkyl) + 60 nm



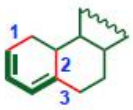
Transoid (base):	214 nm
3 ring residues :	+15
1 exocyclic C=C:	+ 5
Total:	234 nm
Observed:	235 nm



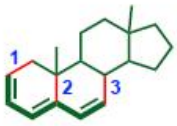
Transoid (base):	214 nm
3 ring residues:	+15
1 exocyclic C=C:	+ 5
-OR:	+ 6
Total:	240 nm
Observed:	241 nm



Transoid (base):	214 nm
3 Ring residues:	+15
1 Alkyl substituent:	+ 5
1 Exocyclic C=C:	+ 5
Total:	239 nm



Cisoid (base):	253 nm
3 ring residues:	+15
1 exocyclic C=C:	+ 5
Total:	273 nm
Observed:	275 nm



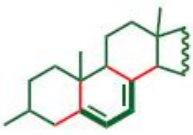
Cisoid (base):	253 nm
3 Ring residues:	+15
1 Exocyclic C=C:	+ 5
Double-bond Extending Conjugation:	+30
Total:	303 nm
Observed:	304 nm

Base value:	214 nm
2 Ring residue	+10
Exocyclic C=C:	+ 5
Total:	229 nm
Observed:	230 nm

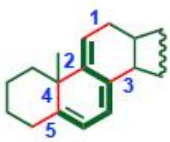
Base value:	214 nm
2 Ring residue:	+10
Exocyclic C=C:	+ 5
Total	229 nm
Observed:	236 nm

Base value:	214 nm
3 Alkyl grs:	+15
Total:	229 nm
Observed:	232 nm

Base value:	214 nm
4 Alkyl grs:	+20
Total:	234 nm
Observed:	235 nm



Base value:	253 nm
4 Ring residues:	+20
2 Exocyclic C=C:	+10
Total:	283 nm
Observed:	282 nm



Base value:	253 nm
5 Ring residues:	+25
3 Exocyclic C=C:	+15
DEC:	+30
Total	323 nm
Observed:	325 nm

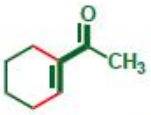
Fig 3: Conjugated compounds

2. Base values Enone&Dienone Absorption

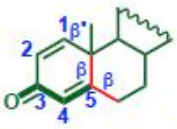
- Acyclic α,β-unsaturated ketones = 215 nm
- 6-membered cyclic α,β-unsaturated ketones = 215 nm
- 5-membered cyclic α,β-unsaturated ketones 202 nm
- α,β-unsaturated aldehydes = 210 nm
- α,β-unsaturated carboxylic acid & esters = 195 nm

Increments for:

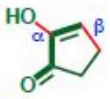
- Double bond extending conjugation (DEC): = +30
- Exocyclic double bond: = + 5
- Homodiene component: = +39
- Alkyl group/ring residue: α = +10, β = +12; γ & higher = +18
- Polar groups: -OH: α = +35; β = +30; δ = +50
    - -OAc: α,β,γ = + 6
    - -OMe: α = +35; β = +30; γ = +17 δ = +31
    - -SAlk: β = +85
    - -Cl: α = +15; β = +12
    - -Br: α = +25; β = +30
    - -NR_2: β = +95



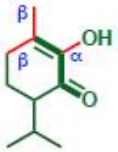
Base value:	215 nm
α substituent:	+10
β substituent:	+12
Total:	237 nm
Observed:	232 nm



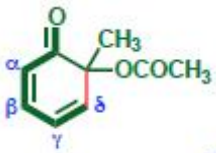
$\Delta^{4,5}$ system (base):	215 nm
2 β substituents:	+24
1 exocyclic C=C:	+ 5
Total:	244 nm
Observed:	245 nm



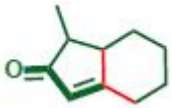
Base value:	202 nm
β substituent:	+12
α-OH:	+35
Total:	249 nm
Observed:	247 nm



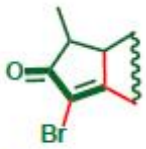
Base value:	215 nm
2 β substituents:	+24
α-OH:	+35
Total:	274 nm
Observed:	270 nm



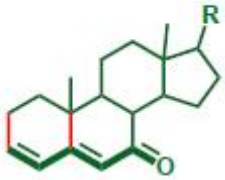
Base value:	215 nm
1 DEC:	+30
Homocyclic diene:	+39
δ ring residue:	+18
Total:	302 nm
Observed:	300 nm



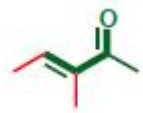
Base value:	202 nm
Exocyclic C=C:	+ 5
2 β-ring residues:	+24
Total:	231 nm
Observed:	226 nm



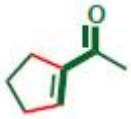
Base value:	202 nm
1 α-Br:	+25
2 β-ring residue:	+24
Exocyclic C=C:	+ 5
Total:	256 nm
Observed:	251 nm



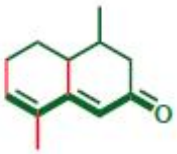
Base value:	215 nm
1 DEC:	+30
β-ring residue:	+12
δ ring residue:	+18
2 Exocyclic C=C:	+ 5
Total:	280 nm
Observed:	280 nm



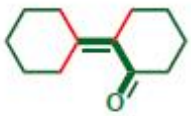
Base value:	215 nm
α alkyl substituent:	+10
β alkyl substituent:	+12
Total:	237 nm



Base value:	215 nm
α alkyl:	+10
β alkyl:	+12
Total:	237 nm



Base value:	215 nm
1 DEC:	+30
Exocyclic C=C:	+ 5
β-alkyl substituent:	+12
γ-alkyl substituent:	+18
δ-alkyl substituent:	+18
Total:	298 nm



Base value:	215 nm
1 α-alkyl:	+10
2 β-alkyl:	+24
2 Exocyclic C=C:	+10
Total:	259 nm

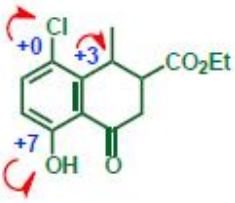
3. Base Value for Aromatic Compound, Parent chromophore: Ar = C_6H_5

- Ar-CO-R = 246 nm
- Ar-CHO = 250 nm
- Ar-COOH or Ar-COOR = 230 nm

Increment for each substituent on Ar:

- Alkyl or ring residue o, m = + 3 nm; p = + 10 nm
- OH, OCH_3, OAlk o, m = + 7 nm; p = + 25 nm
- NH_2 o, m = + 13 nm; p + 58 nm
- $NHCOCH_3$o,m = + 20 nm; p = + 45 nm
- NHMe p = + 73 nm
- NMe_2 o, m = + 20 nm; p = + 85 nm
- Cl o, m = + 0 nm; p = + 10 nm
- Br o, m = + 2 nm; p = + 15 nm

Calc λ_{max}^{EtOH} = 246 (parent chromophore) + 3 (*o*-ring residue) + 25 (*p*-OMe)
= 274 nm
Obs λ_{max}^{EtOH} = 276 nm



Calc λ_{max}^{EtOH} = 246 + 3 (*o*-ring residue) + 7 (*o*-OH)
= 256 nm
Obs λ_{max}^{EtOH} = 257 nm

Calc λ_{max}^{EtOH} = 246 + 25 + 7 + 3 = 281 nm

Obs λ_{max}^{EtOH} = 278 nm

4. Fieser-Kuhn rules for Conjugated Polyenes

λ max = 114 + 5M + n(48.0 – 1.7n) - 16.5R_{endo} – 10R_{exo}

ε max = $(1.74 \times 10^4)^n$

Where n = number of conjugated double bonds

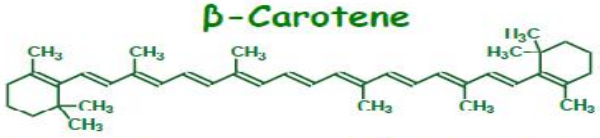
M = number of alkyl or alkyl like substituents on the conjugated system

R_{endo} = number of rings with endocyclic double bonds in the conjugated system

R_{exo} = number of rings with exocyclic double bonds

λ_{max}^{calc} = 114 + 5(8) + 11[48.0 - 1.7(11)] - 0 - 0
= 476 nm
λ_{max}^{obs} = 474 nm (hexane)
ε_{max}^{cal} = 1.74 X 10^4(11) = 19.1 X 10^4
ε_{max}^{obs} = 18.6 X 10^4 (hexane)

β-Carotene



λ_{max}^{calc} = 453.3 nm
λ_{max}^{obs} = 452 nm (hexane)
ε_{max}^{cal} = 19.1 X 10^4
ε_{max}^{obs} = 15.2 X 10^4

Uses of Ultraviolet and Visible Spectroscopy.

1. Determine conjugated group in a compound
2. To determine the geometric isomer of a compound

Application of Ultraviolet and Visible Spectroscopy.

1. Colorimetric and spectrophotometric analysis
2. Kinetic Studies
3. Determination of Pure substance
4. Determination of mixtures of two substance quantitatively.
5. Spectrophotometric titration.

3.4 DETERMINATION OF THE CONCENTRATION OF AN ANALYTE USING UV-VISIBLE SPECTROSCOPY

The absorption of light radiation by solutions can be elucidated by a combination of the laws of Beer and Lambert. These two laws relate the absorption to concentration and to the thickness of the absorbing layer respectively.

Beer's law states that the absorption of light is directly proportional to the number of the absorbing molecules. That is, the transmittance decreases exponentially with the number or concentration of the absorbing molecules. Mathematically, Beer's law is represented as:

$\log_{10}\frac{I_0}{I}$ C or $\log_{10}\frac{I_0}{I} I_0$ εlc

Where, $\log_{10}\frac{I_0}{I}$ is the absorbance (A), C is the concentration and is a constant, I_0 = incident light, I = transmitted light

This can also be represented as: A α C or A = εlC

Lambert's law states that same proportion of incident light is absorbed per unit thickness irrespective of its intensity, and that each successive unit layer absorbs the same proportion of light falling on it. For example, if the incident light is 100% and 50% of it is absorbed per unit layer, the intensity of light will decrease exponentially as follows: 50%, 25%, 12.5%, 6.25%, etc.

Thus, according to this law,

$\log_{10}\frac{I_0}{I}$ α l Or $\log_{10}\frac{I_0}{I} = kl$

Note that: absorbance (A) = $\log_{10}\frac{I_0}{I} = kl$

Where, k is a constant and l is the path length.

The two laws are combined together and called Beer-Lambert's law:

A = $\log_{10}\frac{I_0}{I}\ cl$ or $\log_{10}\frac{I_0}{I} = \varepsilon cl$

Where, is a constant called molar extinction coefficient (or molar absorptivity's) which is numerically equal to the absorbance of a molar solution in a cell of 1cm path length.

Note: While Lambert's law holds for all cases, Beer's law is only obeyed by dilute solutions.

Absorbance and transmittance

The absorbance (A) is the measure of the fraction of light radiation that is absorbed by a given sample solution, while transmittance (T) is the fraction of incident light that is not absorbed (i.e. transmitted by the solution).

Transmittance (T) = $\frac{I}{I_0}$

But, absorbance is related to transmittance as follows:

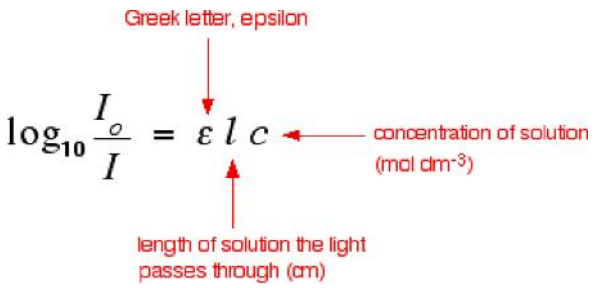
A = $-\log_{10}T = \log_{10}\frac{I_0}{I}$

Note that as the absorbance of a solution increases, the transmittance decreases.

3.4. 1 Using UV- Visible absorption spectra to find concentrations

A = εcl

The **absorbance**($\log_{10}\frac{I_0}{I}$) is measured by a spectrometer or spectrophotometer.



3.4.1.1 Determination of concentration using the molar absorptivity

If you know the molar absorptivity of a solution at a particular wavelength, and you measure the absorbance of the solution at that wavelength, it is easy to calculate the concentration. The only other variable in the expression above is the length of the solution. That's easy to measure and, in fact, the cell containing the solution may well have been manufactured with a known length of 1 cm (most cells are manufactured with a known length of 1 cm).

For example, let's suppose you have a solution in a cell of length 1 cm. You measure the absorbance of the solution at a particular wavelength using a spectrometer. The value is 1.92.
You find a value for molar absorptivity in a table of 19400 for that wavelength.

Substituting those values:

$A = \varepsilon cl$

1.92 = 19400 x 1 x c

C = 1.92

———

19400

= 9.90 x 10^{-5}Mol dm^{-3}

Notice what a very low concentration can be measured provided you are working with a substance with a very high molar absorptivity.

This method, of course, depends on you having access to an accurate value of molar absorptivity. It also assumes that the Beer-Lambert Law works over the whole concentration range.

It is much better to measure the concentration by plotting a calibration curve.

3.4.1.2 Determination of wavelength of absorption for the preparation of calibration curve

In preparing the calibration curve, it is imperative to know the wavelength at which the absorbance of the different standard solutions and the sample solution is to be determined. The wavelength is determined by plotting absorbance against wavelength (measured in nanometers). The wavelength corresponding to the absorbance maximum (or transmittance minimum) is read from the plot and used to prepare the calibration curve. Let us take an example. Suppose you are asked to prepare a calibration curve to determine the concentration of a sample whose concentration is unknown by UV- Visible spectroscopic method. What you will do to determine the wavelength at which this **concentration** is to be carried out is to prepare a standard solution of the sample, after which you measure the absorbance and percentage transmittance over a series of wavelengths e.g wavelengths covering the range 360 nm –640 nm at for instance 10**nm** intervals i.e. 360 nm, 370 nm, 380 nm e.t.c. Plot the graph of absorbance against the wavelength or percentage transmittance. You would obtain a graph as shown in Figure 1

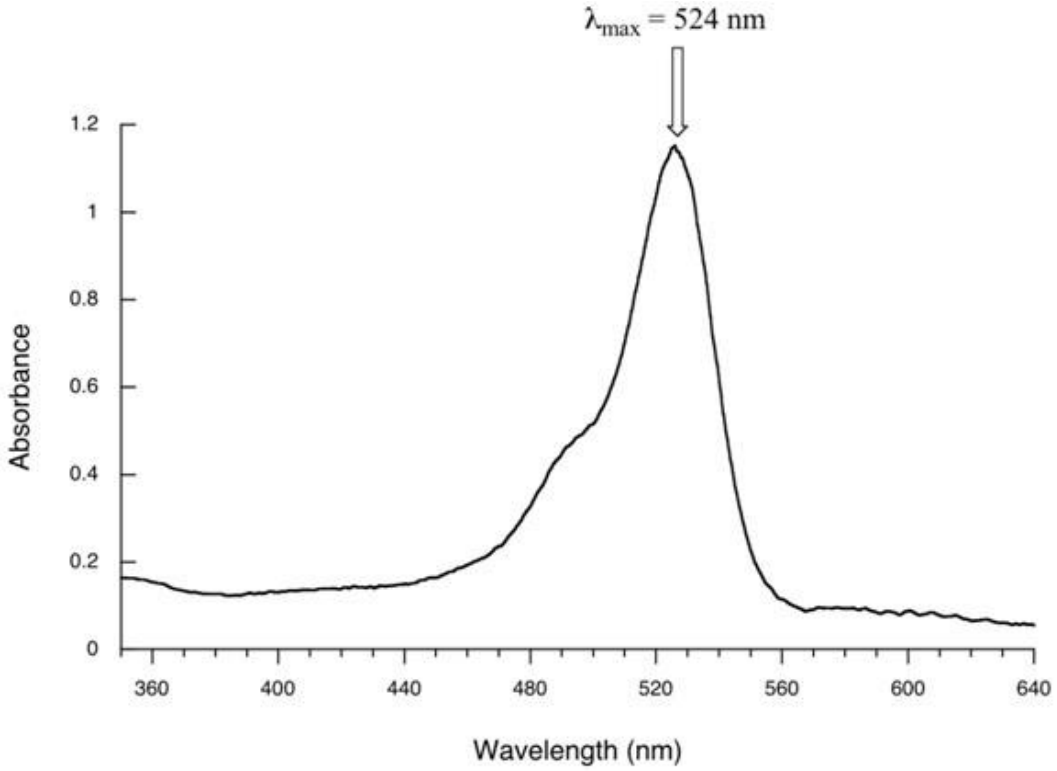


Fig 4: Absorbance against wavelength

The λ_{max} of 524 nm is the wavelength of maximum absorption so the calibration curve will be determined at this wavelength.

3.4.1.3 Finding concentration by plotting a calibration curve

Doing it this way, you don't have to rely on a value of molar absorptivity, the reliability of the Beer-Lambert Law, or even know the dimensions of the cell containing the solution.

What you do is **to** make up a number of solutions of the compound you are investigating - each of accurately known concentration. Those concentrations should bracket the concentration you are trying to find - some less concentrated; some more concentrated.

For each solution, you measure the absorbance at the wavelength of maximum absorption - using the same container for each one. Then you plot a graph of absorbance against concentration. This is a calibration curve.

According to the Beer-Lambert Law, absorbance is proportional to concentration, and so you would expect a straight line. That is true as long as the solutions are dilute, but the Law breaks down for solutions of higher concentration, and so you might get a curve under these circumstances.

As long as you are working from values either side of the one you are trying to find, that is not a problem.

Having drawn a line of best fit, the calibration curve will probably look like Figure 2, and it's what you will probably get if you are working with really dilute solutions.

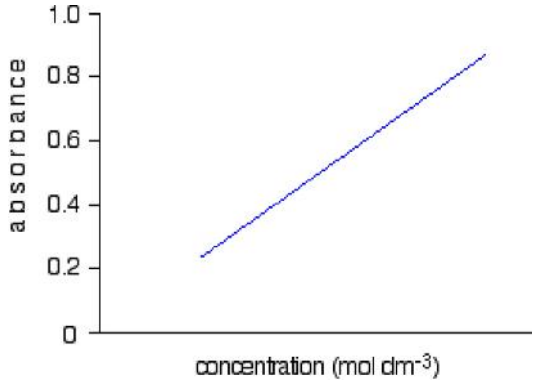


Figure 5: absorbance against concentration

Notice that no attempt has been made to force the line back through the origin. If the Beer-Lambert Law worked perfectly, it *would* pass through the origin, but you can't guarantee that it is working properly at the concentrations you are using.
Now all you have to do is to measure the absorbance of the solution (analyte in solution) with the unknown concentration at the same wavelength as used for the preparation of the calibration curve. If, for example, it had an absorbance of 0.600, you can just read the corresponding concentration from the graph as below (Figure 3).

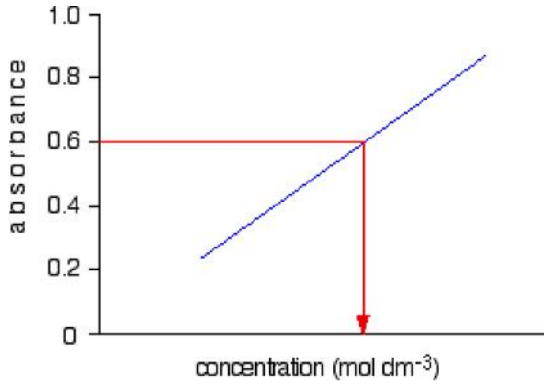


Figure 6: absorbance against concentration

3.5 IDENTIFICATION OF AN ANALTYTE USING UV-VISIBLE SPECTROSCOPY

If you compared the peaks on a given UV-visible absorption spectrum with a list of known peaks, it would be fairly easy to pick out some structural features of an unknown molecule.

Lists of known peaks often include molar absorptivity values as well. That might help you to be even surer. For example using the simple carbon-oxygen double bond of ethanal (CH_3CHO) which has two peaks in its spectrum at 180 and 290nm, data shows that the peak at 290 has a molar absorptivity of only 15, compared with the one at 180 of 10000. If your spectrum showed a very large peak at 180, and an extremely small one at 290, that just adds to your certainty.

3.6 Brief Introduction to Spectrophotometer

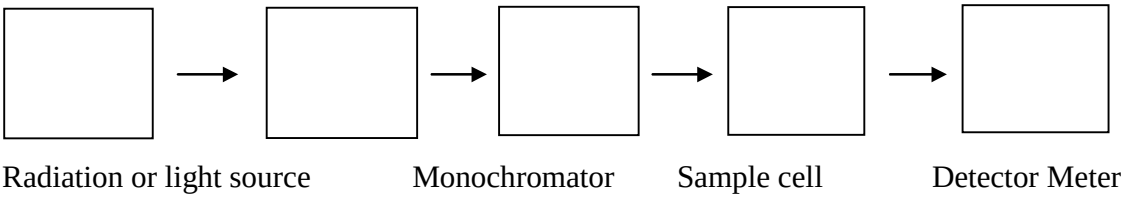


Figure 7: A schematic representation of a spectrophotometer
The schematic diagram above gives brief description of the basic components of a spectrophotometer.

Radiation or light source: a light source produces a polychromatic beam of light. The UV-Visible spectrophotometer uses deuterium, tungsten halogen or xenon lamps or LED as the light source. Deuterium arc lamps measure in the ultraviolet (UV) region 190 – 370 nm. Tungsten halogen also known as quartz iodine lamp measure in the visible region from 320 – 1100nm. Xenon lamp measure in both the UV and visible regions of the electromagnetic spectrum from 190- 1100nm.

Monochromator: is a device which is used to resolve polychromatic radiation into its individual wavelength and isolates these wavelengths into a very narrow band. This device produces light radiation of only particular (single) wavelength. Here, the monochromator selects a particular wavelength for the incident beam of light (I_0).

Sample cell or cuvette: is the container that holds the sample to be analysed.

Detector: measures the intensity of the transmitted light (I).

Meter: The readout is supplied by a meter.

3.7 Brief description of how to use a UV–Visible spectrophotometer

The sample is placed in the cuvette and is then irradiated with an incident beam of light (I_0) of a specific wavelength. A detector then measures the amount of light that is transmitted through the sample (I). The signal from the detector drives a meter that can be calibrated to read transmittance or absorbance.

To use the UV- Visible spectrophotometer, the calibration procedure entails setting 0 Absorbance at a given wavelength with a cuvette containing a reference or blank solution. Typically, the blank solution is just the solvent, i.e., the cuvette is filled with only the solvent used to dissolve the sample to be analyzed, and inserted into the cell holder of the spectrophotometer. 0 (zero) absorbance is pressed on the spectrophotometer to set the blank at 0. After this, the blank is removed, and an identical cuvette containing the solution of interest is then inserted into the spectrometer, and the absorbance is read from a meter on the instrument. Both the calibration and the reading must be done at the same wavelength. The reading for the solution then represents the absorbance at the chosen wavelength due to the component of interest. The calibration has accounted for any absorption (or reflection or scattering) of light by the cuvette and other species in the reference solution.

EXPERIMENT 1 – Determination of Absorption Curve and Concentration of Potassium Nitrate

Purpose: To prepare absorption curve for potassium nitrate and use it to determine the concentration of potassium nitrate

Discussion: Potassium nitrate is an example of an inorganic compound which absorbs mainly in the ultraviolet. The absorbance and percentage transmittance of an approximately 0.1m potassium nitrate solution are measured over the wavelength range 240-360 nm at 5 nm intervals and at smaller intervals in the vicinity of the maxima or minima. Manual spectrophotometers are calibrated to read both absorbance and percentage transmittance on the dial settings, whereas the automatic recording double-beam spectrophotometers usually use chart paper printed with both scales. The linear conversion chart is useful for visualizing the relationship between these two quantities. The three normal means of presenting the spectrophotometric data are described below; by far the most common procedure is to plot absorbance against wavelength (measured in **nanometers**). The wavelength corresponding to the absorbance maximum (or transmittance minimum) is read from the plot and used to prepare the calibration curve. This point is chosen for two reasons: (1) it is the region in which the greatest difference in absorbance between any two different concentrations will be obtained, thus giving the maximum sensitivity for concentration studies, and (2) as it is a turning point on the curve it gives the least alteration in absorbance value for any slight variation in wavelength. No general rule can be given concerning the strength of the solution to be prepared, as this will depend upon the spectrophotometer used for the study. Usually a 0.001-0.01M solution is sufficiently concentrated for the highest **absorbance**, and other concentrations are prepared by dilution. The concentrations should be selected such that the

absorbance lies between about 0.3 and 1.5. For the determination of the concentration of a substance, select the wavelength of maximum absorption for the compound (e.g 302.5 to 305 nm for potassium nitrate) and construct a calibration curve by measuring the absorbances of four or five concentrations of the substance (e.g 2, 4, 6, 8, and $10gl^{-1}KNO_3$) at the selected wavelength. Plot absorbance against concentration. If the compound obeys Beer's law, the result will be a linear calibration curve passing through the origin. If the absorbance of the unknown solution is measured, the concentration can be obtained **by extrapolation**from the calibration curve.

If it is known that the compound obeys Beer's law, the molar absorption coefficient e can be determined from one measurement of the absorbance of a standard solution. The unknown concentration is then calculated using the value of the constant e and the measured value of the absorbance under the same conditions.

Table 1: Reagent/Equipment / Materials:

Potassium nitrate
Beakers
Stirring rod
Dessicator
Distilled water
UV-Visible spectrophotometer

Experimental Procedure

Dry some pure potassium nitrate at 110^0C for 2-3h and cool in a desiccator. Prepare an aqueous solution containing $10.000gl^{-1}$. With the aid of a spectrophotometer and matched 1cm rectangular cells, measure the absorbance and the percentage transmittance over a series of wavelengths covering the range 240-350 nm. Plot the data in three different ways:

(a) absorbance against wavelength

(b) percentage transmittance against wavelength

(c) **Log** (molar absorptivity, or extinction coefficient ( ) against wavelength.

From the curves, evaluate the wavelength of maximum absorption (or minimum transmission). Use this value of the wavelength to determine the absorbance of solutions of potassium nitrate containing 2.000, 4.000, 6.000 and **$8.000gl^{-1}$** KNO_3. Run a blank on the two cells, filling them both with distilled water; if the cells are correctly matched, no difference in absorbance should be discernible. Plot absorbance against concentration for each cell. Determine the absorbance of an unknown solution of potassium nitrate and read the concentration from the calibration.

EXPERIMENT 2 – Spectrophotometric Determination of Iron

Purpose: To prepare absorption curve for iron and use it to determine the concentration of Iron

Discussion: A complex of iron (II) is formed with 1, 10-phenanthroline **[Fe ($C_{12}H_8N_2$)$_3^{2+}$]**, and the absorbance of this coloured solution is measured with a spectrophotometer. The spectrum is plotted to determine the absorption maximum. Hydroxylamine (as the hydrochloride salt to increase solubility) is added to reduce any Fe^{3+} to Fe^{2+} and to maintain it in that state. Equation. $4Fe^{3+} + 2NH_2OH \rightarrow 4Fe^{2+} + N_2O + 4H^+ + H_2O$

Table 2: Materials /Reagents /Equipments:

1 litre volumetric flask	Ferrous ammonium sulphate	UV – Visible spectrophotometer
Beakers	Concsulphuric acid	Weighing balance
Stirring rod	Hydroxylammonium chloride	
Pipets	Sodium acetate	
Distilled water	1, 10 – phenanthroline monohydrate	

Experimental Procedure:

Solution Preparation

1. Standard iron (II) solution. Prepare a standard iron solution by weighing 0.0702 g of ferrous ammonium sulphate, **Fe (NH_4)$_2$(SO_4)$_2$**.$6H_2O$. Quantitatively transfer the weighed sample to a one-litre volumetric flask and add sufficient water to dissolve the salt. Add 2.5 ml of concentrated sulphuric acid, dilute exactly to the mark with distilled water, and mix thoroughly. This solution contains 10.0 mg of iron per litre (10 ppm); if the amount weighed is different than that above, calculate the concentration.
2. 1, 10-phenanthroline solution. Dissolve 100mg of 1, 10-phenanthroline monohydrate in 100 ml of water
3. Hydroxylammonium chloride solution. Dissolve 10 g of hydroxylammonium chloride in 100 ml of water.
4. Sodium acetate solution. Dissolve 10 g of sodium acetate in 100 ml of water.

Into a series of 100 ml volumetric flasks, add with pipettes 1.00, 5.00, 10.00, and 25.00ml of the standard iron solution. Into another 100 ml volumetric flask, place 50 ml of distilled water for a blank. The unknown sample will be furnished in another 100-ml volumetric flask. To each of the flasks (including the unknown)add 1.0ml of the hydroxylammonium chloride solution and 5.0 ml of the 1, 10-phenanthroline solution. Buffer each solution by the addition of 8.0 ml of the sodium acetate solution to produce the red color of ferrous **1, 10**-phenanthroline. [The iron (ii) phenanthroline complex forms at pH 2 to 9. The sodium acetate neutralizes the acid present and adjusts the pH to a value at which the complex forms]**.** Allow at least 15 minutes after adding the reagents before making absorbance measurements so that the colour of the complex can fully develop. Once developed, the colour is stable for days. Dilute each solution to exactly 100 ml. The standards will correspond to 0.1, 0.5; 1, and 2.5 ppm of iron, respectively. Obtain the absorption spectrum of the 2.5-ppm solution by measuring the absorbance from about 400 nm to 700 nm (or the range of your instrument). Take reading at 25-nm intervals except near the vicinity of the absorption maximum, where you should take readings at 5 or 10 nm intervals. Follow your instructor's directions for the operation of your spectrophotometer. The blank solution should be used as the reference solution. Plot the absorbance against the wavelength and select the wavelength of maximum absorption. Calculate the molar absorptivity of the iron (ii)phenanthroline complex at the absorption maximum.

Prepare a calibration curve by measuring the absorbance of each of the standard solutions at the wavelength of maximum absorbance. Measure the unknown in the same way. Plot the absorbance of the standards against concentration in ppm. From this plot and the absorbance of the unknown, determine the final concentration of iron in your unknown solution. Report the number of micrograms of iron in your unknown along with the molar absorptivity and the spectrum of the iron (ii)-phenanthroline complex.

EXPERIMENT 3 – Spectrophotometric Determination of Aspirin (2-(acetylbenzoic acid) by Iron (III)

Purpose: To determine the amount of aspirin in a commercial aspirin product.

Discussion: A coloured complex is formed between aspirin (2-(acetylbenzoic acid) and the iron (III) ion. The intensity of the colour is directly related to the concentration of aspirin present; therefore, spectrophotometric analysis can be used. A series of solutions with different aspirin concentrations will be prepared and complexed. The absorbance of each solution will be measured and a calibration curve will be constructed. Using the standard curve, the amount of aspirin in a commercial aspirin product can be determined. The complex is formed by reacting the aspirin with sodium hydroxide to form the salicylate dianion.

Table 3: Materials /Reagents/Equipment's:

125 ml Erlenmeyer flasks	Acetylsalicylic acid	UV – Visible spectrophotometer
2 cuvettes	50 ml volumetric flask	Commercial aspirin
10 ml graduated cylinder	1 M NaOH	
5 ml pipet	Analytical balance	
250 ml volumetric flask	0 02M Iron (III) buffer	

Be careful while boiling the sodium hydroxide solution. NaOH solutions are dangerous, especially when hot.

Experimental Procedure:

Part I: Making Standards.

1. Weigh 400 mg of acetylsalicylic acid (aspirin) in a 125 mL Erlenmeyer flask. Add 10 mL of a 1 M NaOH solution to the flask, and heat until the contents begin to boil.
   Quantitatively transfer the solution to a 250 mL volumetric flask, and dilute with distilled water to the mark.

2. Pipette a 2.5 mL sample of this aspirin standard solution to a 50 mL volumetric flask. Dilute to the mark with a 0.02 M iron (III) solution. Label this solution "A," and place it in a 125 mL Erlenmeyer flask.

3. Prepare similar solutions with 2.0, 1.5, 1.0, and 0.5 mL portions of the aspirin standard. Label these "B, C, D, and E."

Part II: Making an unknown from a tablet.

1. Place one aspirin tablet in a 125 mL Erlenmeyer flask. Add 10 mL of a 1 M NaOH solution to the flask, and heat until the contents begin to boil.

2. Quantitatively transfer the solution to a 250 mL volumetric flask, and dilute with distilled waterto the mark.

3. Pipette a 2.5 mL sample of this aspirin tablet solution to a 50 mL volumetric flask. Dilute to the mark with a 0.02 M iron (III) solution. Label this solution "unknown," and place it in a 125 mL Erlenmeyer flask.

Part III: Testing the Solutions.

Turn on the spectrophotometer. Press the **A/T/C** button on the Spectrophotometer to select absorbance. Adjust the wavelength to **530** nm by pressing the **nm** arrow up or down.

Insert the blank (0ppm – cuvette of iron buffer) into the cell holder and close the door. Position the cell so that the light passes through clear walls. *****Remember to wipe off the cuvette with a tissue paper before inserting it into the instrument.

Press **0 ABS/100% T** to set the blank to 0 (zero) absorbance. Record the absorbance of the 0ppm solution. Obtain absorbance readings for each of the other standard solutions. Record the results on the data sheet. Obtain an absorbance reading for the unknown sample(s). Make a graph of concentration (x-axis) vs. absorbance (y-axis). From the standard curve, determine the concentration of aspirin in the unknown.

In-text Question

The structures of organic molecules may be classified in terms of the ———

Answer

Functional groups which they contain.

4.0Self-Assessment Exercises

1. Spectroscopy is the study of the interaction between ——— and ——
2. What are chromophores?
3. The ultraviolet and visible absorption is based on molecules containing ———
4. Why does vacuum ultraviolet region occur?
5. With good structural examples, define a chromatogen
6. State the function of a monochromator

Answers

1. Matter and electromagnetic radiation
2. Chromophores are molecules that contains functional groups that absorb UV or visible radiation
3. Pi- electrons or non-bonding electrons
4. Vacuum ultraviolet region occur because at below 200 nm, the air absorbs appreciably and so the instruments are operated under a vacuum; hence, this wavelength region is called the vacuum ultraviolet region.
5. A chromatogen is a molecule containing a chromophores, structural examples include azo (–N=N-); carbonyl (-C=O), methine (-CH=), nitro (-NO_2)
6. Monochromator is a device which is used to resolve polychromatic radiation into its individual wavelength and isolates these wavelengths into a very narrow band

5.0 CONCLUSION

UV-Visible spectroscopy refers to absorption spectroscopy. It involves the absorption of radiation at the near ultraviolet region 200 nm to 800 nm. It is routinely used in analytical chemistry for the quantitative and qualitative determination of different analytes, such as highly conjugated organic compounds, transition metal ions and biological macromolecules.

6.0 SUMMARY

UV-Visible spectroscopy is an analytical technique which involves the absorption of electromagnetic radiation at the near ultraviolet (200 nm) region and the visible region. The ultraviolet and visible absorption is based on molecules containing pi- electrons or **non-bonding** electrons (n- electrons) which can absorb the energy in the form of ultraviolet or visible light to excite these electrons to higher anti-bonding molecular orbitals. UV-Visible spectroscopy is particularly important for the qualitative and quantitative determination of many organic compounds especially those with a high degree of conjugation and transition metal ions. The basic principle of quantitative determination by UV-Visible spectroscopy lies in comparing the extent of absorption of a sample solution with that of a set of standards under radiation of a selected wavelength through the application of Beer- Lambert law.

CLASS ACTIVITY (THE TUTOR TO DIRECT)

1. What type of electrons in a molecule is generally involved in the absorption of UV or visible radiation?

2. Describe how the wavelength of maximum absorption can be determined.

3. What are the most frequent electronic transitions during absorption of electromagnetic radiation which results in more intense absorption?

4. How would you obtain a calibration curve?

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UNIT 2 - COLORIMETRY

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1.0 INTRODUCTION

A colorimeter is a light-sensitive device used for measuring the transmittance and absorbance of light passing through a liquid sample. The device measures the intensity or concentration of the colour which develops when a specific reagent is introduced into a solution. Two types of colorimetersexist, colour densitometers – which measures the density of primary colors, and color photometers – the type that measures the colour reflection and transmission while colorimetry is an analytical technique (spectroscopic method) used to determine the concentrations of coloured substances in solution. It relies on the fact that a coloured substance absorbs light (at the visible region) of a colour complementary to its own and the amount of light it absorbs (absorbance) is proportional to its concentration.Colorimetric determinations are carried out by the use of an instrument called colorimeter.

2.0 Intended Learning Outcomes (ILOs)

After studying this unit, you should be able to:

- Define and explain colorimetric analysis
- Describe or state the principle of colorimetry
- Explain the mode of operation of a colorimeter
- Explain how the concentration of a coloured compound can be determined using a colorimeter
- Carry out colorimetric determinations

3.0 MAIN CONTENT

Design of a colorimeter

The three main components of a colorimeter are a light source, a cuvette containing the sample solution, and a photocell for detecting the light passed through the solution. The instrument is also equipped with either coloured filters or specific LEDs to generate colour. The output from a colorimeter may be displayed by an analog or digital meter in terms of transmittance or absorbance. In addition, a colorimeter may contain a voltage regulator for protecting the instrument from power fluctuation. Some colorimeters are portable and useful for on-site tests whileothers are larger, bench-top instruments useful for laboratory testing.

3.1 Principle of colorimetry

Colorimetric analysis is based on Beer- Lambert law, **stating that the absorption of light transmitted through the medium is directly proportional to the concentration of the medium.**The concentration of the coloured compound is related to the amount of visible radiation absorbed by the coloured compound. The coloured compound absorbs white light at the visible region of a colour complementary to its own. **With the knowledge** that white light is made up of different colours; red, orange, green, yellow, blue, indigo and violet. These colours occur at particular wavelengths, e.g. blue occurs at the wavelength 435- 480 nm, and so, in colorimetry the complimentarycolour absorbed by a coloured solution occurs at particular wavelength. **With a colorimeter, a beam of light with a specific wavelength is passed**

through a solution via series of lenses, which navigate the coloured light to the measuring device. This analyses the colourcompared to an existing standard.

The colour of the compound is usually due to the formation of a coloured compound by the addition of an appropriate reagent or it may be inherent in the desired constituent itself. The basic principle of most colorimetric measurements consists in comparing, under well-defined conditions, the colour produced by the substance in the unknown concentration with the same colour produced by a known amount (standard solution) of the same substance being determined.

In-text Question

State the three main components of a colorimeter and their functions

Answer

The three main components of a colorimeter are a light source, a cuvette containing the sample solution, and a photocell for detecting the light passed through the solution.

3.2 Colorimetric determinations

Generally, in order to determine the concentration of an unknown sample, several sample solutions of a known concentration are first prepared and tested. The concentrations are then plotted on a graph against absorbance, thereby generating a calibration curve. The results of the unknown sample are compared to that of the known sample on the curve to measure the concentration.

The determination is similar to spectrophotometric determination **and will normally require the following steps.**

1. A weighed quantity of the material under investigation in an appropriate solvent
2. A standard solution of the compound being determined in the same solvent
3. The requisite reagent
4. Any ancillary reagents such as buffers, acids or alkalis necessary to establish the correct conditions for formation of the required coloured product
5. Preparation of calibration curve
6. Estimation of the unknown concentration of the test solution from the calibration curve.

In view of the sensitivity of colorimetric and spectrophotometric methods, the absorbance measurements are usually made on very dilute solutions. In order to take sufficient material for an accurate weight to be achieved when preparing the original solution of analyte and the corresponding standard solution, it is commonly necessary to prepare solutions which are too concentrated for the absorbance measurements, and these must then be diluted accurately to the appropriate strength.

Solutions of colour producing reagents are frequently unstable and normally should not be stored for more than a day or so.

The colorimeter consists of light source, monochromator, slit, optical cell or cuvette, photoelectric cell and galvanometer.

3.3 Mode of operation

White light from a tungsten lamp passes through a condenser lens to give a parallel beam which falls on the filter that is positioned to select radiation of specific wavelength to impinge on a glass cuvette containing the solution. As the light is passing through the solution, some part of it is absorbed by the sample component, while the part that is not absorbed is transmitted, and detected by a photo electric cell (detector). In order to measure the absorbance of a solution, the meter reading is first adjusted to 100% transmittance (zero absorbance) with a blank solution. The sample is then inserted in place of the blank and the absorbance is read directly. The concentration corresponding to the absorbance of the sample is then obtained from the standard or calibration curve. The filter is usually a complimentary colour of the test solution.

The filter is chosen to select the band of wavelengths which are most strongly absorbed by the coloured solution e.g. this is illustrated in the table below, by using a yellow filter to use in measuring the concentration of a blue coloured solution like copper (II) sulphate or its ammine/amine complex.

Table 4:showing wavelength of colour in relation to observed and complimentary colour of solution

The wavelength (nm) of the observed transmitted colour of the solution	The observed transmitted colour of the solution	The complementary colour of the solution i.e. the colour of the filter
400-435	violet	yellowish-green
435-480	blue *	yellow *
480-490	greenish-blue	orange
490-500	bluish-green	red
500-560	green	purple
560-580	yellowish-green	violet
580-595	yellow	blue
595-610	orange	greenish-blue
610-750	red	bluish-green

EXPERIMENT 1 – Colorimetric determination of manganese in steel

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Purpose: To determine the concentration of manganese in steel

Discussion: Colorimetry is particularly suited to the determination of manganese in steel because the manganese can be converted into permanganate ions, which are coloured. The conversion is achieved in two stages. Using nitric acid, the managanese is first oxidised to manganese (II) ions, which are then oxidised to permanganate ions by the more powerful oxidising agent, potassium periodate.

Table 5: Equipment / Materials/ Reagents:

Measuring cylinders (50cm^3 and 10 cm3)	Dropper	Potassium persulphate
Clock glass	Wire cutters	Standard flask (50 cm^3 and 100 cm^3)
Filter funnel	Propanone	Potassium permanganate
Tweezers	Deionised water	Green filter
Wash bottle	Anti-bumping granules	Optical matched cuvettes
Glass beakers (50 cm^3 and 250 cm^3)	Analytical balance (accurate to 0.001g)	Bunsen burner, tripod stand,wire gauze
Steel paper chips	Colorimeter	Acidified 85% phosphoric acid
Acidified potassium periodate(5g potassium periodate per 100 cm^3 of 2 mol 1^{-1} nitric acid		

CAUTION

Wear eye protection and if any chemical splashes on your skin wash it off immediately. The acidified 0.0010 **M**ol l^{-1} potassium permanganate is harmful if ingested and irritates the eyes and skin. Wear gloves.
Both 2 **M**ol l^{-1} nitric acid and its vapour are corrosive and toxic, causing severe burns to the eyes, digestive and respiratory systems. Wear gloves.
85% phosphoric acid is corrosive: it burns and irritates the eyes and skin. It is a systemic irritant if inhaled and if swallowed causes serious internal injury. Wear gloves.

Acidified potassium periodate solution is harmful if swallowed and is an irritant to the eyes, skin and respiratory system. It is also corrosive. Wear gloves.
Potassium persulfate is harmful if swallowed or inhaled as a dust. It irritates the eyes, skin and respiratory system, causing dermatitis and possible allergic reactions. Wear gloves.
Propanone is volatile and highly flammable, and is harmful if swallowed. The vapour irritates the eyes, skin and lungs, and is narcotic in high concentrations. Wear gloves.

Experimental Procedure

Part A – Calibration graph

1. Rinse the burette, including the tip, with 0.0010 $Moll^{-1}$ acidified potassium permanganate and fill it with the same solution.
2. Run 2 cm^3 of the permanganate solution into a 50 cm^3 standard flask and make up to the graduation mark with deionized water.
3. Stopper the flask and invert it several times to ensure the contents are completely mixed.
4. Rinse a cuvette with some of the solution and fill it.
5. Using a colorimeter (fitted with a green filter) measure the absorbance of the solution in the cuvette. If you have more than one green filter, choose the one that gives maximum absorbance.
6. Repeat steps 2 to 5 with 4, 6, 8, 10, 12 and 14 cm^3 of the permanganate stock solution in the burette.
7. Use dilution formula to calculate the concentration of the $2cm^3$ – 14 cm^3 of the diluted stock solution.
8. Plot a calibration graph of 'absorbance' against 'concentration of potassium permanganate'.

Part B – Conversion of manganese to permanganate

1. Degrease a steel paper clip by swirling it with a little propanone in a beaker. Using tweezers remove the paper clip and leave it to dry for a minute or so on a paper towel.

2. Cut the paper clip into small pieces.

3. Weigh **accurately** about 0.2 g of the paper clip pieces and transfer them to a 250 cm^3 glass beaker.

4. Add approximately 40 cm^3 of 2 mol l^{-1} nitric acid to the beaker and cover it with a clock glass.

5. Heat the mixture cautiously, in a fume cupboard, until the reaction starts. Continue heating gently to maintain the reaction, but remove the source of heat if the reaction becomes too vigorous.

6. Once the steel has reacted, allow the solution to cool a little. Add a couple of anti- bumping granules and then boil the solution until no more brown fumes are given off.

7. Once this solution has cooled considerably – no more than 'hand hot' – adds about 5 cm^3 of 85% phosphoric acid, approximately 0.2 g of potassium persulfate and a couple of fresh anti-bumping granules. Boil the mixture for about 5 minutes.

8. To this solution, add approximately 15 cm^3 of acidified potassium periodate solution plus a couple of fresh anti-bumping granules and then gently boil the mixture. The solution will start to turn pink. Continue gently boiling until the intensity of the pink colour remains constant. This should take about 5 minutes.

9. Allow the pink solution to cool to room temperature and then transfer it to a 100 cm^3 standard flask, leaving the anti-bumping granules in the beaker.

10. Rinse the beaker several times with a little deionised water and add the rinsings (but not the anti-bumping granules) to the flask.

11. Make up the solution to the graduation mark with **deionized** water.

12. Stopper the flask and invert it several times to ensure the contents are completely mixed.
13. Using a colorimeter fitted with the appropriate green filter, measure the absorbance of the solution.
14. Use your calibration graph to convert the absorbance to permanganate concentration and then calculate the percentage by mass of manganese in the steel paper clip.

In-text Question

State whysolutions of colour producing reagents are not be stored for more than a day or so.

Answer

They are unstable

4.0Self-Assessment Exercises

1. A colorimeter measures two important parameters, explain.
2. Explain why a glove should be worn when working with acidified potassium periodate
3. The plot of concentration against absorbance gives?
4. Why is colorimeters particularly suitable for the determination of manganese in steel

Answers

1ai. A colorimeter measures the transmittance and absorbance of light passing through a liquid sample

1aii. It also measures the intensity or concentration of the colour which develops when a specific reagent is introduced into a solution.

2. Acidified potassium periodate solution is harmful if swallowed and is an irritant to the eyes, skin and respiratory system. It is also corrosive.

3. It gives a straight line graph

4. Colorimetry is particularly suited for the determination of manganese in steel because the manganese can be converted into permanganate ions, which are coloured.

5.0 CONCLUSION

Colorimetry is a spectroscopic method of analysis which involves the measurement of the absorption of electromagnetic radiation at the visible region by a coloured compound. The principle is based on the application of Beer- Lambert law. The amount of visible radiation absorbed by the coloured compound is related to the concentration of the analyte in the solution.

6.0 SUMMARY

Colorimetry is an analytical technique (spectroscopic method) used to determine the concentrations of coloured substances in solution. It relies on the fact that a coloured substance absorbs lightat the visible region of the electromagnetic radiation, of a colour complementary to its own and the amount of light it absorbs (absorbance) is proportional to its concentration.Colorimetric determinations are carried out by the use of an instrument called colorimeter. The unknown concentration of the test sample solution is obtained from the calibration curve of the standard solutions of the test solution.

CLASS ACTIVITY (THE TUTOR TO DIRECT)

1. In what region of the electromagnetic spectrum is colorimetric analysis carried out

2. Why is it necessary to prepare fresh solution of the coloured sample to be analyzed

3. Describe the mode of operation of a colorimeter

4. Can colorimeter be used to analyse dilute coloured solutions.

5. Outline the function and basic features that must be considered in the design of a colorimter

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9. Mode of operation
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UNIT 3 - INFRARED SPECTROSCOPY

1.0 INTRODUCTION

The light our eyes see is but a small part of a broad spectrum of electromagnetic radiation. On the immediate high energy side of the visible spectrum lies the ultraviolet, and on the lower energy side is the infrared. The portion of the infrared region most useful for analysis of organic compound is not immediately adjacent to the visible spectrum. But is that having a wavelength range from 2.500 to 16, 000 nm, with a corresponding frequency range from $1.9^{*}10^{13}$to $1.2^{*}10^{14}$Hz

Infrared spectroscopy is a spectroscopic method of analysis used qualitatively to identify and study chemicals and quantitatively to measure concentrations. When a molecule interacts/absorbs radiation at the infrared region, it causes the molecule to undergo vibrational transitions. Let us pause here to get a clearer picture or understanding of what happens when a molecule absorbs radiation.

There are three basic processes by which a molecule can absorb radiation: all involve raising the molecule to a higher internal energy level, the increase in energy being equal to the energy of the absorbed radiation (hv). The three types of internal energy are quantized; that is, they exist at discrete levels. Firstly, the molecules rotates about various axes, the energy of rotation being at definite energy levels, so the molecule may absorb radiation and be raised to a higher rotational energy level, in a rotational transition. This type of transition (rotational transition) occurs when molecules absorb radiation at the far infrared region and microwave region of the electromagnetic spectrum. Secondly, the atoms or groups of atoms within a molecule vibrate relative to each other, and the energy of this vibration occurs at definite quantized levels. The molecule may then absorb a discrete amount of energy and be raised to a higher vibrational energy level, in a vibrational transition. This type of transition occurs with absorption of near infrared radiation. Third, the electrons of a molecule may be raised to a higher electron energy, corresponding to an

electronic transition. This type of transition occurs at the ultraviolet and visible region. These transitions occur only at definite wavelengths corresponding to an energy equal to the difference of the discrete energy levels involved in the transition.

The infrared portion of the electromagnetic spectrum is usually divided into three regions; the near-, mid- and far- infrared. The higher-energy near-IR, approximately 14000–4000 cm^{-1} (0.8–2.5 μm wavelength) can excite overtone or harmonic vibrations. The mid-infrared, approximately 4000–400 cm^{-1} (2.5–25 μm) may be used to study the fundamental vibrations and associated rotational-vibrationalstructure. The far-infrared, approximately 400–10 cm^{-1} (25– 1000 μm), lying adjacent to the microwave region, has low energy and may be used for rotational spectroscopy. Most of the analytical applications are confined to the middle IR region because absorption of organic molecules are high in this region.

The method or technique of infrared spectroscopy uses an instrument called an **infrared spectrometer** to produce an infrared spectrum. A basic IR spectrum is essentially a graph of infrared light absorbance (or transmittance) on the vertical axis vs. frequency or wavelength on the horizontal axis. Typical units of frequency used in IR spectra are reciprocal centimeters (sometimes called wave numbers), abbreviated as cm^{-1}. Units of IR wavelength are commonly given in microns, abbreviated as μm, which are related to wave numbers in a reciprocal way.

2.0 INTENDED LEARNING OUTCOMES (ILOs)

After studying this unit, you should be able to:

- Explain the principle of infrared spectroscopy
- Give account of the kinds of molecules that absorb infrared radiation
- State the types of vibration
- Carry out IR spectroscopy practical

3.0 MAIN CONTENT

3.1 Principle of Infrared Spectroscopy

When molecules absorb radiation at the infrared region, the energy of the wavelength absorbed causes a vibrational transition if the energy absorbed is equal to the quantized jump in the internal energy i.e. the energy difference between the vibrational energy levels of the atoms or group of atoms within the molecule. The vibrational energy of the atoms or groups of atoms within the molecule is raised to a higher level. The energy absorbed appears as absorption peaks at the wavelength it corresponds to on the IR spectrum.

Not all molecules can absorb in the infrared region. For absorption to occur there must be change in the dipole moment (polarity) of the molecule. A diatomic molecule must have a permanent dipole (polar covalent bond in which a shared pair of electrons is shared unequally) in order to absorb.

Different functional groups absorb characteristics frequencies of IR radiation. Hence gives the characteristic peak value. Therefore IR spectrum of a chemical substance is a finger print of a molecule for its identification.

In-text Question

The infrared portion of the electromagnetic spectrum is usually divided into three regions, namely;

Answer

The near- (14000–4000 cm^{-1} (0.8– 2.5 μm wavelength), mid- (4000–400 cm^{-1} (2.5–25 μm) and far- infrared (400–10 cm^{-1} (25– 1000 μm)**.**

3.2 Types of Vibrations

In an organic molecule there are two major types of fundamental vibrations. These are stretching and bending vibrations. The stretching vibration could either be symmetrical or asymmetrical. Bending vibration is of four different types namely scissoring, rocking, wagging and twisting. The exact frequency at which a given vibration occurs is determined by the strength of the bonds involved and the mass of the component atoms. In practice, infrared spectra do not normally display separate absorption signals for each fundamental vibrational modes of a molecule. The energy required to bend a bond is not great and falls within the range of 400 – 1300 cm^{-1}. This region is called the finger print region because absorption in this region is very dependent on the molecular environment. Thus, this region is used to establish the identity of the chemical compounds. The energy required to stretch a bond is a little bit higher. This falls within the region 0f 1300 – 4000 cm^{-1}. Absorption in this region is caused by functional groups and is independent of other parts of the molecule and is used to detect the functional groups in molecules. Some general trends include:

i) Stretching frequencies are higher than corresponding bending frequencies. (It is easier to bend a bond than to stretch or compress it).
ii) Bonds to hydrogen have higher stretching frequencies than those to heavier atoms.
iii) Triple bonds have higher stretching frequencies than corresponding double bonds which in turn have higher frequencies than single bond. (Except for bonds to hydrogen)

3.3 Group frequencies

Group frequencies are the absorption bands or signals that occurs at certain frequencies due to stretching or bending vibration within a molecule. For example, the bands at 3300 cm_{-1} and 1050 cm_{-1} are characteristics of the OH group in alcohols.

3.4 Correlation of structure and frequency

Many thousands of infrared spectra have been recorded and from these, it has been possible to empirically tabulate correlations between absorption frequencies and types of bonds or chemical groups. Table 6, summaries some of the correlations for various types of vibrations. Table 2:1 also contains Group Frequencies.

Table 6: Correlations of various types of vibrations and group frequencies

Vibration	Type of molecule	Group frequencies (cm_{-1})
C – H $_{stretch}$	Alkanes, alcohols	2800 - 3000
C – H $_{stretch}$	Aldehydes	2700 - 2900
C – H $_{stretch}$	Alkenes	3010 - 3095
O – H $_{stretch}$	Alcohols, phenols	3200 - 3600
O – H $_{stretch}$	Acids	2500 - 3000
O – H $_{bend}$	Alcohol, phenol	1260 - 1410
N – H $_{stretch}$	Amines	3300 - 3500
C = C $_{stretch}$	Alkenes	1620 - 1680
C = O $_{stretch}$	Aldehydes	1720 - 1740
C = C $_{stretch}$	Alkynes	2100 - 2140
C = $N_{stretch}$	Nitriles	2000 - 2500
C = $O_{stretch}$	Ketones	1705 - 1725

The intensities of IR spectra provides quantitative information while the absorption positions reveal qualitative characteristics about the nature of chemical bonds, their structure and their chemical environment Though quantitation in IR is not as straight forward as UV/visible owing to the multiplicity of spectral bands in IR, however, the use of high resolution grating IR instruments increases the scope and reliability of quantitative IR analysis.

3.5 IR Spectroscopy Experimental Procedures

The infrared spectrum of a sample is recorded by passing a beam of infrared light through the sample. When the frequency of the IR is the same as the vibrational frequency of a bond, absorption occurs. The energy absorbed appears as absorption peaks at the wavelength it corresponds to on the IR spectrum. A basic IR spectrum is essentially a graph of infrared light absorbance (or transmittance) on the vertical axis vs. frequency or wavelength on the horizontal axis. Well resolved and sharp peak/peaks at wavelength/wavelengths it corresponds to, is/are matched with the wavelength range on the group frequency table to identify the functional group/groups present.

Analysis of a sample by IR spectroscopy involves:

Sample preparation

Gaseous samples require a sample cell with a long **path length**to compensate for the diluteness. The **path length** of the sample cell depends on the concentration of the compound of interest. A simple glass tube with length of 5 to 10 cm equipped with infrared-transparent windows at the both ends of the tube can be used for concentrations down to several hundred ppm. Sample gas concentrations well below ppm can be measured with a White's cell in which the infrared light is guided with mirrors to travel through the gas. White's cells are available with optical **pathlength** starting from 0.5 m up to hundred meters.

Liquid samples can be sandwiched between two plates of a salt (commonly sodium chloride, or common salt, although a number of other salts such as potassium bromide or calcium fluoride are also used).The plates are transparent (do not absorb in the IR region) to the infrared light and do not introduce any lines onto the spectra.

Solid samples can be prepared in a variety of ways. One common method is to crush the sample with an oily mulling agent (usually Nujol) in a marble or agate mortar, with a pestle. A thin film of the mull is smeared onto salt plates and measured. The second method is to grind a quantity of the sample with a specially purified salt (usually potassium bromide) finely (to remove scattering effects from large crystals). This powder mixture is then pressed in a mechanical press to form a translucent pellet through which the beam of the spectrometer can pass. A third technique is the "cast film" technique, which is used mainly for polymeric materials. The sample is first dissolved in a suitable, **non-hygroscopic** solvent. A drop of this solution is deposited on surface of KBr or NaCl cell. The solution is then evaporated to dryness and the film formed on the cell is **analyzed** directly.

Simple spectra are obtained from samples with few IR active bonds and high levels of purity.
More complex molecular structures lead to more absorption bands and more complex spectra.

Comparing to a reference

To take the infrared spectrum of a sample, it is necessary to measure both the sample and a "reference" (or "control"). This is because each measurement is affected by not only the lightabsorption properties of the sample, but also the properties of the instrument (for example, what light source is used, what infrared detector is used, etc.). The reference measurement makes it possible to eliminate the instrument influence. Mathematically, the sample transmission spectrum is divided by the reference transmission spectrum.

The appropriate "reference" depends on the measurement and its goal. The simplest reference measurement is to simply remove the sample (replacing it by air). However, sometimes a different reference is more useful. For example, if the sample is a dilute solute dissolved in water in a beaker, then a good reference measurement might be to measure pure water in the same beaker. Then the reference measurement would cancel out not only all the instrumental properties (like what light source is used), but also the light-absorbing and light-reflecting properties of the water and beaker, and the final result would just show the properties of the solute (at least approximately).

A common way to compare to a reference is sequentially: first measure the reference, then replace the reference by the sample and measure the sample.

Infrared Spectroscopy is a spectroscopic technique in which a compound irradiated with infrared radiation, absorption of which causes covalent bonds to change from a lower vibration state to a higher one. Infrared spectroscopy is particularly valuable for determining the kinds of functional groups present in a molecule. Infrared spectroscopy is useful to organic chemists for the determination of molecular structure in an unknown compound

but also for many other applications. For example, forensic scientists use infrared spectroscopy to identify illegal substances and toxins in a substance etc.

Infrared Spectra range infrared region from 12500 to 50cm^{-1} which is divided into three infrared region of 12500 to 4000cm^{-1} called the near infrared; the region of 4000 to 400 cm^{-1} called the mid infrared and the region of 400 to 50 cm^{-1} called the far infrared. However, the most useful infrared region of concern is the mid infrared region of 4000 to 400cm^{-1} that is usually explored commercially in infrared instruments.

Theory of Infrared Spectroscopy

1. Origin of Molecular Spectra:

The energy if a molecule can be resolved into:

(i) The energy associated with a rotation of the molecule as a whole (rotational energy)

(ii) The energy associated with a vibrations of the constituents atoms (vibrational energy)

(iii) The energy associated with a motion of the electrons in a molecule (transitional energy)

If a molecule is placed in an electromagnetic field, a transfer of energy from the electromagnetic field to the molecule occurs when, $\Delta E = E'' - E' = hv$ where E' is lower energy state; E'' is higher energy state; h is Planck's constant ($6.624 \times 10^{-27}\ erg.sec.$) and v is the difference in energy between two quantized state.

Radiation in this infrared region is referred to its frequency in wavenumbers $\bar{v}$, the frequency of electromagnetic radiation expressed as the number of waves per centimetre, with units cm^{-1} or the frequency v in hertz divided by c, speed of light. $\bar{v} = \frac{1}{\lambda} = \frac{v}{c}$

2. Vibrational Spectra: Organic molecule is flexible and not rigid. Consider a heterogeneous diatomic molecule AB; the constituent atoms in this molecule vibrate with frequencies that depends on the masses of the atoms, the restoring force brought into play when the molecules are disturbed from its equilibrium configuration. The frequency of vibration v is given by:

$$v = \frac{1}{2\pi}\sqrt{\frac{K}{\mu}} or \qquad \bar{v}(cm^{-1}), = \frac{1}{2\pi C}\sqrt{\frac{K}{\mu}} where\ \mu = \frac{m_A \times m_B}{m_A + m_B}$$

$$\therefore,\ \bar{v}(cm^{-1}) = \frac{1}{2\pi C}\sqrt{\left(\frac{K\,(m_A+m_B)}{m_A \times m_B}\right)}. \qquad \bar{v}(cm^{-1}) = 4.12\sqrt{\left(\frac{K\,(m_A+m_B)}{m_A \times m_B}\right)}.$$

$$K = 5 \times 10^5 dynes.cm^{-1}\ for\ single\ bond\ (A-B);\quad 10 \times 10^5 dynes.cm^{-1}\ for\ double\ bond\ (A=B);$$

$$15 \times 10^5 dynes.cm^{-1}\ for\ triple\ bond\ (A \equiv B)$$

Where $\bar{v}(cm^{-1})$ is wavenumber; μ is reduced mass of a molecule AB and K is force constant.

For example, we can calculate the frequency of vibration of a single bond between ^{12}C and ^{1}H as follows:

$$Reduced\ mass\ \mu = \frac{12 \times 1}{12 + 1} = \frac{0.923g}{atom}\ and\ \bar{v} = 4.12\sqrt{\frac{5 \times 10^5}{0.923}} = 3032cm^{-1}$$

INSTRUMENTATION

Infrared instruments uses a mono-chromator for wavelength selection are constructed using double-beam optics similar to that shown in the Figure below. Double beam optics are preferred over single-beam optical infrared radiation. In addition, it is easier to correct for the absorption of infrared radiation by atmospheric CO_2 and H_2O vapour when using double-beam optics. Resolutions of 1–3 cm^{-1} are typical formost instruments.

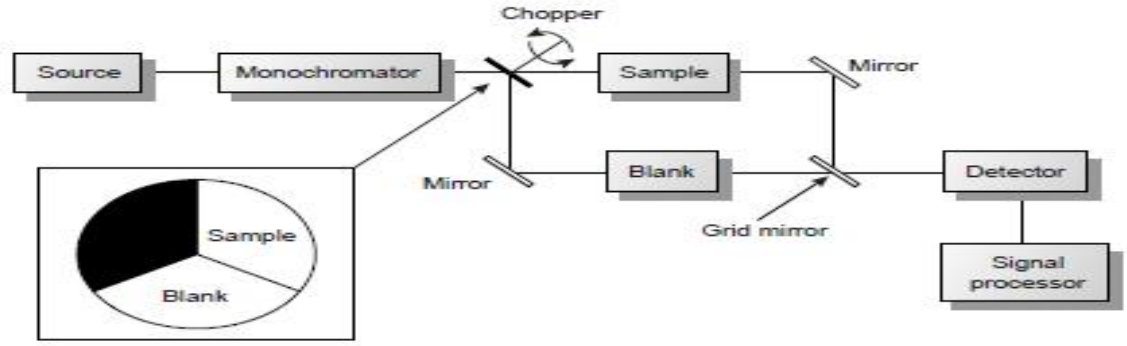


Fig 8: Infrared instruments with a monochromator with double beam optics

There is also the Fourier transform, infrared spectrometer, or FT–IR, the monochromator is replaced with an interferometer (see Figure 9). Because an FT–IR includes only a single optical path, it is necessary to collect a separate spectrum to compensate for the absorbance of atmospheric CO_2 and H_2O vapour. This is done by collecting a background spectrum without the sample and storing the result in the instrument's computer memory. The background spectrum is removed from the sample's spectrum by rationing the two signals. In comparison to other IR instruments, an FT–IR provides for rapid data acquisition, allowing an enhancement in signal-to noise ratio through signal averaging.

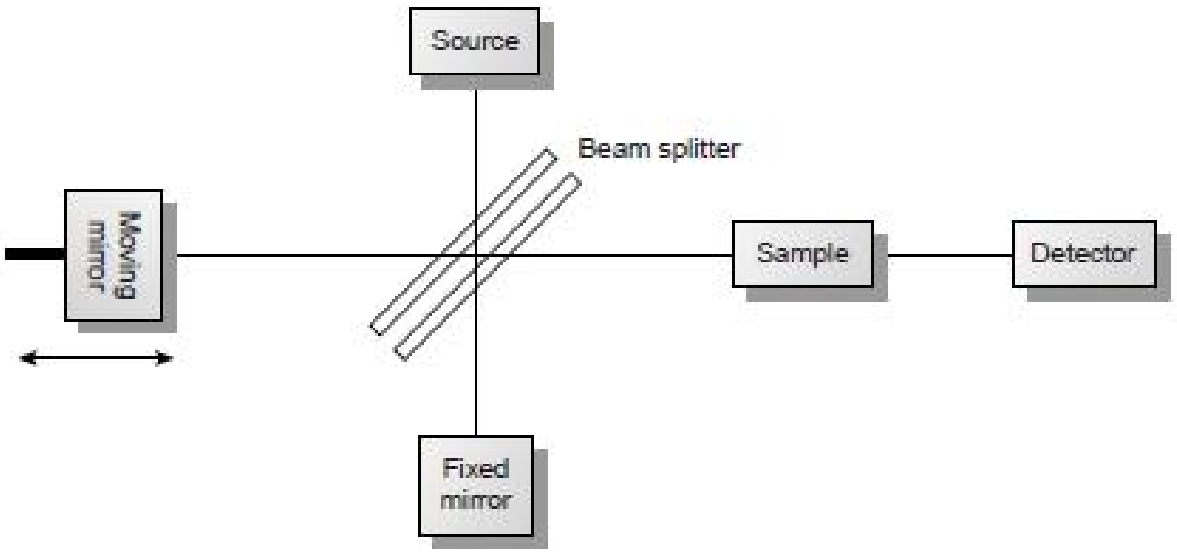


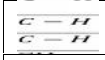
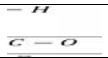
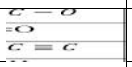
Fig 9: Fourier transform, infrared spectrometer, FT–IR, with interferometer.

Infrared spectroscopy is routinely used for the analysis of samples in the gas, liquid, and solid states. Sample cells are made from materials, such as NaCl and KBr that are transparent to infrared radiation. Gases are analysed using a cell with a path-length of approximately 10cm. Longer path-lengths are obtained by using mirrors to pass the beam of radiation through the sample several times. Liquid samples are analysed in one of two ways. For non-volatile liquids, a suitable sample can be prepared by placing a drop of the liquid between two NaCl plates, forming a thin film that typically is less than 0.01 mm thick. Volatile liquids must be placed in a sealed cell to prevent their evaporation. Solid samples also can be analysed by means of reflectance. Transparent solid samples can be analysed directly by placing them in the IR beam. Most solid samples, however, are opaque and must be dispersed in a more transparent medium before recording a traditional transmission spectrum. If a suitable solvent is available, then the solid can be analyzed by preparing a solution and analysing as described earlier. When a suitable solvent is not available, solid samples may be analysed by preparing a mull of the finely powdered sample with a suitable oil. Alternatively, the powdered sample can be mixed with KBr and pressed into an optically transparent pellet.

CORRELATION TABLES OF INFRARED SPECTRA

Table 7: The absorption pattern of functional group are given below:

Bond	Wave Number ($\frac{\text{unit of } \nu}{cm^{-1}}$)	Mode of vibration	Intensity

	2700 – 3300	Stretching	Weak to medium
	1300 – 1500	Bending	Medium to small
CH_2	1450–1475	Bending	Medium
CH_3	1375 and 1450	Bending	Weak to medium
	3200–3650	Stretching	Weak to strong (strongest when H-bonded)
	1000–1250	Stretching	Strong
C=O	1630–1820	Stretching	Strong
	1600–1680	Stretching	Weak to medium
N–H	3100–3550	Stretching	Medium

APPLICATION OF INFRARED SPECTROMETRY

1. It is applied in quantitative analysis of sample in environmental chemistry, clinical chemistry; industrial chemistry and forensic chemistry are numerous.
2. It is applied in qualitative assessment to access the presence of functional group in a compound.

3.6 Measuring IR absorption bands

As with electronic **(UV-Visible**) spectra, the use of infrared spectra for quantitative determinations depends upon measuring the intensity of either the transmission or absorption of the infrared radiation at a specific wavelength, usually the maximum of a strong, sharp, narrow, **wellresolved** absorption band. Most organic compounds will possess several peaks in their spectra which satisfy these criteria and which can be used so long as there is no substantial overlap with the absorption peaks from other substances in the sample matrix. The background to any spectrum does not normally correspond to a 100% transmittance at all wavelengths, so measurements are best made by what is known as the baseline method.

This involves selecting an absorption peak to which a tangential line can be drawn, as shown in Figure. This is then used to establish a value for I_0 by measuring vertically from the tangent through the peak to the wavenumber scale. Similarly, a value for I is obtained by measuring the corresponding distance from the absorption peak maximum. So, for any peak, the absorbance

will not be the value corresponding to the height of the absorption, measured from the horizontal axis of the chart paper; instead it will be the value of A_{calc} obtained from the equation

$$A_{calc} = \log_{10} \frac{1}{T} = \frac{I_0}{I}$$

Where I_0 and I are values measured using the tangential baseline.

This procedure has the great advantage that some potential sources of error are eliminated. The measurements do not depend upon accurate wavelength positions as they are made with respect to the spectrum itself, and any cell errors are avoided by using the same cell of fixed path length. Measuring A_{calc} eliminates any variation in the source intensity, the instrument optics or the sensitivity.

3.7 Beer's law: Quantitative IR spectra

Infrared spectra are recorded using either or both absorbance (A) and percentage transmittance

(T)**, just** as they are in visible ultraviolet electronic spectra, and Beer's law,

A = $cl = \log \frac{1}{T} = \log \frac{I_0}{I}$ applies equally to infrared spectra as it does to electronic spectra.

Use of a calibration graph

A calibration curve overcomes any problems created due to non-linear absorbance or concentration features, and it means that any unknown concentration run under the same conditions as the series of standards can be determined from the graph. The procedure requires that all standards and samples are measured in the same cell of fixed path length, although the dimensions of the cells and the molar absorptivity for the chosen absorption band are not needed; they are constant for all the measurements.

EXPERIMENT 1 – The Identification of Functional Groups of an Unknown Substance

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Purpose: This experiment involves the instrumental technique to obtain the spectrum as well as the analysis of the spectral data to determine the functional groups present in the unknown sample.

Discussion:

Infrared spectrometers, similar in principle to the UV-Visible spectrometer, permit chemists to obtain absorption spectra of compounds that are a unique reflection of their molecular structure.

A critical part of the infrared experiment is getting the infrared radiation to interact with the sample without losing a significant part of the infrared radiation from non-sample interactions (mirrors which absorb light rather than reflect, scratches on any optical surface which reflect light in the wrong direction, sample surfaces which reflect light, etc.). Classically, liquids are analyzed either neat (suspended between two sodium chloride plates (sodium chloride does not absorb infrared radiation in the spectral range of concern)) or in solution in a solvent such as carbon tetrachloride which does not absorb too much infrared radiation in the spectral range of concern. Solids, with problems associated with crystal surfaces reflecting away most of the radiation, are analyzed either in solution (at least the few solids which dissolved in suitable IR solvents) or more commonly as a mull, a KBr pellet, or a melt (if the melting point was low enough). Such sampling techniques are necessary to provide adequate sample for the classical dispersive optical-null double-beam prism and (later) grating spectrometers. However, the ready availability of low cost powerful laboratory computing has allowed the routine utilization of more sensitive no dispersive Fourier Transform Infrared Spectrometers (FT-IR). FT-IR allows for the collection of all the spectral data in seconds compared to 3-10 minutes for the classical grating **spectromete**r. However, FT-IR requires powerful computing to mathematically analyze the collected data. Computers also allow for the collection of many spectra in a short time and the averaging of the spectra to eliminate most random noise.

Experimental Procedure:

NOTE: Suggestions (detailed instructions for the operation of our spectrometer will be given by your instructor in lab).

Normally you will not have to run a "background". (A background measures the amount of energy that actually gets to the detector without any sample in the sampling device. The energy reaching the detector is not constant at all wavelengths due to: absorption by spectrometer mirrors and windows; scattering by flaws, scratches, and dirt; absorption by condensed compounds and the **atmospheres**; variable output by the infrared source; etc. The computer in the spectrometer subtracts the background from your sample data to produce the spectrum.) However, if you are the first person to use the spectrometer for the day, or if the spectrometer has been run for quite **awhile**, or if your spectrum is problematic, you should run a background.

Obtaining a spectrum of a liquid using salt plates.

a. Obtain the salt plates, holder, and O-rings from the desiccator.
b. Clean the salt plates by wiping with a Kim-wipe moistened with absolute alcohol. Be extremely careful not to touch the surface of the salt plates with your fingers. (Your fingers are wet enough to dissolve the salt!) c. Place an O-ring on the salt plate holder.
d. Place a clean salt plate on the O-ring. Again, do not touch the flat surface of the salt plate!!
e. Place a drop or two of a dry liquid sample on the salt plate.
f. Place the other clean salt plate on top of the sample. Be sure there are no air bubbles in the sample.
g. Place the other O-ring on the upper salt plate.
h. Place the other metal holder on the O-ring.
i. Lightly tighten the four knurled nuts. If you tighten too hard you may crack the salt plates or squeeze all of your sample out from between the salt plates.

j. Place the holder in the spectrometer. Obtain your spectrum. Print a hard copy and save your spectrum on the network.
k. Disassemble the sample holder and clean the salt plates again by wiping with a Kimwipe moistened with absolute alcohol.
l. Return the clean salt plates in their container to the desiccator. Also, return the salt plate holder and O-rings to the **desiccator**.

From the IR spectrum, determine the functional group of your unknown.

EXPERIMENT 2 – Determination of Concentration of Cyclohexane Using IR Spectroscopy

Purpose: To determine the concentration of cyclohexane using IR spectroscopy

Experimental Procedure:

Run infrared spectra for pure cyclohexane and pure **nitro methane**. From the spectra select a cyclohexane absorption which is not affected by, or overlapping with, those of the **nitromethane**. Prepare a series of solutions of known concentrations of cyclohexane in **nitromethane** covering the range from 0% to 20%(w/v). Using a cell of fixed path length 0.1 mm, measure the absorbance for the solutions at the chosen peak absorption using the baseline method and plot the calibration graph. Use this graph to determine the unknown concentration of cyclohexane in the sample.

In-text Question

State the simple analysis Infrared Spectroscopy is routinely used for

Answer

It is used in the analysis of samples in the gas, liquid, and solid states.

4.0Self – Assessment Exercises

1. State and explain the portion of the infrared region most useful for analysis of organic compound.

2. Sate true or false

a. Triple bonds have higher stretching frequencies than corresponding double bonds.

b. The intensities of IR spectra provides quantitative information while the absorption positions reveal qualitative characteristics about the nature of chemical bonds.

C .Fourier Transform Infrared Spectrometers (FT-IR) does not allows for the collection of all the spectral data in seconds compared to 3-10 minutes for the classical grating spectrometer**.**

d. Absorption spectra of compounds are a unique reflection of their molecular structure.

3. Explain the criteria for a compound to absorb IR radiation

Answers

1. It is the portion of infrared region that is having a wavelength range from 2.500 to 16, 000 nm, with a corresponding frequency range from $1.9*10^{13}$ to $1.2*10^{14}$ Hz

2a. True (b) True (c) False (d) True

3. The criteria for a compound to absorb IR radiation include the correct frequency/wavelength of radiation which possess the right amount of energy that matches the vibrational transition energy of the atoms or group of atoms involved, and change in dipole moment of the atoms or group of atoms involved.

5.0 CONCLUSION

Infrared spectroscopy is a useful analytical technique used in the identification of functional groups in a molecule. It is also useful for quantitative analysis of complex mixtures of similar compounds because some absorption peaks for each compound will occur at a definite and selective wavelength, with intensities proportional to the concentration of absorbing species. Infrared spectroscopy exploits the fact that molecules absorb specific frequencies that are **characteristic** of their structure. These absorptions are resonant frequencies i.e the frequency of the absorbed radiation matches or is equal to the transition energy of the bonds or group that vibrates.

6.0 SUMMARY

IR spectroscopy is concerned with the study of absorption of infrared radiation, which causes vibrational transition in the molecule. Hence, IR spectroscopy is also known as vibrational spectroscopy. IR spectra are mainly used in structure elucidation to determine the functional groups. The IR region is subdivided into three; the near, middle and far infrared regions. Most of the analytical applications are confined to the middle IR region because absorption of organic molecules are high in this region. When the applied energy in the form of infrared radiation is equal to the vibrational transition energy of the atoms in the molecule, absorption of IR radiation takes place and a peak is observed. Different functional groups absorb characteristic frequencies of IR radiation. Hence gives the characteristic peak value. Therefore, IR spectrum of a chemical substance is a finger print of a molecule for its identification. The criteria for a compound to absorb IR radiation are; Correct frequency/wavelength of radiation that has the right amount of energy that matches the vibrational transition energy of the atoms or group of atoms involved, and change in dipole moment of the atoms or group of atoms involved.

CLASS ACTIVITY (THE TUTOR TO DIRECT)

1. Explain briefly infrared spectroscopy

2. What are group frequencies?

3. Explain how you can obtain the functional group present in a molecule

4. State the uses of infrared spectroscopy.

5. Explain the advantage of FT-IR over infrared spectroscopy

7.0 REFERENCES/ FURTHER READING

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9. Types of Vibrations
https://www.youtube.com/watch?v=0liFNXs03mY
10. Group frequencies
https://www.youtube.com/watch?v=Ou3cKwz1y0k
11. IR Spectroscopy Experimental Procedures
https://www.youtube.com/watch?v=oHggbow0RQk
12. Measuring IR absorption bands
https://www.youtube.com/watch?v=2VHrN8_rqL8
13. Beer's law: Quantitative IR spectra
https://www.youtube.com/watch?v=zuUvQN8KXOk

UNIT 4 – ATOMIC ABSORPTION SPECTROSCOPY

3.1 Principle of Atomic Absorption Spectroscopy
https://www.youtube.com/watch?v=5fvWhCk7x6U

3.2.1 Preparation of calibration curve

https://www.youtube.com/watch?v=Yzan11nP6Ls
3.3 Uses of Atomic Absorption Spectroscopy
https://www.youtube.com/watch?v=SGFZxFIX9gk

UNIT 4 – ATOMIC ABSORPTION SPECTROSCOPY

1.0 INTRODUCTION

2.0 Intended Learning Outcomes (ILOs)

3.0 MAIN CONTENT

3.1 Principle of Atomic Absorption Spectroscopy

In-text Question
3.2 Experimental Preliminaries

3.2.1 Preparation of calibration curve

3.2.2 Preparation of sample solutions

3.2.3 Preparation of standard solutions

3.3 Uses of Atomic Absorption Spectroscopy

3.4 Experimental

In-text Question

4.0 SELF – ASSESSMENT EXERCISES

5.0 CONCLUSION

6.0 SUMMARY

7.0 REFERENCES/ FURTHER READING

UNIT 4 – ATOMIC ABSORPTION SPECTROSCOPY

3.1 Principle of Atomic Absorption Spectroscopy
https://www.youtube.com/watch?v=5fvWhCk7x6U

3.2.1 Preparation of calibration curve
https://www.youtube.com/watch?v=Yzan11nP6Ls

3.3 Uses of Atomic Absorption Spectroscopy
https://www.youtube.com/watch?v=SGFZxFIX9gk

1.0 INTRODUCTION

The first commercial atomic absorption (AA) spectrometer was introduced in 1959, and its use after that grew extensively. Atomic absorption contains the same basic components as an instrument designed for molecular absorption measurements. Most measurements in AAS are made with instruments equipped with an ultraviolet/visible grating monochromator.

Atomic Absorption Spectroscopy (AAS) is a technique in which the absorption of light by free gaseous atoms in flame or furnace is used to measure the concentration of atoms. Since the atoms are single, they do not vibrate or rotate, only electronic transitions occur.

Consider a solution containing a metallic salt, e. g sodium chloride, if it is aspirated into a flame for example, acetylene burning in air, a vapour which contains atoms of the metal may be formed. Some of these gaseous metal atoms may be raised to an energy level which is sufficiently high to permit the emission of radiation characteristics of the metal e.g. the characteristics yellow colour imparted to flames by compounds of sodium. However, a much larger number of the gaseous metal atoms will normally remain in an unexcited state or, in other words in the ground state. These ground state atoms are capable of absorbing radiant energy of their own specific resonance wavelength, i.e., the wavelength of the radiation that the atoms would emit if excited from the ground state. Hence, if light of the resonance wavelength is passed through a flame containing the atoms in question, then part of the light will be absorbed, and the extent of absorption will be proportional to the number of ground state atoms present in the flame.

2.0 INTENDED LEARNING OUTCOMES (ILOs)

After studying this unit, you should be able to:

- Explain Atomic Absorption Spectroscopy (AAS)
- Explain the principle of AAS
- Describe how the concentration of an element can be determined by AAS
- Carry out practical determination of the concentration of some elements.

3.0 MAIN CONTENT

3.1 Principle of Atomic Absorption Spectroscopy

The sample solution is aspirated into a flame and the sample element is converted to atomic vapour. Most of the atoms in a flame remain in the ground state and it is these ground state atoms that are measured in atomic absorption. These ground state atoms can absorb radiation of a particular wavelength that is produced by a special source made from that element (i.e. the element been **analyzed)**. The wavelength of radiation given off by the source is the same that this sample element would give off if it were to emit radiation, since it is the same element with the source. The absorption follows Beer's law, that is, the absorbance is directly proportional to the path length in the flame and to the concentration of atomic vapour in the flame.

In-text Question

State the main aim of this study unit

Answer

It is explain the function and the principles of Atomic Absorption Spectroscopy (AAS)

3.2 Experimental Preliminaries

The following procedures are followed when carrying out determinations of the concentration of elements by AAS; preparation of calibration curve, preparation of sample solutions, preparation of standards.

3.2.1 Preparation of calibration curve

A calibration curve for use in atomic absorption measurements is plotted by aspirating into the flame samples of solutions containing known concentrations of the element to be determined, measuring the absorption of each solution, and then constructing a graph in which the measured absorption is plotted against the concentration of the solutions. If we are dealing with a test solution which contains a single component, then the standard solutions are prepared by dissolving a weighed quantity of a salt of the element to be determined in a known volume of distilled **(deionized)** water in a graduated flask. But if other substances are present in the test solution, they should also be incorporated in the standard solutions and at a similar concentration to whatever exists in the test solution.

At least four standard solutions should be used covering the optimum absorbance range 0.1- 0.4; and if the calibration curve proves to be non- linear (this often happens at high absorbance values), then measurements with additional standard solutions should be carried out. In common with all absorbance measurements, the readings must be taken after the instrument zero has been adjusted against a blank, which may be distilled water or a solution of similar composition to the test solution but minus the component to be determined. It is usual to examine the standard solutions in order of increasing concentration, and after making the measurements with one solution; distilled water is aspirated into the flame to remove all traces of solution before proceeding to the next solution. At least two, and preferably three, separate absorption readings

should be made with each solution, and an average value taken. If necessary, the test solution must be suitably diluted using a pipette and a graduated flask, so it too gives absorbance readings in the range 0.1-0.4.

Using the calibration curve it is a simple matter to interpolate from the measured absorbance of the test solution the concentration of the relevant element in the solution. All modern instruments include a microcomputer which stores the calibration curve and allows a direct read-out of concentration.

3.2.2 Preparation of sample solutions

For application of flame spectroscopic methods the sample must be prepared in the form of a suitable solution unless it is already presented in this form.

Aqueous solutions may sometimes be **analyzed** directly without any pretreatment, but it is a matter of chance that the given solution should contain the correct amount of material to give a satisfactory absorbance reading. If the existing concentration of the element to be determined is too high, then the solution must be diluted quantitatively before commencing the absorption measurements. Conversely, if the concentration of the metal in the test solution is to low, then a concentration procedure must be carried out which entails using separation methods. The separation methods most commonly used with flame spectrophotometric methods are solvent extraction and ion exchange.

Solid samples will need some form of dissolution procedure prior to measurement. Many dissolution procedures are available; here are some of them.

1. Wet ashing: The usual method is to treat the solid sample by acid digestion, producing a clear solution with no loss of the element to be determined. Hydrochloric acid, nitric acid or aqua regia (3:1 hydrochloric **acid:nitric acid**) will dissolve many inorganic substances. Hydrofluoric acid must be used to decompose silicates, and perchloric acid is often used to break up organic complexes. The instruction manual normally **supplied** with the instrument will give guidance on acceptable acid concentrations. Biological samples usually only require simple dilution prior to measurement, or they can be measured directly using **furnace** atomic absorption.

2. Fusions: A weighed sample is mixed with a flux in a metal or graphite crucible. The sample and flux mixture is heated over a flame, or in a furnace, and the resulting fused material is leached with either water or an appropriate acid or alkali. The most widely used flux is sodium peroxide. Fusions with this substance are normally carried out in a zirconium crucible and cooled melt is then leached with dilute mineral acid. Lithium metaborate is a good flux for silicate rocks

3. Dry ashing: The sample is weighed into a crucible, heated in a muffle furnace and then the residue is dissolved in a suitable acid. This technique is often used to remove organic substances from the analyte material. Care must be taken to ensure that volatile elements such as mercury, arsenic and even lead are not removed in the ashing process.

4. Microwave dissolution:

Microwave ovens have been used for sample dissolution. The sample is sealed in a specially designed microwave digestion vessel with a mixture of the appropriate acids. The high frequency microwave temperature, typically 100-250^{o}C and the increased pressure assist in the considerable reduction in the time taken for sample dissolution. The method has been used for the dissolution of samples of coal, fly ash, biological and geological materials.

3.2.3 Preparation of standard solutions

In flame spectrophotometric measurements we are concerned with solutions having very small concentrations of the element to be determined. It follows that the standard sol0utions which will be required for the analyses must also contain very small concentrations of the relevant elements, and it is rarely practicable to prepare the standard solutions by directly weighing out the required reference substance. The usual practice, therefore, is to prepare stock solutions which contain about 1000ugml^{-1} of the required element, and then the working standard solutions are prepared by suitable dilution of the stock solutions. Solutions which contain less than 10ugml^{-1} are often found to deteriorate on standing, owing to adsorption of the solute on to the walls of glass vessels. Consequently, standard solutions in which the solute concentration is of this order should not be stored for more than 1-2 days. The stock solutions are ideally prepared from the pure metal or from the pure metal oxide by dissolution in a suitable acid solution; the solids used must be of the highest purity.

THEORY

Atomic absorption spectroscopy (AAS) is an analytical technique for the quantitative determination of chemical elements using the absorption of optical radiation (light) by free atoms in the gaseous state. Atomic absorption spectroscopy is based on absorption of light by free metallic ions. Atomic absorption is so sensitive that it can measure down to parts per billion of a gram (μg.dm^{-3}) in a chemical sample. The technique makes use of the wavelengths of light specifically absorbed by chemical elements. They correspond to the energies needed to promote electrons from one energy level to another, higher, energy level.

Guystav Kirchhoff and Robert Bunsen first used atomic absorption spectroscopy in 1859 and 1860 as a means for identify atoms in flames and hot gases. Modern atomic absorption spectroscopy has its beginnings in 1955 as a result of the independent work of Sir A. C. Walsh and C. T. J. Alkemade. Commercial instruments were in place by the early 1960s, and the importance of atomic absorption as an analytical technique was soon evident.

Plate 1: AAS Spectrophotometer with a Computer System

WORKING PRINCIPLE

The AAS consists of Light Source, Atomizer, Monochromator, Detector, Signal Processor (computer data system)

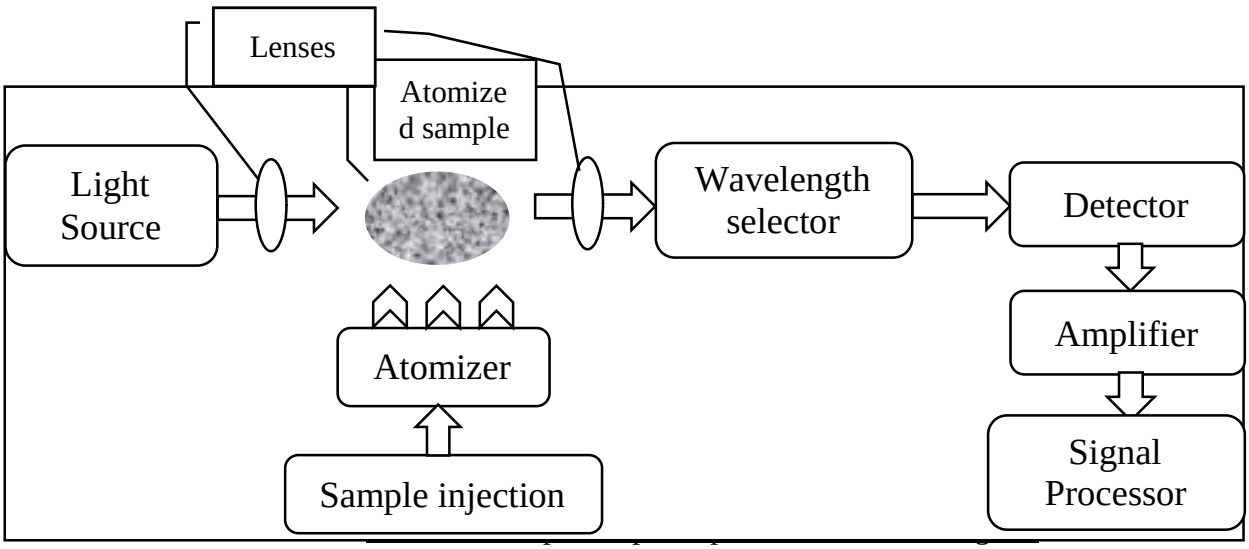


Fig 10: The process of atomic absorption spectroscopy (AAS) involves:

1. Atomization of the sample
2. Absorption of radiation from a light source by the free atoms

3. Wavelength Selection (Monochromator)
4. Detector
5. Output Signal Processing

- In order to analyze a sample for its atomic constituents, it has to be atomized. The atomizers most commonly used nowadays are flames (nebulizer) or electro thermal (graphite tube) atomizers. The atoms are irradiated by optical radiation from a radiation source which could be an element-specific line radiation source or a continuum radiation source (Hallow cathode lamb, Deuterium lamb, Xenon lamb etc.). Upon the absorption of ultraviolet or visible light, the free atoms undergo electronic transitions from the ground state to excited electronic states.
- The radiation then passes through a monochromator (wavelength selector) in order to separate the element-specific radiation from any other radiation emitted by the radiation source (This stage provides both sensitivity and selectivity since other elements in the sample will not generally absorb the chosen wavelength and thus, will not interfere with the measurement.).

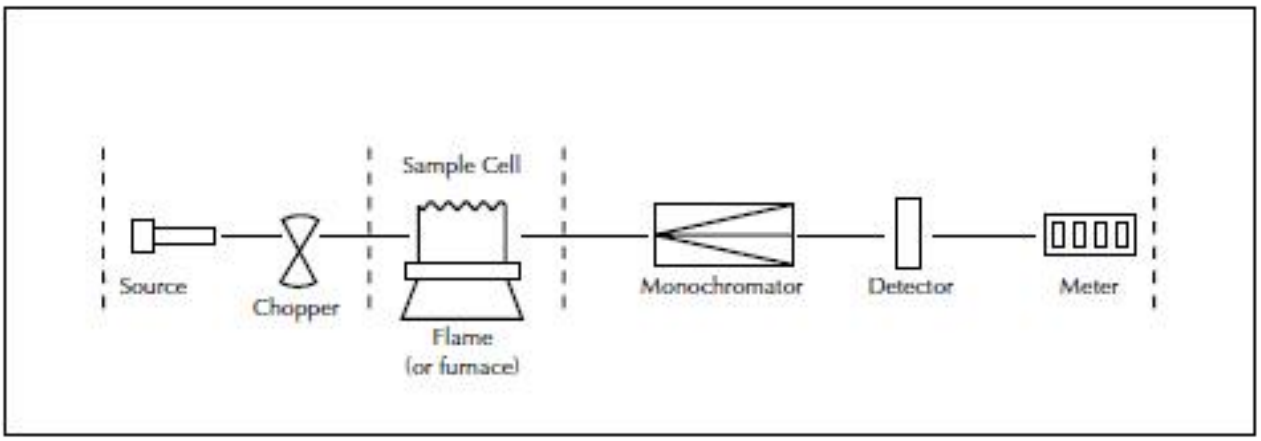


Fig 11: Single Beam AAS

Modern spectrophotometer incorporates a beam splitter so one part of the beam passes through the sample cell and the other is the reference. The intensity of the light source may not stay constant during an analysis. If only a single beam is used to pass through the atom cell, a blank reading containing no analyte (substance to be analyzed) would have to be taken first, setting the absorbance at zero. If the intensity of the source changes by the time the sample is put in place, the measurement will be inaccurate. In the double beam instrument there is a constant monitoring between the reference beam and the light source. To ensure that the spectrum does not suffer from loss of

sensitivity, the beam splitter is designed as high as possible of the energy of the lamp beam passes through the sample.

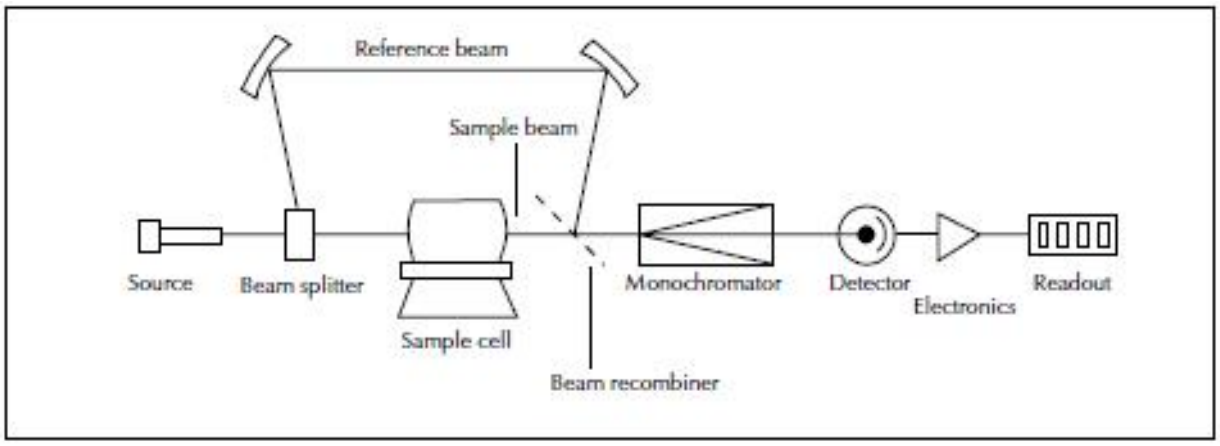


Fig 12: Double Beam AAS

- The detector is typically a photomultiplier tube which measures the intensity of the beam of light which is recorded as electrical signal; then transmitted to output signal processor (computer data system).

SAMPLING PROCEDURE AND ANALYSIS

A) Sample preparation: Depending on the analysis, total recoverable metals, dissolved metals, suspended metals, and total metals could be obtained from a certain environmental matrix. Appropriate acid digestion is employed in these methods. Hydrochloric acid digestion is not suitable for samples, which will be analyzed by graphite furnace atomic absorption spectroscopy because it can cause interferences during furnace atomization, (Nitric acid is suitable).

B) Calibration and standard curves: As with other analytical techniques, atomic absorption spectroscopy requires careful calibration. QA/QC demands calibration through several steps including interference check sample, calibration verification, calibration standards, blank control, and linear dynamic range.

If the sample concentration is too high to permit accurate analysis in linearity response range, there are three alternatives that may help bring the absorbance into the optimum working range:

1) Sample dilution
2) Using an alternative wavelength having a lower absorptivity
3) Reducing the path length by rotating the burner hand.

C) Interferences:

Since the concentration of the analyte element is considered to be proportional to the ground state atom population in the flame, any factor that affects the ground state population of the analyte element can be classified as

interference. Factors that may affect the ability of the instrument to read this parameter can also be classified as interference. The following are the most common interferences:

i. Spectral interferences are due to radiation overlapping that of the light source. The interference radiation may be an emission line of another element or compound, or general background radiation from the flame, solvent, or analytical sample. This usually occurs when using organic solvents, but can also happen when determining sodium with magnesium present, iron with copper or iron with nickel.

ii. Formation of complex compounds that do not dissociate in the flame. The most common example is the formation of calcium and strontium phosphates.

iii. Ionization of the analyte reduces the signal. This commonly happens to barium, calcium, strontium, sodium and potassium.

iv. Matrix interferences due to differences between surface tension and viscosity of test solutions and standards.

APPLICATION OF ATOMIC ABSORPTION SPECTROSCOPY

Atomic absorption spectroscopy is ideally suited for the analysis of trace and ultra-trace samples. AAS can be used for the analysis of over 60 elements at concentrations at or below the level of µg/L. AAS is very fast in an ideal automated system and gives an accuracy level of 0.5 – 5%

1.5 USE OF ATOMIC ABSORPTION SPECTROSCOPY

AAS has many uses in different areas of chemistry:

- **Clinical analysis.** Analyzing metals in biological fluids such as blood and urine.
- **Environmental analysis.** Monitoring our environment – *e.g.* finding out the levels of various elements in rivers, seawater, drinking water, air, petrol and drinks such as wine, beer and fruit drinks.
- **Pharmaceuticals.** In some pharmaceutical manufacturing processes, minute quantities of a catalyst used in the process (usually a metal) are sometimes present in the final product. By using AAS the amount of catalyst present can be determined.
- **Industry.** Many raw materials are examined and AAS is widely used to check that the major elements are present and that toxic impurities are lower than specified – *e.g.* in concrete, where calcium is a major constituent, the lead level should be low because it is toxic.
- **Mining.** By using AAS the amount of metals such as gold in rocks can be determined to see whether it is worth mining the rocks to extract the gold.
- **Other Include:** Toxicology, Forensic, Archaeology research

ATOMIC EMISSION SPECTROSCOPY

THEORY

Atomic emission spectroscopy (AES) is a method of chemical analysis that uses the intensity of light emitted from (thermal excitation) via flame, plasma, arc, or spark at a particular wavelength to determine the quantity of an element in a sample. The wavelength of the atomic spectral line in the emission spectrum gives the identity of the element while the intensity of the emitted light is proportional to the number of atoms of the element.

Atomic emission spectroscopy has a long history:

- Qualitative applications based on the color of flames were used in the smelting of ores as early as 1550 and were fully developed around 1830 with the observation of atomic spectra generated by flame emission and spark emission.
- Quantitative applications based on the atomic emission from electric sparks were developed by Lockyer in the early 1870 and quantitative applications based on flame emission were pioneered by Lundegardh in 1930. Atomic emission based on emission from a plasma was introduced in 1964.

Plate 2: Inductively coupled plasma atomic emission spectrometer

There are various types of Adsorption Emission Spectrometer:

1. Inductively coupled plasma atomic emission spectroscopy (ICP-AES): uses an inductively coupled plasma to produce excited atoms and ions that emit electromagnetic radiation at wavelengths characteristic of a particular element.
2. Direct Current plasma (Spark and Arc) atomic emission spectroscopy (DCP-AES): is used for the analysis of metallic elements in solid samples. For non-conductive materials, the sample is ground with graphite powder to make it conductive during analysis. An electric arc or spark is passed through the sample,

heating it to a high temperature to excite the atoms within it. The excited analyte atoms emit light at characteristic wavelengths that can be dispersed with a monochromator and detected.

The most important is the inductively coupled plasma (ICP - AES).

WORKING PRINCIPLE

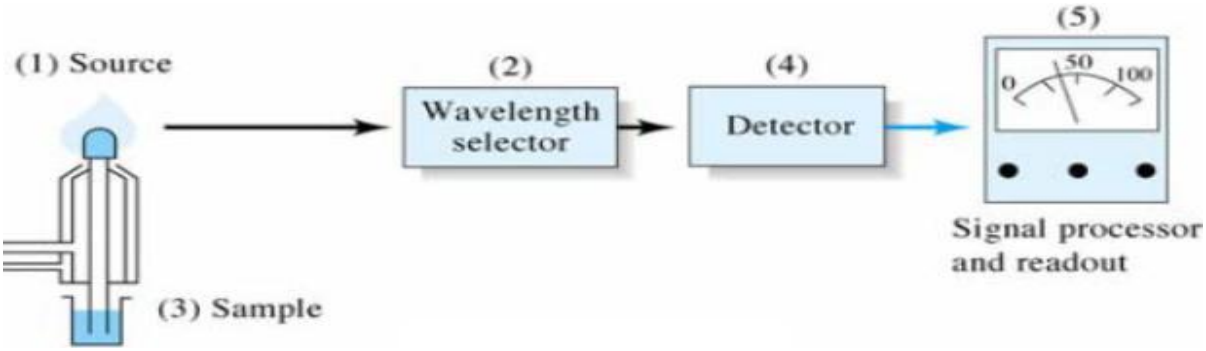


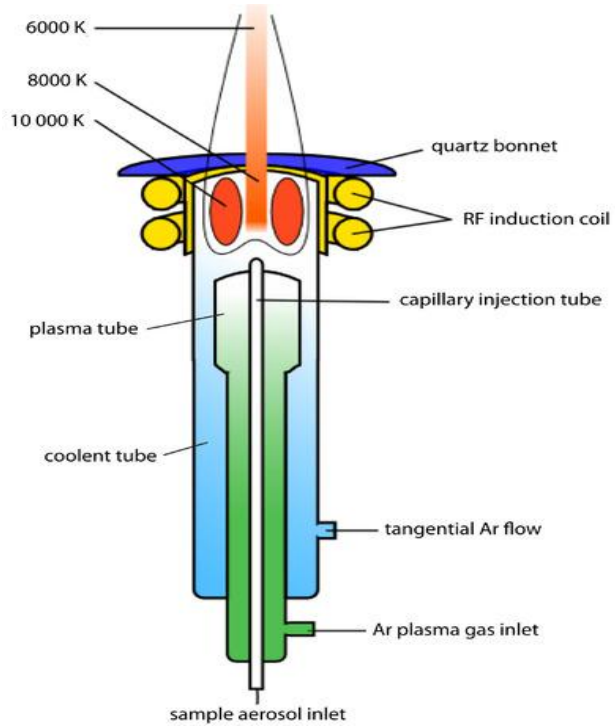
Fig 13: Schematic block diagram of aes

The process of atomic emission spectroscopy (AES) involves:

1. Thermal Excitation (atomizer) of the sample
2. Emission of radiation by the free atoms
3. Wavelength Selection (Monochromator)
4. Detector
5. Output Signal Processing

➢ A sample of a material (analyte) is brought into the flame as a gas, sprayed solution, or directly inserted into the flame or plasma atomizer (others includes: arc, spark, glow discharges, laser) by use of a small loop of wire, usually platinum. The heat from the flame evaporates the solvent and breaks intramolecular bonds to create free atoms. The thermal energy also excites the atoms into excited electronic states that subsequently emit light when they return to the ground electronic state. Each element emits light at a characteristic wavelength, which is dispersed by a grating or prism, detector to transmit electrical signal from emission of light and then transmitted to output signal processor (computer data system).

Plate 3: Inductively coupled plasma atomic emission source



A schematic diagram of the inductively coupled plasma source (ICP) is shown above. The ICP torch consists of three concentric quartz tubes, surrounded at the top by a radio-frequency induction coil. The sample is mixed with a stream of Argon using a nebulizer, and is carried to the plasma through the torch's central capillary tube. Plasma formation is initiated by a spark from a Tesla coil. An alternating radio-frequency current in the induction coils creates a fluctuating magnetic field that induces the argon ions and the electrons to move in a circular path. The resulting collisions with the abundant unionized gas give rise to resistive heating, providing temperatures as high as 10 000 K at the base of the plasma, and between 6000 and 8000 K at a height of 15–20 mm above the coil, where emission is usually measured. At these high temperatures the outer quartz tube must be thermally isolated from the plasma.

SAMPLING PROCEDURE AND ANALYSIS

A. Preparing the Sample: Flame and plasma sources are best suited for samples in solution and liquid form. Although a solid sample can be analyzed by directly inserting it into the flame or plasma, they usually are first brought into solution by digestion or extraction.

B. Minimizing Spectral Interferences: The most important spectral interference is broad, background emission from the flame or plasma and emission bands from molecular species. This background emission is particularly severe for flames because the temperature is insufficient to break down refractory compounds, such as oxides and hydroxides.

C. Minimizing Chemical Interferences: Flame emission is subject to the same types of chemical interferences as atomic absorption. These interferences are minimized by adjusting the flame's composition and adding protecting agents, releasing agents, or ionization suppressors

MULTI-ELEMENTAL ANALYSIS: Atomic emission spectroscopy is ideally suited for multi-elemental analysis because all analytes in a sample are excited simultaneously. If the instrument includes a scanning monochromator, we can program it to move rapidly to an analyte's desired wavelength, pause to record its emission intensity, and then move to the next analyte's wavelength. This sequential analysis allows for a sampling rate of 3–4 analytes per minute.

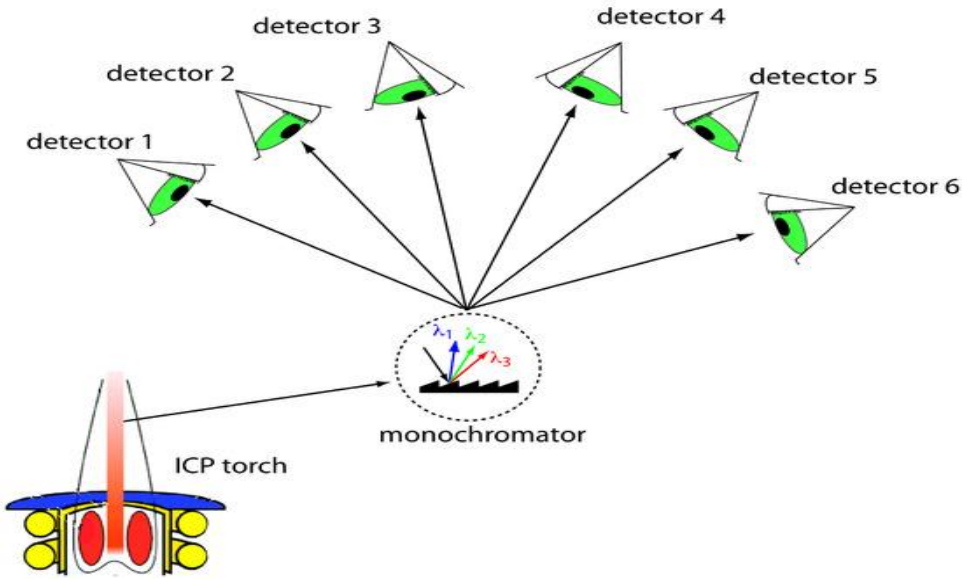


Fig 14: Schematic diagram of a multichannel AES for the simultaneous analysis of several elements modified from Xvlun(commons.wikipedia.org). Instruments may contain as many as 48–60 detectors.

APPLICATION OF ATOMIC EMISSION SPECTROSCOPY

Atomic emission is widely used for the analysis of trace metals in a variety of sample matrices. The development of a quantitative atomic emission method requires several considerations, including choosing a source for atomization and excitation, selecting a wavelength and slit width, preparing the sample for analysis, minimizing spectral and chemical interferences, and selecting a method of standardization.

USE OF ATOMIC EMISSION SPECTROSCOPY

AES is used in emission measurement with the flame is the regulation of alkali metals and heavy metals for Pharmaceutical, Mining, Cement Manufacturing Analytics etc.

ATOMIC FLUORESCENCE SPECTROSCOPY

THEORY

Fluorescence spectroscopy is a type of electromagnetic spectroscopy that analyzes fluorescence from a sample. It involves using a beam of light, usually ultraviolet light, that excites the electrons in molecules of certain compounds and causes them to emit light; intensity fluctuations from the emitted light are measured from either single fluorophores, or pairs of fluorophores.

AFS is not as popular as absorption or emission spectroscopy. Over the years, significant research effort has been devoted to the development of analytical methods based on atomic fluorescence. To date, however, the procedure has not found widespread use because of the overwhelming successes of atomic emission, and especially atomic absorption methods, which were developed prior to atomic fluorescence by more than a decade. As mentioned earlier, these successes have led to the availability of absorption and emission instruments from numerous commercial sources.

In recent years, a number of manufacturers have introduced atomic fluorescence spectrometers useful for determining elements that form vapors and hydrides, such as heavy metals. (– thus no High Temperature atomization is required for AFS only).

Plate 4: Atomic Fluorescence Spectrometer

WORKING PRINCIPLE

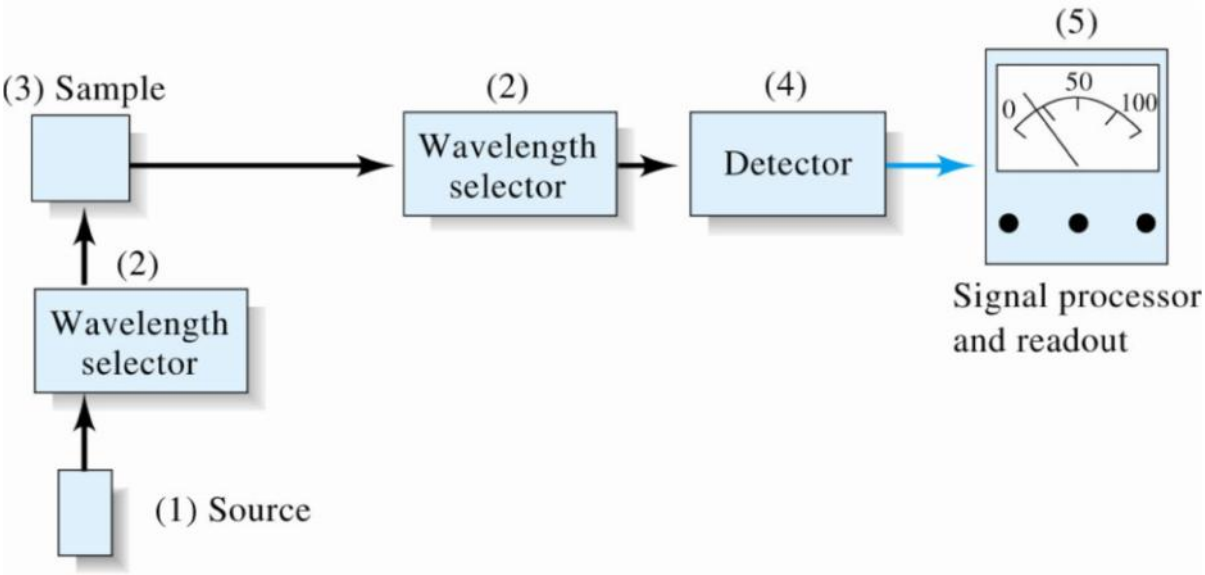


Fig 15: Depicts the working principles of AFS

The process of atomic fluorescence spectroscopy (AFS) involves:

1. Monochromatic excitation (atomizer) of the sample
2. Emission of radiation by the free atoms
3. Wavelength Selection (Monochromator)

4. Detector
5. Output Signal Processing

➢ In atomic fluorescence, the high intensity monochromatic discharge lamp (LED, lasers and lamps; Xenon arcs and mercury-vapor lamps) provides the excitation energy which is filtered and strike the sample, a proportion of the incident light is absorbed by the sample, and some of the molecules in the sample fluoresce. The fluorescent light is emitted in all directions. Some of this fluorescent light passes through a second filter or monochromator and reaches a detector, which is usually placed at 90° to the incident light beam to minimize the risk of transmitted or reflected incident light reaching the detector.

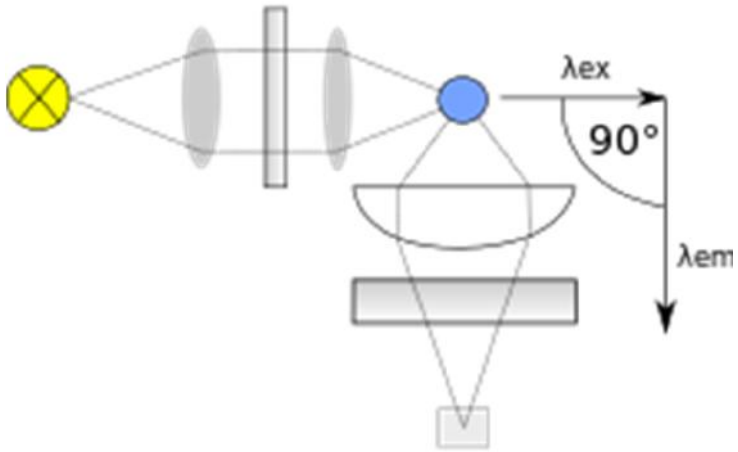


Fig 16: Schematic design of the components of a fluorimeter

➢ The detector can either be single-channeled or multi-channeled. The single-channeled detector can only detect the intensity of one wavelength at a time, while the multi-channeled detects the intensity of all wavelengths simultaneously, making the emission monochromator or filter unnecessary.

➢ After detecting, the signal is processed and reads output results.

SAMPLING PROCESS AND ANALYSIS

Samples is digested prior to analysis to ensure for accurate analyte measurement. The sample is then atomized and any free atoms are excited by light source emitted by a lamp. Consequently, the excited atoms re-radiate the absorbed energy at particular wavelength which allows for quantification and analysis.

APPLICATION OF ATOMIC FLUORESCENCE SPECTROSCOPY

This technique is sensitive and linear over a wide range of concentrations. Providing enhanced sensitivities, reduced interferences, and extremely low detection limits for the determination of sub-trace levels of hydride-forming metals

USE OF ATOMIC FLUORESCENCE SPECTROSCOPY

Atomic Fluorescence Spectroscopy (AFS) is used in, Public health and disease control, Metallurgical and geological industries. Petrochemical industries, Pharmaceutical industries, Clinical diagnostics, Agriculture, Environmental monitoring research work for analyzing organic compounds.

AFS is useful in other kinds of analysis/measurement of a compound present in air or water, which is used for heavy metals detection, such as mercury. Additionally, Fluorescence spectroscopy can be adapted to the microscopic level using micro-fluorimetry. In analytical chemistry, fluorescence detectors are used with HPLC.

EXPERIMENT 1 – Determination of the concentration of magnesium in tap water

Purpose: To determine the concentration of magnesium in tap water

Discussion: The determination of magnesium in potable water is very straightforward; very few interferences are encountered when using an acetylene-air flame.

Table 8: Reagents/Equipment / Materials:

Magnesium Metal	Deionized water
Hydrochloric Acid	Tap water
1 L graduated flask	Atomic Absorption spectrophotometer
Distilled water	Magnesium hollow cathode lamp
Pipette	Analytical weighing balance

Preparation of the standard solutions: A magnesium stock solution ($1000mgL^{-1}$) is prepared by dissolving 1.000g magnesium metal in 50ml of 5M hydrochloric acid. After dissolution of the metal, the solution is transferred to a 1 L graduated flask and made up to the mark with distilled water. An intermediate stock solution containing $50mgL^{-1}$ is prepared by pipetting 50mL of the

stock solution into a 1 L graduated flask and diluting to the mark. Dilute accurately four portions of this solution to give four standard solutions of magnesium with known magnesium concentrations lying within the optimum working range of the instrument to be used (typically 0.1-0.4ugmL^{-1} Mg^{2+}).

Experimental Procedure: Although the precise mode of operation may vary according to the particular instrument used, the following procedure may be regarded as typical. Place a magnesium hollow cathode lamp in the operating position, adjust the current to the recommended value (usually 2- 3Ma), and select the magnesium line at 285.2 nm using the appropriate monochromator slit width. Connect the appropriate gas supplies to the burner following the instructions detailed for the instrument, and adjust the operating conditions to give a fuel- lean acetylene-air flame.
Starting with the least concentrated solution, aspirate in turn the standard magnesium solutions into the flame and for each take three readings of the absorbance; between each solution, and remember to aspirate **deionized** water into the burner. Finally, read the absorbance of the sample of tap water; this will usually require considerable dilution in order to give an absorbance reading lying within the range of values recorded for the standard solutions. Plot the calibration curve and use this to determine the magnesium concentration of the tap water. If the magnesium content of the water is greater than 5ug mL^{-1} it might be considered preferable to work with the less sensitive magnesium line at wavelength 202.5 nm.

EXPERIMENT 2 – Determination of the Concentration of Vanadium in Lubricating Oil

Purpose: To determine the concentration of vanadium in lubricating oil

Discussion: The oil is dissolved in white spirit and the absorption of this solution is compared with the absorption of standards made up from vanadium naphthenate dissolved in white spirit.

Table 9: Reagents/Equipment / Materials:

Vanadium Naphthenate	Atomic Absorption spectrophotometer
White spirit	Lubricating oil
100 mL graduated flask	
50 mL burette	
Vanadium hollow cathode lamp	

Preparation of the standard solutions: The standard solutions are prepared from a solution of vanadium naphthenate in white spirit which contains about 3% of vanadium. Weigh out

accurately about 0.6g of the vanadium naphthenate into a 100mL graduated flask and make up to the mark with white spirit; this stock solution contains about 180ug mL^{-1} of vanadium. Dilute portions of this stock solution measured with the aid of a grade A 50 mL burette to obtain a series of working standards containing 10-40ug mL^{-1} of vanadium.

Experimental Procedure: Weigh out accurately about 5g of the oil sample, dissolve in a small volume of white spirit and transfer to a 50 mL graduated flask; using the same solvent, wash out the weighing bottle and make up the solution to the mark. Set up a vanadium hollow cathode lamp selecting the resonance line of wavelength 318.5 nm, and adjust the gas controls to give a fuel-rich acetylene-nitrous oxide flame in accordance with the instruction manual. Aspirate successively into the flame the solvent blank, the standard solutions, and finally the test solution, in each case recording the absorbance reading. Plot the calibration curve and ascertain the vanadium content of the oil.

In-text Question

Explain the need for sample preparation in atomic fluorescence

Answer

Samples are prepared by digested prior to analysis to ensure for accurate analyte measurement. The sample is then atomized and any free atoms are excited by light source emitted by a lamp.

4.0Self-Assessment Question

1. Explain the dependent factor responsible for AAS measurement
2. State the principle of AAS that shows that it follows Bear's law
3. State the type of dissolution that are necessary in preparation of a solid sample for an AAS analysis.
4. With examples explain the feature which makes microwave dissolution suitable for sample preparation.

Answers

1. Atomic absorption spectrophotometer contains the same basic components as an instrument designed for molecular absorption measurements, therefore most measurements in AAS are made with instruments equipped with an ultraviolet/visible grating monochromator.
2. The absorbance AAS is directly proportional to the path length in the flame and to the concentration of atomic vapour in the flame.
3. The type of dissolutions used in preparing solid samples for AAS analysis include wet ashing, Fusions, Dry ashing, Microwave dissolution.
4. The high frequency microwave temperature, typically 100-250^{o}C and the increased pressure assist in the considerable reduction in the time taken for sample dissolution. This method has been used for the dissolution of samples of coal, fly ash, biological and geological materials.

5.0 CONCLUSION

Atomic Absorption Spectroscopy (AAS) is a technique in which the absorption of light by free gaseous atoms in flame or furnace is used to determine the concentration of atoms. It is sensitive; it can detect trace amounts of metals/ heavy metals in samples. It is useful in the estimation of the concentration of trace metals/ heavy metals in a sample. This makes it a useful analytical technique for environmental monitoring.

6.0 SUMMARY

Atomic Absorption Spectroscopy is a useful spectroscopic analytical technique in the determination of the concentration of trace metals/heavy metals. It is based on the principle of the absorption of radiation by atoms in flame or furnace in an unexcited state. The energy of the radiation absorbed by the atoms is that of its own specific resonance wavelength, i.e., the radiation absorbed by the atom is the radiation it would emit if its electrons were excited from the ground state. The absorption follows Beer's law, hence, the number of the absorbing free gaseous atoms is proportional to the concentration of the atomic vapour in the flame. The estimation of the concentration of an element by AAS involves preparation of calibration curve from which the unknown concentration of the test element is determined by interpolation.

CLASS ACTIVITY (THE TUTOR TO DIRECT)

1. What is Atomic Absorption Spectroscopy (AAS)?

2. Draw and label the diagram of a simple atomic absorption spectroscopy (AAS)

3. Discuss the principle of AAS

4. Outline the procedures involved in carrying out determination of the concentration of elements by AAS

5. Distinguish between wet ashing and dry ashing

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MODULE TWO
UNIT 1 - PRECIPITATION GRAVIMETRY

3.1 Principle of Precipitation gravimetry
https://www.youtube.com/watch?v=uy6uGSt7aQs

3.2 Steps Involved in Gravimetric Analysis
https://www.youtube.com/watch?v=ffVX0G4lVGI

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MODULE TWO (INORGANIC)

UNIT 1 - PRECIPITATION GRAVIMETRY

1.0 INTRODUCTION

2.0 INTENDED LEARNING OUTCOMES (ILOS)

3.0 MAIN CONTENT

3.1 Principle of Precipitation Gravimetry.

In-text Question

3.1.1 Solubility Considerations

3.1.2 How to Obtain Precipitate of High Purity

3.1.3 Controlling Particle Size

3.2 Steps Involved in Gravimetric Analysis

3.3 Experiments

In-text Question

4.0 Self – Assessment Exercises

5.0 CONCLUSION

6.0 SUMMARY

7.0 REFERENCES/ FURTHER READING

MODULE TWO
UNIT 1 - PRECIPITATION GRAVIMETRY
3.1 Principle of Precipitation gravimetry

https://www.youtube.com/watch?v=uy6uGSt7aQs

3.2 Steps Involved in Gravimetric Analysis
https://www.youtube.com/watch?v=ffVX0G4lVGI

1.0 INTRODUCTION

Precipitation gravimetry is a type /form of gravimetric methods of analysis. Before we proceed to discuss precipitation gravimetry, it is important we understand what gravimetry is all about. Recall **that in** CHM 202, you were introduced and taught gravimetric analysis. Gravimetric analysis is a quantitative analysis which involves estimation of the weight of an element or definite compound of the element. The process entails isolating and weighing an element or a definite compound of the element in a pure form as possible. The element or compound is separated from a weighed portion of the substance being examined. The weight of the element or radical may then be readily calculated from knowledge of the formula of the compound and the atomic weights of the constituent elements. Though gravimetric analysis is a method of quantitative analysis, a separation is involved and the techniques employed are sometimes used for preliminary separations. Since weight can be measured with greater accuracy than almost any other fundamental property, gravimetric analysis is potentially one of the most accurate and precise analytical methods available. There are four fundamental types of gravimetric analysis: particulate gravimetry, volatilization gravimetry, precipitation gravimetry and electrodeposition gravimetry.

2.0 INTENDED LEARNING OUTCOMES (ILOS)

After studying this unit, you should be able to:

- Discuss/ explain the principle of precipitation gravimetry
- State and discuss the conditions for an analytical precipitate
- State and explain the steps involved in precipitation gravimetric determination
- Apply the theory of precipitation gravimetry by performing experiments involving precipitation gravimetry

3.0 MAIN CONTENT

3.1 Principle of Precipitation gravimetry

In precipitation gravimetry, **the analyte is converted to a sparingly soluble precipitate or**an insoluble compound forms when a precipitating reagent is added, or precipitant, to a solution containing our analyte. In most methods the precipitate is the product of a simple metathesis reaction (exchange reaction, or double replacement reaction) between the analyte and the precipitant; however, any reaction generating a precipitate can potentially serve as a gravimetric method. The precipitating reagent or precipitant is the reagent added, that reacts with the analyte in solution to form the precipitate, while the precipitate is the insoluble compound formed.**This precipitate is then filtered, washed free of impurities, converted to a product of known composition by suitable heat treatment and weighed.**Precipitation gravimetry is used for the separation of elements from samples and for the determination of the weight of elements in a given sample.

All precipitation gravimetric analysis share two important attributes. First, the precipitate must be of low solubility, of high purity, and of known composition if its mass is to accurately reflect the analyte's mass. Second, the precipitate must be easy to separate from the reaction mixture.

In-text Question

State the reason for precipitation gravimetry analysis

Answer

In precipitation gravimetry, the analyte is converted to a sparingly soluble precipitate or an insoluble compound forms when a precipitating reagent is added, or precipitant to a solution containing our analyte.

3.1.1 Solubility Considerations

To provide accurate results, a precipitate's solubility must be minimal. The accuracy of a total analysis technique typically is better than ±0.1%, which means that the precipitate must account for at least 99.9% of the analyte. Extending this requirement to 99.99% ensures that the precipitate's solubility does not limit the accuracy of a gravimetric analysis.

We can minimize solubility losses by carefully controlling the conditions under which the precipitate forms. This, in turn, requires that we account for every equilibrium reaction affecting the precipitate's solubility.

Another important parameter that may affect a precipitate's solubility is the pH of the solution in which the precipitate forms. For example, hydroxide precipitates such as Fe $(OH)_3$, are more soluble at lower pH levels at which the concentration of OH^- is small. It is important therefore, to adjust the pH of a solution to maintain low solubility of the precipitate.

Solubility can often be decreased by using a **non-aqueous** solvent. A precipitate's solubility is generally greater in aqueous solutions because of the ability of water molecules to stabilize ions through solvation. The poorer solvating ability of **non-aqueous** solvents, even those that are polar, leads to a smaller solubility product. For example, $PbSO_4$ has a K_{SP} of 1.6×10^{-8} in water, whereas in a 50:50 mixture of H_2O /Ethanol the k_{sp} is four orders of magnitude smaller.

3.1.2 How to obtain precipitate of high purity

In addition to having a low solubility, the precipitate must be free from impurities, **for the fact that** precipitation usually occurs in a solution that is rich in dissolved solids, the initial precipitate is often impure. We must remove these impurities before determining the precipitate's mass.

The greatest source of impurities is the result of chemical and physical interactions occurring at the precipitate's surface. A precipitate is generally crystalline—even if only on a microscopic scale—with a well-defined lattice of cations and anions. Those cations and anions at the precipitate's surface carry, respectively, a positive or a negative charge because they have incomplete coordination spheres. In a precipitate of AgCl, for example, each silver ion in the precipitate's interior is bound to six chloride ions. A silver ion at the surface, however, is bound to no more than five chloride ions and carries a partial positive charge (Figure 17). The presence of these partial charges makes the precipitate's surface an active site for the chemical and physical interactions that produce impurities.

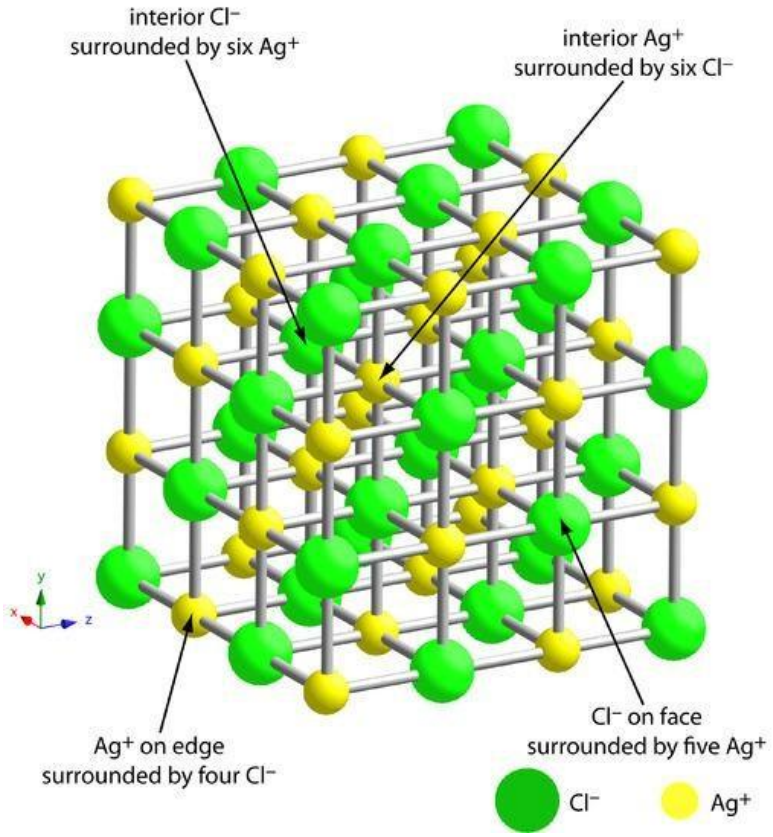

Figure 17: Lattice structure of AgCl

Ball-and-stick diagram showing the lattice structure of AgCl. Each silver ion in the lattice's interior binds with six chloride ions, and each chloride ion in the interior binds with six silver ions. Those ions on the lattice's surface or edges bind to fewer than six ions and carry a partial charge. A silver ion on the surface, for example, carries a partial positive charge. These charges make the surface of a precipitate an active site for chemical and physical interactions.

One common impurity is an **inclusion**. A potential interfering ion whose size and charge is similar to a lattice ion, may substitute into the lattice structure, provided that the interferent precipitates with the same crystal structure. The probability of forming an inclusion is greatest when the concentration of the interfering ion is substantially greater than the lattice ion's concentration. An inclusion does not decrease the amount of analyte that precipitates, provided that the precipitant is present in sufficient excess. Thus, the precipitate's mass is always larger than expected.

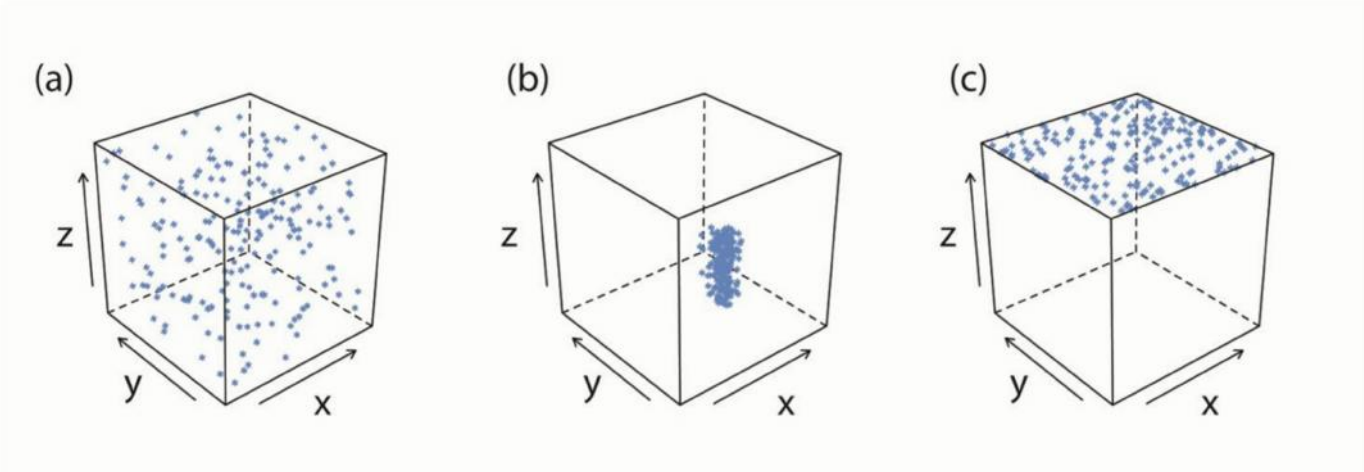

Figure 18 Three examples of impurities that may form during precipitation. The cubic frame represents the precipitate and the blue marks are impurities: (a) inclusions, (b) occlusions, and (c) surface adsorbates. Inclusions are randomly distributed throughout the precipitate. Occlusions are localized within the interior of the precipitate and surface adsorbates are localized on the precipitate's exterior. For ease of viewing, in (c) adsorption is shown on only one surface. An inclusion is difficult to remove since it is chemically part of the precipitate's lattice. The only way to remove an inclusion is through **reprecipitation**. After isolating the precipitate from its supernatant solution (the solution remaining after the precipitate is formed), we dissolve it by heating in a small portion of a suitable solvent. We then allow the solution to cool, reforming the precipitate. Because the interferent's concentration is less than that in the original solution, the amount of included material is smaller. We can repeat the process of reprecipitation until the inclusion's mass is insignificant. The loss of analyte during reprecipitation, however, can be a significant source of error.

Occlusions form when interfering ions become trapped within the growing precipitate. Unlike inclusions, which are randomly dispersed within the precipitate, an occlusion is localized, either along flaws within the precipitate's lattice structure or within aggregates of individual precipitate particles (Figure 18). An occlusion usually increases a precipitate's mass; however, the mass is smaller if the occlusion includes the analyte in a lower molecular weight form than that of the precipitate.

We can minimize occlusions by maintaining the precipitate in equilibrium with its supernatant solution for an extended time. This process is called a **digestion**. During digestion, the dynamic nature of the solubility–precipitation equilibrium, in which the precipitate dissolves and reforms, ensures that the occlusion is re-exposed to the supernatant solution. Because the rates of dissolution and reprecipitation are slow, there is less opportunity for forming new occlusions.

After precipitation is complete the surface continues to attract ions from solution. These **surface adsorbates** comprise a third type of impurity. We can minimize surface adsorption by decreasing the precipitate's available surface area. One benefit of digesting a precipitate is that it increases the average particle size, because the probability of a particle completely dissolving is inversely proportional to its size, during digestion larger particles increase in size at the expense of smaller

particles. One consequence of forming a smaller number of larger particles is an overall decrease in the precipitate's surface area. We also can remove surface adsorbates by washing the precipitate, although the potential loss of analyte cannot be ignored.

Inclusions, occlusions, and surface adsorbates are examples of **coprecipitates**—otherwise soluble species that form within the precipitate containing the analyte. Another type of impurity is an interferent that forms an independent precipitate under the conditions of the analysis. For example, the precipitation of nickel dimethylglyoxime requires a slightly basic pH. Under these conditions, any Fe^{3+} in the sample precipitates as $Fe(OH)_3$. In addition, because most precipitants are rarely selective toward a single analyte, there is always a risk that the precipitant will react with both the analyte and an interferent.

We can minimize the formation of additional precipitates by carefully controlling solution conditions. If an interferent forms a precipitate that is less soluble than the analyte's precipitate, we can precipitate the interferent and remove it by filtration, leaving the analyte behind in solution. Alternatively, we can mask the analyte or the interferent to prevent its precipitation.

Example: Both of the above-mentioned approaches are illustrated in Fresenius' analytical method for determining Ni in ores containing Pb^{2+}, Cu^{2+}, and Fe^{3+}. Dissolving the ore in the presence of H_2SO_4 selectively precipitates Pb^{2+} as $PbSO_4$. Treating the supernatant with H_2S precipitates the Cu^{2+} as CuS. After removing the CuS by filtration, adding ammonia precipitates Fe^{3+} as $Fe(OH)_3$. Nickel, which forms a soluble amine complex, remains in solution.

3.1.3 Controlling Particle Size

Size matters when it comes to forming a precipitate. Larger particles are easier to filter, and, as noted earlier, a smaller surface area means there is less opportunity for surface adsorbates to form. By carefully controlling the reaction conditions we can significantly increase a precipitate's average particle size.

Precipitation consists of two distinct events: nucleation, the initial formation of smaller stable particles of precipitate, and particle growth. Larger particles form when the rate of particle growth exceeds the rate of nucleation. Understanding the conditions favoring particle growth is important when designing a gravimetric method of analysis.

Von Wiermarn discovered that the particle size of precipitates is inversely proportional to the relative supersaturation of the solution during the precipitation process, we define a solute's **relative supersaturation**, *RSS*, as

$$RSS=Q-S/S$$

Where*Q* is the concentration of the mixed reagents before precipitation occurs and is the degree of **super saturation**, and *S* is the solubility of the precipitate at equilibrium. A solution with a large, positive value of *RSS* has a high rate of nucleation, producing a precipitate with many small particles and high surface area. When the *RSS* is small, precipitation is more likely to occur by

particle growth than by nucleation, producing a precipitate with few larger crystals and low surface area.

High relative **supersaturation** ----- many small crystals
(High surface area)
Low relative **supersaturation** ------ fewer larger crystals
(Low surface area)

Examining equation above shows that we can minimize *RSS* by decreasing the solute's concentration, *Q*, or by increasing the precipitate's solubility, *S*. Several steps are commonly taken to keep Q low and increase S.

1. Precipitation from dilute solution. This keeps Q low.
2. Add dilute precipitating reagents slowly, with effective stirring. This also keeps Q low. Local excess of the reagent are prevented by stirring.
3. Precipitation from hot solution. This increases S. The solubility should not be too great or the precipitation will not be quantitative. The bulk of the precipitation may be performed in the hot solution, and then the solution may be cooled to make the precipitation quantitative.
4. Precipitate at as low a pH as possible to still maintain quantitative precipitation. Many precipitates are more soluble in acid medium, and this slows the rate of precipitation. They are more soluble because the anion of the precipitate combines with protons in the solution.

Most of these operations also often decrease the degree of contamination. The concentration of impurities is kept lower and their solubility is increased, and the slower rate of precipitation decreases their chance of being trapped. The larger crystals have a smaller specific surface area and so less chance of adsorption of impurities.

There are practical limitations to minimizing *RSS*. Some precipitates, such as $Fe(OH)_3$ and PbS, are so insoluble that *S* is very small and a large *RSS* is unavoidable. Such solutes inevitably form small particles. In addition, conditions favoring a small *RSS* may lead to a relatively stable supersaturated solution that requires a long time to fully precipitate.

A visible precipitate takes longer to form when *RSS* is small both because there is a slow rate of nucleation and because there is a steady decrease in *RSS* as the precipitate forms. One solution to the latter problem is to generate the precipitant in situ as the product of a slow chemical reaction. This maintains the *RSS* at an effectively constant level. Because the precipitate forms under conditions of low *RSS*, initial nucleation produces a small number of particles. As additional precipitant forms, particle growth supersedes nucleation, resulting in larger precipitate particles.
This process is called homogeneous precipitation**.**

3.2 Steps Involved in Gravimetric Analysis

1. Preparation of the solution
2. Precipitation
3. Digestion
4. Filtration
5. Washing
6. Drying or Ignition
7. Weighing
8. Calculation

Preparation of the Solution: Although some form of preliminary separation may be necessary to eliminate interfering materials, in other instances the precipitation step in gravimetric analysis is sufficiently selective that other separations are not required. The substance to be estimated must be in solution form. For this, accurately weigh a suitable quantity of substance and dissolve it in distilled water or suitable solvent, heat the solution if necessary. The solution conditions must be adjusted to maintain low solubility of the precipitate and to obtain it in a form suitable for filtration. Proper adjustment of the solution conditions prior to precipitation may also mask potential interferences. Factors that must be considered include the volume of the solution during precipitation, the concentration range of the test substance, the presence and concentration of other constituents, the temperature and the pH.

Precipitation: This step involves reaction with a precipitant to give precipitate.
When the precipitation is performed, a slight excess of precipitating reagent is added to decrease the solubility by mass action (common ion effect and to assure complete precipitation). If the approximate amount of analyte is known, a 10 percent excess of the reagent is generally added. Completeness of precipitation is checked by waiting until the precipitate has settled and then adding a few drops of precipitating reagent to the clear solution above it. If no new precipitate forms, precipitation is complete.

Digestion: When a precipitate is allowed to stand in the presence of the mother liquor (the solution from which it was precipitated), the larger crystals grow at the expense of the small ones. This is known as digestion or Ostwald ripening. The small particles tend to dissolve and precipitate on the surfaces of the larger crystals. In addition, individual particles agglomerate. This results in an appreciable decrease in surface area. Also, imperfections of the crystals tend to disappear, and adsorbed or trapped impurities tend to go into solution. Digestion is usually done at elevated temperatures to speed the process, although in some cases, it is done at room temperature. It improves the filterability of the precipitate and its purity.

Filtration: After precipitating and digesting the precipitate, we separate it from solution by filtering. The most common filtration method uses filter paper, which is classified according to its speed, its size, and its ash content on ignition. Speed, or how quickly the supernatant passes through the filter paper, is a function of the paper's pore size. A larger pore allows the supernatant to pass more quickly through the filter paper, but does not retain small particles of

precipitate. Filter paper is rated as fast (retains particles larger than 20–25 μm), medium–fast (retains particles larger than 16 μm), medium (retains particles larger than 8 μm), and slow (retains particles larger than 2–3 μm). The proper choice of filtering speed is important. If the filtering speed is too fast, we may fail to retain some of the precipitate, causing a negative determinate error. On the other hand, the precipitate may clog the pores if we use a filter paper that is too slow.

Because filter paper is hygroscopic, it is not easy to dry it to a constant weight. When accuracy is important, the filter paper is removed before determining the precipitate's mass. After transferring the precipitate and filter paper to a covered crucible, we heat the crucible to a temperature that coverts the paper to CO_2 (g) and H_2O (g), a process called **ignition**.

Igniting a poor quality filter paper leaves behind a residue of inorganic ash. For quantitative work, we use a low-ash filter paper. This grade of filter paper is pretreated with a mixture of HCl and HF to remove inorganic materials. Quantitative filter paper typically has an ash content of less than 0.010% w/w.

Gravity filtering is accomplished by folding the filter paper into a cone and placing it in a longstem funnel (Figure 3). A seal between the filter cone and the funnel is formed by dampening the paper with water or supernatant, and pressing the paper to the wall of the funnel. When properly prepared, the funnel's stem fills with the supernatant, increasing the rate of filtration.

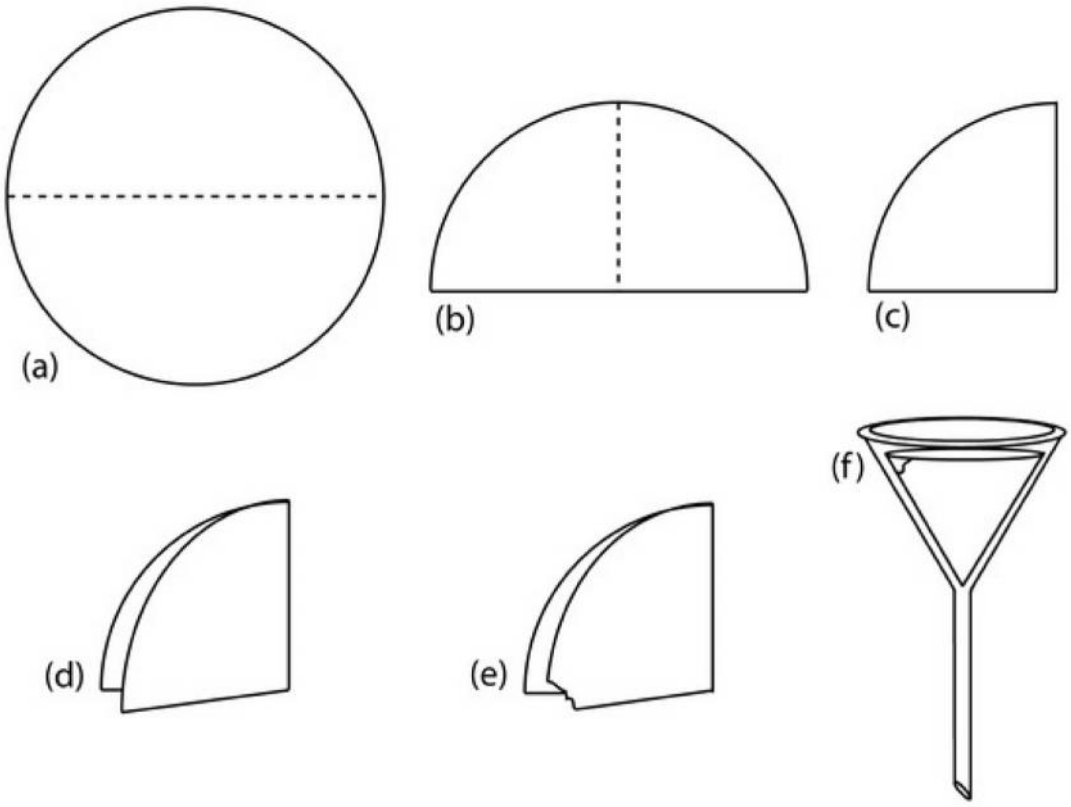

Figure 19: Preparing a filter paper cone. The filter paper circle in (a) is folded in half (b), and folded in half again (c). The folded filter paper is parted (d) and a small corner is torn off (e). The filter paper is opened up into a cone and placed in the funnel (f).

The precipitate is transferred to the filter in several steps. The first step is to decant the majority of the **supernatant** through the filter paper without transferring the precipitate. This prevents the filter paper from clogging at the beginning of the filtration process. The precipitate is rinsed while it remains in its beaker, with the rinsing decanted through the filter paper. Finally, the precipitate is transferred onto the filter paper using a stream of rinse solution. Any precipitate clinging to the walls of the beaker is transferred using a rubber policeman (a flexible rubber spatula attached to the end of a glass stirring rod).

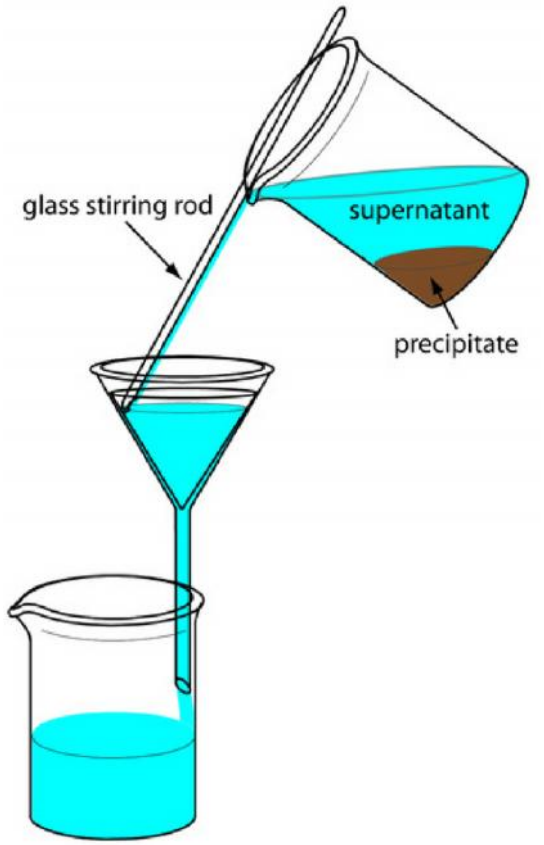

Figure 20: Proper procedures for transferring the supernatant to the filter paper cone.

An alternative method for filtering a precipitate is a filtering crucible. The most common is a fritted-glass crucible containing a porous glass disk filter. Fritted-glass crucibles are classified by their porosity: coarse (retaining particles larger than 40–60 μm), medium (retaining particles greater than 10–15 μm), and fine (retaining particles greater than 4–5.5 μm). Another type of filtering crucible is the Gooch crucible, which is a porcelain crucible with a perforated bottom. A glass fiber mat is placed in the crucible to retain the precipitate. For both types of crucibles, the precipitate is transferred in the same manner described earlier for filter paper. Instead of using

gravity, the supernatant is drawn through the crucible with the assistance of suction from a vacuum aspirator or pump (Figure 21).

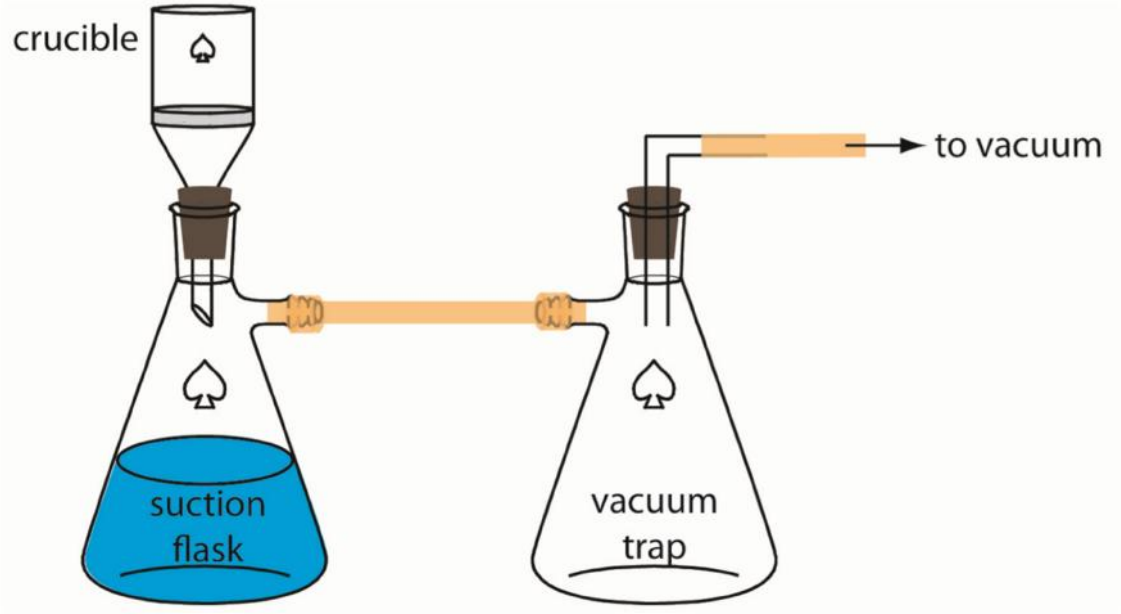

Figure 21: Procedure for filtering a precipitate through a filtering crucible. The trap prevents water from an aspirator from back-washing into the suction flask.

Washing: Coprecipitated impurities, especially those on the surface, can be removed by washing the precipitates after filtering. The precipitate will be wet with the mother liquor, which is also removed by washing. Many precipitates cannot be washed with pure water, because peptization occurs (process of passing of a precipitate into colloidal particles on adding suitable electrolyte). Prevention consists in adding an electrolyte to the wash liquid. The electrolyte must be one that is volatile at the temperature to be used for drying or ignition, and it must not dissolve the precipitate.

Drying or igniting the precipitate:

After separating the precipitate from its supernatant solution, the precipitate is dried to remove residual traces of rinse solution and any volatile impurities. The temperature and method of drying depend on the method of filtration and the precipitate's desired chemical form. Placing the precipitate in a laboratory oven and heating to a temperature of 110^{o}C is sufficient when removing water and other easily volatilized impurities. Higher temperatures require a muffle furnace, a Bunsen burner, or a Meker burner, and are necessary if we need to thermally decompose the precipitate before weighing.

Because filter paper absorbs moisture, we must remove it before weighing the precipitate. This is accomplished by folding the filter paper over the precipitate and transferring both the filter paper and the precipitate to a porcelain or platinum crucible. Gentle heating first dries and then chars

the filter paper. Once the paper begins to char, we slowly increase the temperature until all traces of the filter paper are gone and any remaining carbon is oxidized to CO_2.

Fritted-glass crucibles cannot withstand high temperatures and must be dried in an oven at temperatures below 200°C. The glass fiber mats used in Gooch crucibles can be heated to a maximum temperature of approximately 500°C. To ensure that drying is complete the precipitate is repeatedly dried and weighed until a constant weight is obtained.

Weighing and Calculation: The residue after drying and ignition is weighed and the weight of the precipitate is obtained using the formula:

Weight of the precipitate = Weight of crucible along with precipitate – Weight of empty crucible.

From the weight of the precipitate one can determine percentage of analyte present in the sample. Calculations are usually made on a percentage basis.

The general formular for calculating the percentage of the substance sought (analyte) is:

$$\% \text{ sought (analyte)} = \frac{\text{Weight of precipitate (g) x gravimetric factor}}{\text{Weight of sample (g)}} \times 100\%$$

$$\text{Gravimetric factor} = \frac{\text{f. w of substance sought or analyte}}{\text{f.w of substance weighed or sample weighed}}$$

Is always important to write a balanced equation of the reaction between the sample and the precipitant

Example: An ore is analyzed for the manganese content by converting the manganese to Mn_3O_4 and weighing it. If a 1.52g sample yields Mn_3O_4 weighing 0.126 g, what would be the percent Mn in the sample?

Solution

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

$$= \frac{0.126\text{g} \times [3(54.94)/228.8]}{1.52 \text{ g}} \times 100\% = 5.97\%$$

Before we round off and go to our practical section, it is important to note that many of the possible problems associated with gravimetric analysis are overcome by following wellestablished procedures as stipulated below:

1. Precipitation should be carried out in dilute solution. This keeps Q low.

2. The reagents should be mixed slowly and with constant stirring. This will keep the degree of supersaturation small and will assist the growth of large crystals. A slight excess of the reagent is all that is generally required; in exceptional cases a large excess may be necessary. In some instances the order of mixing the reagents may be important. Precipitation may be effected under conditions which increase the solubility of the precipitate, further reducing the degree of supersaturation.

3. Precipitation is effected in hot solutions, provided the solubility and the stability of the precipitate permit. Either one or both of the solutions should be heated to just below the boiling point or other more favourable temperature. At the higher temperature: (a) the solubility is increased with a consequent reduction in the degree of supersaturation,(b) coagulation is assisted and the sol formation decreased, and (c) the velocity of crystallization is increased, thus leading to better-formed crystals.

4. Crystalline precipitates should be digested for as long as practical, preferably overnight, except in those cases where post-precipitation may occur. As a rule, digestion on the steam bath is desirable. This process decreases the effect of co-precipitation and gives more readily filterable precipitates. Digestion has little effect upon amorphous or gelatinous precipitates.

5. The precipitate should be washed with the appropriate dilute solution of an electrolyte. Pure water may tend to cause peptisation.

6. If the precipitate is still appreciably contaminate as a result of coprecipitation or other causes, the error may often be reduced by dissolving it in a suitable solvent and then reprecipitating it. The amount of foreign substances present in the second precipitation will be small; hence the amount of entrainment by the precipitate will also be small.

7. Precipitation from a homogeneous solution is commonly employed to prevent supersaturation. The precipitating agent is generated within the solution by means of a homogeneous reaction at a rate similar to that required for precipitation of the species.

   In CHM 303 you studied the chemistry of the elements of different groups of the periodic table. Now in this practical section we want to use our knowledge of precipitation gravimetry to isolate and determine the weight of some of the elements studied in CHM 303 in given samples.

1 Gravimetric Determination of Chloride as Silver Chloride

Purpose: To separate the chloride content from a given sample
To determine the amount/ quantity of chloride present in a given sample

Discussion: The aqueous solution of the chloride is acidified with dilute nitric acid in order to prevent the precipitation of other silver salts, such as the phosphate and carbonate, which might form neutral solution, and also to produce a more readily filterable precipitate. A slight excess of silver nitrate solution is added, whereupon silver chloride is precipitated:

$Cl^- + Ag+ = AgCl$

The precipitate, which is initially colloidal, is coagulated into curds by heating the solution and stirring the suspension vigorously; the supernatant liquid becomes almost clear. The precipitate is collected in a filtering crucible, washed with very dilute nitric acid, in order to prevent it from becoming colloidal, dried at $130 - 150^0$ C, and finally weighed as AgCl. If silver chloride is washed with pure water, it may become colloidal and run through the filter. For this reason the wash solution should contain an electrolyte. Nitric acid is generally employed because it is without action on the precipitate and is readily volatile; its concentration need not be greater than 0.01 M. Completeness of washing of the precipitate is tested for by determining whether the excess of the precipitating agent, silver nitrate, has been removed. This may be done by adding one to two drops of 0.1 M hydrochloric acid to 3–5 mL of the washings collected after the washing process has been continued for some time; if the solution remains clear or exhibits only a very slight opalescence, all the silver nitrate has been removed.

Silver chloride is light-sensitive; decomposition occurs into silver and chlorine, and the silver remains colloidally dispersed in the silver chloride and thereby imparts a purple colour to it. The decomposition by light is only superficial, and is negligible unless the precipitate is exposed to direct sunlight and is stirred frequently. Hence the determination must be carried out in as subdued a light as possible, and when the solution containing the precipitate is set aside, it should be placed in the dark (e.g in a locker), or the vessel containing it should be covered with thick brown paper.

Table 10: Reagents /Equipment / Materials:

NaCl	Distilled water	Sintered-glass filtering crucible	Test tube
250 ML beaker	Conc. Nitric acid	Dessicator	Hydrochloric acid
Stirring rod	Silver nitrate	Weighing balance	Oven
Clock glass	Heating mantle	Rubber policeman	

Experimental Procedure

Weigh out accurately three samples of 0.2g of the solid chloride into three separate 250ml beakers provided with a stirring rod and cover each beaker with a clock glass. Add about 150ml of water to each beaker, stir until the solid has dissolved, and add 0.5ml of conc nitric acid to each beaker. To each cold solution add 0.1M silver nitrate slowly and with constant stirring. Only a slight excess should be added; this is readily detected by allowing the precipitate to settle and adding a few drops of silver nitrate solution, when no further precipitate should be obtained. Carry out the determination in subdued light. Heat the suspensions nearly to boiling, while stirring constantly, and maintain each at this temperature until the precipitates coagulates and the supernatant liquid is clear (2-3 min). Make certain that precipitation is complete by adding a few drops of silver nitrate solution to the supernatant liquid. If no further precipitate appears, set each beaker aside in the dark, and allow the solution to stand for about 1h before filtration. In the meantime prepare a sintered-glass filtering crucible; the crucible must be dried at the same temperature as is employed in heating the precipitate ($130 - 150^0$ C) and allowed to cool in a dessicator. Collect the precipitates in the weighed filtering crucible. Wash each precipitate two or three times by decantation with about 10 ml of cold very dilute nitric acid (0.5 ml of the concentrated acid added to 200ml of water) before transferring the precipitate to the crucible. Remove the last small particles of silver chloride adhering to the beaker with a policeman. Wash the precipitates in the crucible with very dilute nitric acid added in small portions until 3-5 ml of the washings, collected in a test tube, give no turbidity with one or two drops of 0.1 M hydrochloric acid. Place the crucible and contents in an oven at $130 - 150^0$ C for 1h, allow to cool in a dessicator, and weigh. Repeat the heating and cooling until constant weight is attained.

1. Calculate the percentage of chlorine in the sample

   Gravimetric factor = Cl/AgCl = 0.24737

2. Report also the average deviation, variance and standard deviation.

3. What is digestion of a precipitate and why is it necessary.

2 Determination of Nickel as the Dimethylglyoximate

Purpose: To separate an analyte of interest (Nickel) from a given sample
To determine the amount/ quantity of analyte (Nickel) present in a given sample

Discussion: Nickel is precipitated by the addition of an ethanolic solution of dimethylglyoxime (H_2DMG) to a hot, faintly acid solution of the nickel salt, and then adding a slight excess of aqueous ammonia solution (free from carbonate). The preciptitate is washed with cold water and then weighed as nickel dimethylglyoximate after drying at 110-120^{0}C. With large precipitates, or in work of high accuracy, a temperature of 150^{0}C should be used; this volatilizes any reagent that may have been carried down by the precipitate. The equation is

$$Ni^{2+} + 2H_2DMG = Ni(HDMG)_2 + 2H^+$$

The precipitate is insoluble in dilute ammonia solutions, in solutions of ammonium salts, and in dilute ethanoic acid-sodium ethanoate solutions. Large amount of aqueous ammonia and of cobalt, zinc or copper retard the precipitation, extra reagent must be added, because these elements consume dimethylglyoxime to form various soluble compounds. Dimethylglyoxime is almost insoluble in water, and is added in the form of a 1% solution in 90% ethanol (rectified spirit) or absolute ethanol; 1ml of this solution is sufficient for the precipitation of 0.0025g of nickel. The reagent is added to a hot feebly acid solution of a nickel salt, and the solution is then rendered faintly ammoniacal. This procedure gives a more easily filterable precipitate than direct precipitation from cold or from ammoniacal solutions. Only a slight excess of the reagent should be used, since dimethylglyoxime is not very soluble in water or in very dilute ethanol and may precipitate; if a very large excess is added (such that the alcohol content of the solution exceeds 50%), some of the precipitate may dissolve.

Table 11: Reagents/Equipment / Materials:

Pure ammonium nickel sulphate	Dilute hydrochloric acid	Oven
Beakers	Dimethylglyoxime	Steam bath
Stirring rod	Sintered-glass or porcelain filtering crucible	Weighing balance
Clock glass	Dessicator	
Distilled water	Ammonia solution	

Experimental Procedure

Weigh out accurately 0.3-0.4g of pure ammonium nickel sulphate $(NH_4)_2SO_4.NiSO_4.6H_2O$ into a 500ml beaker provided with a cockglass cover and stirring rod. Dissolve it in water, and 5ml of dilute hydrochloride acid (1:1) and dilute to 200ml. Heat to 70-80^{0}C, add a slight excess of the dimethylglyoxime reagent (at least 5ml for every 10mg of Ni present), and immediately add dilute ammonia solution dropwise, directly to the solution and not down the beaker wall, and with constant stirring until precipitation takes place, and then in slight excess. Allow to stand on the steam bath for 20-30min, and test the solution for complete precipitation when the red precipitate has settled out. Allow the precipitate to stand for 1h, cooling at the same time. Filter the cold solution through a sintered-glass or porcelain filtering crucible, previously heated to 110-120^{0}C and weighed after cooling in a desiccator. Wash the precipitate with cold water until free from chloride, and dry it at 110-120^{0}C for 45-50min. Allow to cool in a desiccator and weigh. Repeat the drying until constant weight is attained. Weigh as $Ni(C_4H_7O_2N_2)_2$.

1. Calculate and report the percentage of nickel in the sample.

   Gravimetric factor = $Ni/Ni(C_4H_7O_2N_2)_2$ =0.20319

2. What is coprecipitation? , list the different types of coprecipitation and indicate how they may be minimized or treated for.

3 Gravimetric Determination of Lead as Chromate

Purpose: To separate an analyte of interest (lead) from a given sample
To determine the amount/ quantity of analyte (lead) present in a given sample

Discussion: Although this method is limited in its applicability because of the general insolubility of chromates, it is a useful procedure for gaining experience in gravimetric analysis. The best results are obtained by precipitating from homogenous solution using the homogenous generation of chromate ion produced by slow oxidation of chromium (III) by bromate at 90 - 95^0 C in the presence of an ethoanate buffer.

Table 12: Reagents/Equipment / Materials:

Sodium hydroxide	0.6 M sodium ethanoate	Laboratory oven
Beakers	Chromium nitrate	Analytical weighing balance
Stirring rod	Sintered-glass or porcelain filtering crucible	
Sample solution containing 0.1 – 0.2g lead	Potassium bromate	
6 M ethanoic acid	1% nitric acid	

Experimental Procedure

Use a sample solution containing 0.1 – 0.2 g lead. Neutralize the solution by adding sodium hydroxide until a precipitate just begins to form. Add 10 mL ethanoate buffer solution (6M in ethanoic acid and 0.6M in sodium ethanoate); 10mL chromium nitrate solution (2.4 g per 100ml); and 10 mL potassium bromate solution (2.0g per 100ml). Heat to 90 - 95^0C. After generation (of chromate) and precipitation are complete (about 45 min) as shown by a clear supernatant liquid, cool, filter through a weighed sintered-glass or porcelain filtering crucible, wash with a little 1% nitric acid, and dry at 120^0 C. Weigh as $PbCrO_4$.

1. Calculate the percentage of lead in the sample

   Gravimetric factor = $Pb/PbCrO_4$ = 0.641108

2. Why was the precipitate obtained washed with 1% nitric acid.

In-text Question

State how you can separate an analyte of interest (Nickel) from a given sample

Answer

By addition of ethanolic solution of dimethylglyoxime (H_2DMG) to a hot, faintly acid solution of the nickel salt, and then adding a slight excess of aqueous ammonia solution (free from carbonate)

In-text Question

Explain the reason for lengthy time of digestion of crystalline precipitates

Answer
Crystalline precipitates is digested for as long time as practical, preferably overnight, except where post-precipitation may occur. As a rule, digestion on the steam bath is desirable. This process decreases the effect of co-precipitation and gives more readily filterable precipitates.

4.0SELF- ASSESSMENT EXERCISES

1. **What do you understand by precipitation gravimetry?**

2. **Enumerate the various steps involved in gravimetric analysis**

3. **What is gravimetric analysis?**

Answers

1. Precipitation gravimetry is one in which **the analyte is converted to a sparingly soluble precipitate or** an insoluble compound forms when a precipitating reagent is added, or precipitant, to a solution containing the analyte. All precipitation gravimetric analysis have two important attributes. First, the precipitate must be of low solubility, of high purity, and of known composition if its mass is to accurately reflect the analyte mass.
   Second, the precipitate must be easy to separate from the reaction mixture.

2. **Steps Involved in Gravimetric Analysis include**

   Preparation of the solution
   Precipitation
   Digestion
   Filtration
   Washing
   Drying or Ignition
   Weighing
   Calculation

3. Gravimetric analysis is a quantitative analysis which involves estimation of the weight of an element or definite compound of the element. It entails isolating and weighing an element or a definite compound of the element in a pure form.

5.0 CONCLUSION

Precipitation gravimetric method is an accurate and precise analytical method for the quantitative determination of the amount/mass of an analyte, for it to be a useful analytical tool, the precipitate must accurately reflect the mass of the analyte. To achieve this, the solubility of the precipitate must be low, of high purity and of known composition. Secondly, the precipitate should be of large crystal size to be easily filterable.

6.0 SUMMARY

Precipitation gravimetry is a useful analytical technique used for the separation and quantitative determination of an analyte in a sample. The important attributes of an analytical precipitate that ensures the precipitate's accuracy and precision is that, the precipitate should be of low solubility, high purity, known composition and easily filterable.

To obtain a precipitate of low solubility;

- The precipitation equilibrium of the precipitate should be taken into account
- The pH of the solution in which the precipitate forms should be adjusted to maintain low solubility of the precipitate.
- Solubility can often be decreased by using a non-aqueous solvent.

To obtain a precipitate of high purity;

- The precipitate should be re-precipitated
- Digested
- Washed
- The analyte or the interferent should be masked

The following steps are involved in gravimetric analysis

- Preparation of the solution
- Precipitation
- Digestion
- Filtration
- Washing
- Drying or Ignition
- Weighing
- Calculation

CLASS ACTIVITY (THE TUTOR TO DIRECT)

1. State and explain briefly three common impurities that can occur in a precipitate.
2. What is the von Wiermarn ratio? Define the terms in it.
3. What information concerning optimum conditions of a precipitate does the von Wiermarn ratio give?
4. Why must a wash liquid generally contain an electrolyte?

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UNIT 2 – QUALITATIVE ANALYSIS OF CATIONS

1.0 INTRODUCTION

2.0 INTENDED LEARNING OUTCOMES (ILOs)

3.0 MAIN CONTENT

3.1 Principles of Qualitative Inorganic Analysis

In-text Question

3.2 Detecting Cations

3.4 Experimental

In-text Question

4.0 SELF – ASSESSMENT EXERCISE (s)

5.0 CONCLUSION

6.0 SUMMARY

7.0 REFERENCES/ FURTHER READING

UNIT 2 – QUALITATIVE ANALYSIS OF CATIONS

3.1 Principles of Qualitative Analysis
https://www.youtube.com/watch?v=Y1zWFMBl5vo

3.2 Detecting Cations
https://www.youtube.com/watch?v=jltLlzZ6FqU

1.0 INTRODUCTION

Chemical analysis can be either qualitative or quantitative in nature. Qualitative analysis deals with identification of the substances present in a given sample. For inorganic compounds, qualitative analysis often involves the identification of ions present in a sample. You will be given an aqueous solution containing a mixture of several metal cations that you must identify. The techniques you will learn can be used to identify ions occurring in other types of samples such as minerals, ground water and industrial waste streams. The procedures used will provide you with an opportunity to apply principles learned from your CHEM 202. These principles include those involved in acid-base chemistry, oxidation-reduction reactions, ionic equilibrium, precipitation reactions and complex ion formation.

2.0 INTENDED LEARNING OUTCOMES (ILOs)

After studying this unit, you should be able to:

- Apply principles of qualitative analysis for identification of some of the more common metal ions.

3.0 MAIN CONTENT

3.1 Principles of Qualitative Analysis

1. Separation**:** These are procedures that separate groups of ions from other groups, or individual ions in a mixture of ions.

Focusing on our goal to correctly identify the metal cations that are present in our unknowns, the simplest scheme we can imagine would involve one that has a specific reagent to test for each different cation. In such a scheme, each reagent would be required to give an easily recognized confirmation test, such as color change or precipitate formation, for only one of the cations in the mixture, regardless of the other cations present. However, different metal cations can sometimes exhibit similar behavior and a specific reagent for each separate cation is not possible. In other words, individual components in our unknowns would most likely interfere with one another. Therefore, in the scheme that we will employ, reagents will be used to separate the ions in our samples into groups. Each group will then be analyzed for the presence or absence of individual metal cations. The most common way to subdivide into smaller groups is by selective precipitation, in which a small group of cations is chemically precipitated. The ions in the

precipitate can then be physically separated from those remaining in solution by centrifuging. The precipitate (solid) settles out and the solution (supernatant) is transferred into another container. In this way, the initial large group is separated into smaller and smaller groups until definitive tests can be run to confirm the presence or absence of each specific cation.

It is important to recognize the distinction between each group in qualitative analysis and the groups of the Periodic Table (alkali metals, transition metals, etc.); the cations in each group do not necessarily correlate with groups in the Periodic Table. Periodic Table groups are based upon similarities in electron configurations that result in similar behaviours of the elements within the group. Some of the cations in our groupings do fall within the same Group in the Periodic Table, and others do not. The Groups we use in qualitative analysis are based solely upon the solubility behavior of the cations under specific conditions. For example, Group 1consists of cations that form insoluble chlorides in acidic solution. Within each of these Groups, the analysis may require that there be further separations into subgroups. A specific or confirmatory test will be carried out for each ion when separations have ensured that interfering ions have been removed. Sometimes this will mean isolation of a given ion from all other cations. In other cases, it will be possible to carry out confirmatory tests in the presence of one or more other cations of the same group. To be successful, care must be taken to follow the procedures carefully; components that are not separated correctly may interfere with later tests.

2. Confirmatory Tests: These are tests that determine conclusively that a certain ion is present. Interfering ions are removed before a confirmatory test is done.

In-text Question

Explain the two aspects of chemical analysis

Answer

Chemical analysis can either be qualitative or quantitative in nature. Qualitative analysis deals with identification of the substances present in a given sample.

3.2 Detecting Cations

According to their properties, cations are usually classified into five or six groups. Each group has a common reagent which can be used to separate them from the solution. To obtain meaningful results, the separation must be done in specified sequence, as some ions of an earlier group may also react with the reagent of a later group, causing ambiguity as to which ions are present. This happens because cationic analysis is based on the solubility products of the ions. As the cation gains its optimum concentration needed for precipitation it precipitates and hence allowing us to detect it.

In general, concentrations of reagents and pH are adjusted such that only one group is affected by the precipitating reagent. Once a select group is precipitated out of solution, it is removed by first centrifuging the mixture to get all the precipitate out and then collecting the supernatant

(potentially containing other groups) by a process called decanting. In a mixed solution, the supernatant can be further tested for other groups by selective precipitation and the remaining precipitate can be tested for Group members by further selective precipitation and confirmatory test. The division and precise details of separating into groups vary slightly from one source to another; given below is one of the commonly used schemes.

Group I Cations

This consists of ions that form insoluble chlorides. As such, the reagent used to separate this group is hydrochloric acid, usually used at a concentration of 1–6 M. Concentrated HCl must not be used, because it forms a soluble complex ion ($[PbCl_4]^{2-}$) with Pb^{2+}. Consequently the Pb^{2+}ion would go undetected. The most important cations in 1st group are Ag^+, $H_2^{2+}$and Pb^{2+}. The chlorides of these elements cannot be distinguished from each other by their colour - they are all white solid compounds. $PbCl_2$ is soluble in hot water, and can therefore be differentiated easily. Ammonia is used as a reagent to distinguish between the other two. While AgCl dissolves in ammonia (due to the formation of the complex ion $[Ag(NH_3)_2]^+$, Hg_2Cl_2 gives a black precipitate consisting of a mixture of chloro-mercuric amide and elemental mercury.
Furthermore, AgCl is reduced to silver under light, which gives samples a violet colour.
When the required concentration of HCl is added to a solution containing metal ions, the presence of a white precipitate indicates the presence of one or more Group I cations. If no precipitate forms, there were no Group I cations present in the solution and you can proceed with testing for Group II cations.

$PbCl_2$ is far more soluble than the chlorides of the other two ions, especially in hot water. Therefore, HCl in concentrations which completely precipitate $Hg^{2+}{}_2$ and Ag^+ may not be sufficient to do the same to Pb^{2+}. Higher concentrations of Cl^- cannot be used for the before mentioned reasons. Thus, a filtrate obtained after first group analysis of Pb^{2+} contains an appreciable concentration of this cation, enough to give the test of the second group, viz. formation of an insoluble sulfide. For this reason, Pb^{2+} is usually also included in the 2nd analytical group.

The procedure for determining group I cations involves adding the sample in water and then adding dilute hydrochloric acid. A white precipitate is formed.

The precipitation reactions are:

$Ag^+ + Cl^- \longrightarrow AgCl$ (white)
$Hg^{2+} + 2\ Cl^- \longrightarrow Hg_2Cl_2$ (white)

$Pb^{2+} + 2\ Cl^- \longrightarrow PbCl_2$ (white)

The precipitate is separated out of solution by centrifuging the solution in a balanced centrifuge and the supernatant is decanted into a separate test tube. Approximately 5 ml of distilled water is added to the precipitate and heated in a **waterbath** for 5 minutes with stirring. The remaining precipitate is centrifuged. The supernatant is decanted into a different test tube leaving behind the precipitate. The precipitate is saved for further testing of Ag^+ and $Hg_2{}^{2+}$. Lead (II), Pb^{2+}, is the

only cation of Group I that is soluble in hot water. Therefore the supernatant must be tested for the presence of **Pb^{2+}**.

Confirmation of the presence of lead

To the supernatant 2-3 drops of 6M acetic acid (CH_3COOH) and 3-4 drops of 1M K_2CrO_4 **is added.** The formation of yellow precipitate of lead chromate, $PbCrO_4$, confirms the presence of lead. It may be necessary to centrifuge the solution in order to see the precipitate as it may be masked by the orange color of the K_2CrO_4 reagent.

$$Pb^{2+} + K_2CrO_4 \rightarrow PbCrO_4 + 2\ K^+$$

Confirmation of the presence of silver

It is now necessary to consider the precipitate which may be comprised of AgCl or Hg_2Cl_2 or a mixture of the two. By adding NH_4OH to the solution, the AgCl and Hg_2Cl_2 can be separated.

$AgCl + 2\ NH_4OH \longrightarrow Ag(NH_3)_2^+ + Cl^- + 2H_2O$

And

$Hg_2Cl_2 + 2NH_4OH \longrightarrow Hg(black) + Hg(NH_2)Cl(white) + 2H_2O + NH_4^+ + Cl^-$

With the addition of ammonium , if the precipitate is insoluble, then Pb^{2+} is present; if the precipitate is soluble, then Ag^+ is present, and if the white precipitate turns black, then Hg_2^{+2} is present.

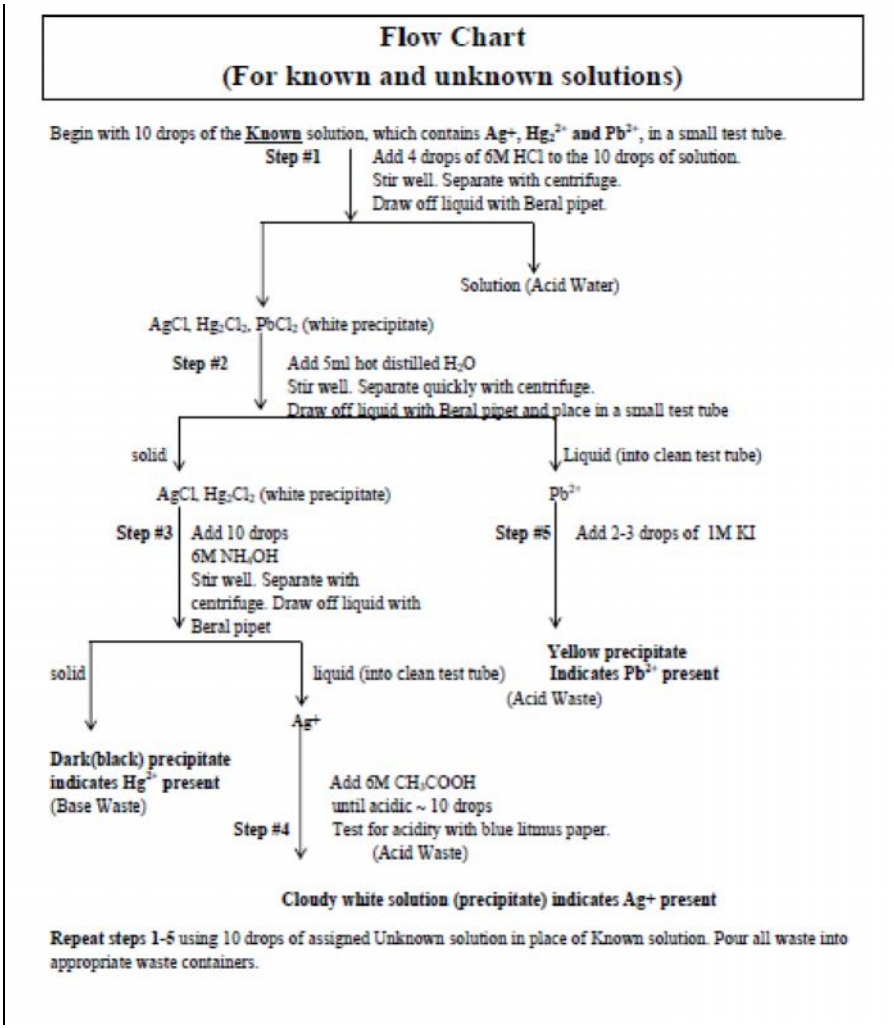

Fig 22: Flow diagram for known and unknown solutions

Group II Cations

This consists of ions that form acid-insoluble sulphides. Cations in the 2nd group include: Cd^{2+}, Bi^{3+}, Cu^{2+}, As^{3+}, As^{5+}, Sb^{3+}, Sb^{5+}, Sn^{2+}, Sn^{4+} and Hg^{2+}. The Group II cations are chloride soluble ions and consequently they are readily separated from the slightly soluble Group I chloride insoluble cations. They can be further separated into groups through selective precipitation of a number of sulphides. HgS, Bi_2S_3, CuS, SnS and SnS_2 precipitate from reaction with H_2S in 0.3M H^+. Because any of the Group I cations (**$Ag^+$and Hg^{2+}**) have already been removed with the Group I precipitation, we do not have to worry about precipitation of Ag_2S or Hg_2S, even though they will react with H_2S**.**

Note: Even though Pb_{2+} ions are precipitated and filtered off as $PbCl_2$ in the Group 1 analysis, there may be enough residual Pb_{2+} in solution to precipitate as PbS. Consequently, many analytical schemes will place Pb_{2+} in both groups I and II.

None of the other sulphides of the other groups will precipitate out from H_2S at 0.3M H+ as they have high equilibrium constants. Consequently, by adding H_2S to the solution after the Group I cations have been removed and adjusting the pH to 0.3M H_+, we can remove **Hg^{2+}, Bi^{3+}, Cu^{2+}, Cd^{2+}, Pb^{2+}, $Sn^{2+}$and Sn^{4+}**according to the following precipitation reactions:

$Hg^{2+} + H_2S \longrightarrow HgS\ (black) + 2H^+ + 2Cl^-$

Or

$HgCl_2\ (aq) + H_2S \longrightarrow HgS + 2H^+ + 2Cl^-$

$2Bi^{3+} + 3H_2S \longrightarrow Bi_2S_3\ (brown) + 6H^+$

$Cu^{2+} + H_2S \longrightarrow CuS\ (black) + 2H^+$

$Cd^{2+} + H_2S \longrightarrow CdS\ (yellow) + 2H^+$

$Sn^{2+} + H_2S \longrightarrow SnS\ (brown) + 2H^+$

And

$Sn^{4+} + 2H_2S \longrightarrow SnS_2\ (yellow) + 4H^+$

The precipitation procedure will result in a mixture of a number of sulphides. It is necessary to separate and identify the components of the sulphide mixture.

If Sn is present, or thought to be present, it is first necessary to treat the solution with a little H_2O_2 in order to oxidize Sn_{2+} to Sn_{4+} before the Group II sulphides are precipitated by H_2S. Once the Group II cations are precipitated, SnS can be removed from the bulk by dissolving it in ammonium sulphide $(NH_4)_2S$ as it is the only Group II sulphide that is soluble in ammonium sulphide.

Note: HgS, Bi_2S_3, PbS, CdS and CuS can be separated by differential solubility. HgS is insoluble in nitric acid while the rest of the group II cations are soluble. Therefore, when the sulphide precipitate is treated with HNO_3, HgS and S should remain as a precipitate while the rest of the cations should remain in solution. Although HgS does not dissolve in HNO_3, it will dissolve in aqua regia (HCl and HNO_3 mixed) and the resultant $HgCl_2$ can be used to confirm its presence. The reaction equation is as follows:

$3HgS + 2NO_3^- + 6Cl^- + 8H^+ \longrightarrow 3HgCl_2\ (aq) + 2NO + 3S + 4H_2O$

$SnCl_2$ (stannous chloride) is then added to the resultant $HgCl_2$. Sn_{2+} is oxidized to Sn_{4+} and disproportionationoccurs when $HgCl_2$ is reduced to $Hg_2Cl_{2\ (s)}$ (white) and $Hg_{\ (s)}$ (black).

Pb^{2+}can be removed from the cation mixture by precipitation with $(NH_4)_2SO_4$ as $PbSO_4$. The $PbSO_4$ can then be dissolved in ammonium acetate ($NH_4C_2H_3O_2$) and the lead precipitated out as yellow $PbCrO_4$ upon reaction with K_2CrO_4.

$Pb^{2+} + (NH_4)_2SO_4 \longrightarrow PbSO_4 + 2NH_4^+$

Bi^{3+}can be removed from $Cu^{2+}$and $Cd^{2+}$by the addition of NH_4OH to the solution. Bi^{3+}forms a white precipitate ($Bi(OH)_3$) while $Cu^{2+}$and Cd^{2+}remain in solution. Reaction of $Bi(OH)_3$with sodium stannite gives rise to black elemental bismuth. The $Cu(NH_3)_4^{2+}$ formed, when copper ispresent, gives the solution a blue color.

Separation of $Cu^{2+}$from Cd^{2+} is done by the reduction of $Cu^{2+}$to elemental copper using sodium dithionite as a reducing agent. Reaction of the isolated cadmium with thioacetamide gives rise to the yellow sulphide precipitate of CdS.

$Bi^{3+} + 3NH_4OH \longrightarrow Bi(OH)_3(white) + 3NH_4^{2+}$

$Bi(OH)_3(s) + 2Sn(OH)_3^-(aq) + 3\ OH^- \longrightarrow 2Bi\ (s)\ (black) + 3Sn(OH)_6^{2-}(aq)$
(Stannite) (Stannate)

$Cu^{2+} + 4NH_4OH \longrightarrow Cu(NH_3)_4^{2+}(blue) + 4H_2Oor$

$Cu^{2+} + 4NH_3 \longrightarrow Cu(NH_3)_4^{2+}$

$Cu2+ + Na2S2O4 \longrightarrow Cu(s) + SO32- + 2Na+$

$Cd^{2+} + H_2S \longrightarrow CdS + 2H^+$

Group III Cations

This group includes ions that form hydroxides which are insoluble even at low concentrations. The reagents are similar to those of the 2nd group, but separation is conducted at pH of 8–9. Occasionally, a buffer solution is used to ensure this pH.

Cations in the 3rd group are, among others: Fe^{2+}, Fe^{3+}, Al^{3+}, and Cr^{3+}.

The group is determined by making a solution of the salt in water and adding ammonium chloride and ammonium hydroxide. Ammonium chloride is added to ensure low concentration of hydroxide ions.

The formation of a reddish brown precipitate indicates Fe^{3+}; a gelatinous white precipitate indicates $Al^{3\pm}$; and a green precipitate indicates Cr^{3+} or Fe^{2+}. These last two are distinguished by adding sodium hydroxide in excess to the green precipitate. If the precipitate dissolves, Fe^{2+} is indicated; otherwise, Cr^{3+} is present.

Group IV Cations

The fourth group of cations includes Zn^{2+},Ni^{2+},Co^{2+}, and Mn^{2+}. Of these, Zinc salts are colourless, Manganese salts are faint pink or colourless, and nickel and cobalt salts may be brightly coloured, often blue-green. The precipitate, washed in water is reacted with extremely dilute hydrochloric acid. This precipitates nickel salts, if any. The supernatant liquid is filtered and reacted with excess of Sodium Hydroxide. This precipitates any Manganese salts. Hydrogen sulphide is passed through the supernatant liquid. If a white precipitate forms, Zinc is present.

Some sources group Group III and Group IV cations as Group III cations.

Group V Cations

Ions in 5th analytical group of cations form carbonates that are insoluble in water. The reagent usually used is $(NH_4)_2CO_3$(at around 0.2 M), with a neutral or slightly basic pH. All the cations in the previous groups are separated beforehand, since many of them also form insoluble carbonates.

The most important ions in the 5th group are Ba^{2+}, Ca^{2+}, and Sr^{2+}. After separation, the easiest way to distinguish between these ions is by testing flame colour: barium gives a yellow-green flame, calcium gives orange-red, and strontium, deep red.

Group VI Cations

Cations which are left after carefully separating previous groups are considered to be in the sixth analytical group. The most important ones are Mg^{2+}, Li^{+}, $Na^{+}$and K^{+}. All the ions are distinguished by flame color: lithium gives a red flame, sodium gives bright yellow (even in trace amounts), potassium gives violet, and magnesium, bright white.

Table 13: Scheme for separation of cations

<table>
<tr><td colspan="7">Scheme for separation of cations</td></tr>
<tr><td colspan="7">HCl or a soluble chloride, preferably NH_4Cl, added to unknown; filtered</td></tr>
<tr><td rowspan="4">precipitate: contains chlorides of lead (Pb), silver (Ag), and mercurous mercury (Hg)

$PbCl_2$ (white)
AgCl (white)
Hg_2Cl_2 (white)

Group I</td><td colspan="6">solution: H_2S passed into the acid solution; filtered</td></tr>
<tr><td colspan="2">precipitate: treated with NH_4OH; ammonium polysulfide $(NH_4)_2S_x$; and $(NH_4)_2S$; filtered</td><td colspan="4">solution: neutralized with NH_4OH and NH_4Cl; filtered</td></tr>
<tr><td rowspan="2">precipitate: contains cupric, lead, cadmium, bismuth, and mercuric sulfides

Group IIa</td><td rowspan="2">solution: contains arsenic, antimony, and tin cations

Group IIb</td><td rowspan="2">precipitate: contains aluminum (Al), chromium (Cr), and ferric (Fe) hydroxides

$Al(OH)_3$ (white)
$Cr(OH)_3$ (gray-green)
$Fe(OH)_3$ (brown)

Group IIIa</td><td colspan="3">solution: H_2S passed into alkaline solution; filtered</td></tr>
<tr><td>precipitate: contains cobalt (Co), nickel (Ni), manganese (Mn), and zinc (Zn) sulfides

CoS (black)
NiS (black)
MnS (buff)
ZnS (white)

Group IIIb</td><td colspan="2">solution: evaporated and NH_4OH and $(NH_4)_2CO_3$ added; filtered</td></tr>
<tr><td>precipitate: barium, strontium, and calcium carbonates (all white)

Group IV</td><td>solution: contains magnesium, sodium, and potassium ions

Group V</td></tr>
</table>

EXPERIMENT 1 – Identification of Cations in an Unknown Mixture

Purpose: To separate and identify individual cations in an unknown solution containing a mixture of two to three cations.

Table 14: Equipment / Materials:

Centrifuge	Hot Plates	1 M KI
Test tubes (6 small, 2 medium)	Small beaker	6 M CH_3COOH
Test tube rack	Red litmus paper	
Stirring rods	6 M HCl	
Pipets	6 M NaOH	

In this experiment use the information gathered from group I cations separation scheme to identify the cations present in the sample given.

Experimental Procedure:

Obtain an unknown solution. The unknown solution contains between 1, 2, and 3 cations (or A,B, and C). After recording the **unknown number**_____ you are to analyze your unknown and identify the cations present. During the analysis you are to take careful notes of the procedures you follow, recording all tests and observations. After completing your analysis, explain which cations are present and which are absent and how you arrived at these conclusions.

- Take 20 drops of the unknown solution in a clean medium test tube and dilute the solution using 5 mL deionized water.
- Add 10-15 drops of 6.0 M HCl. If there is no precipitate, go to next step.

For each cation, one of the tests confirms the presence or the absence of the ion in solution. The test that produced a very dramatic change for one of the ions with little or no change for the others is the confirmatory test for that ion. Briefly summarize the confirmatory test for each ion in the space provided.

Report should state the identity of all cations present in the unknown. Use a **flowchart** to provide the evidence for the presence of the identified cations. Record the cations and record your observations following each experiment in space provided in steps 1-5 on report form.

In-text Question

Hg_2Cl_2 gives a black precipitate consisting of a mixture of

Answer

Chloro-mercuric amide and elemental mercury.

In-text Question

In group 1 cation, $PbCl_2$ is easily differentiated because

Answer

They are soluble in hot water

4.0SELF- ASSESSMENT EXERCISES

1. State which aspect of chemical reaction will qualitative analysis be applied.
2. State the main objective of qualitative analysis
3. The most distinguishing factor in qualitative analysis is ---------?
   Balance the equation below
4. $Cu^{2+} + NH_3 \longrightarrow Cu(NH_3)_4^{2+}$

5. Cu2+ + Na2S2O4 Cu(s) + SO32- + Na+

6. $Cd^{2+} + H_2S \rightarrow CdS + H^+$

Answers

1. It can be applied in acid-base chemistry, oxidation-reduction reactions, ionic equilibrium, complex ion formation etc.
2. The objective of qualitative analysis is to apply the principles of qualitative analysis for identification of some of the more common metal ions.
3. Colour is the most distinguishing factor in qualitative analysis

The equations below is balanced as

4. $Cu^{2+} + 4NH_3 \text{ — } Cu(NH_3)_4^{2+}$
5. Cu2+ + *Na2S2O4*—Cu(s) + SO32- + 2Na+
6. $Cd^{2+} + H_2S$ —CdS + $2H^+$

5.0 CONCLUSION

Qualitative analysis of cations can be used to separate cations from ions in solution. Cations are typically divided into Groups, while each group shares a common reagent that can be used for selective precipitation. The ions in a given group are first separated from each other, and then a characteristic test is performed for each ion in order to confirm the presence of that ion. Qualitative analysis of cations can be employed in the detection of cations in samples. E.g. water sample e.t.c.

6.0 SUMMARY

In carrying out qualitative analysis of cations, a sequence of separation scheme is followed to separate groups of ions from groups. The ion or ions of interest in the group is separated into individual ions in a mixture of ions. This is followed by confirmatory test to identify the separated ion.

CLASS ACTIVITY (THE TUTOR TO DIRECT)

1. Differentiate between Qualitative analytical groups and Groups of the periodic table.

2. A water sample is suspected to be contaminated by Hg (II) ions. How could you determine if the sample is really contaminated?

3. How would you separate Pb^+ from Ag^+?

7.0 REFERENCES/ FURTHER READING

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UNIT 3 – POTENTIOMETRIC TITRATION

1.0 INTRODUCTION

2.0 INTENDED LEARNING OUTCOMES (ILOs)

3.0 MAIN CONTENT

3.1 Principles of Potentiometric Titration

In-text Question

3.2 Potentiometric measurements.

3.3 Location of End Point in Potentiometric Titration.

3.4 Types of Potentiometric Titration.

3.4.1 Redox reaction: determination using potentiometry.

3.5 Advantages of Potentiometric Titrations over Classical Visual Indicator Methods.

3.6 Experimental.

In-text Question

4.0SELF-ASSESSMENT EXERCISES

5.0CONCLUSION

6.0 SUMMARY

7.0 REFERENCES/ FURTHER READING

UNIT 3 – POTENTIOMETRIC TITRATION

3.1 Principle of Potentiometric Titration
https://www.youtube.com/watch?v=JwCeCS2YRVo

3.2 Potentiometric Measurements
https://www.youtube.com/watch?v=0-nbyzUplyU

3.3 Location of End Point in Potentiometric Titration
https://www.youtube.com/watch?v=zDcx-rli3tg
3.4 Types of Potentiometric Titration
https://www.youtube.com/watch?v=oPsPMDWK94g

1.0 INTRODUCTION

An indicator is used to detect the end point of a reaction in titrimetric analysis. However, if no visible indicator is available, the detection of the equivalence point can often be achieved in other ways such as; potentiometric titration, coulometric titration, amperometric titration etc.

Potentiometric titration is an analytical method. As the name implies, it is a titrimetric procedure in which potentiometric measurements are carried out in order to fix the end point. In this procedure we are concerned with changes in electrode potential. In such a titration, the change in cell e.m.f occurs rapidly in the neighborhood of the end point. **Potentiometric titrations offer additional advantages over direct potentiometry, due to the fact that the measurement is based on the titrant volume which causes a rapid change in potential close to the equivalent point.**

In this unit, we shall examine the principle of potentiometric titration, after which we perform some potentiometric titration experiments using the knowledge gathered.

2.0 INTENDED LEARNING OUTCOMES (ILOs)

After studying this unit, you should be able to:

- Explain the principle of potentiometric titration
- Determine the end point of a potentiometric titration
- Carry out potentiometric titration experiments

3.0 MAIN CONTENT

3.1 Principle of Potentiometric Titration

In a potentiometric titration, the potential of an indicator electrode is measured as a function of the volume of titrant added **but they are not dependent on measuring absolute values E_{cell}. This makes the titration relatively free from junction potential uncertainties because the junction potential remains approximately constant during titration.Potentiometric titration involves measurement of the potential of a suitable indicator electrode as a function of titrant volume. It provides information that is not the same as that obtained from a direct potentiometeric measurement. It provides data that are more reliable than data from titration that use chemical indicators and they are particularly useful with coloured or turbid solutions and for detecting the presence of unsuspected species.**The equivalence point of the reaction will be revealed by a sudden change in potential in the plot of e.m.f. readings against the volume of the titrating solution; any method which will detect this abrupt change of

potential may be used. One electrode must maintain a constant, but not necessarily known potential; the other electrode, which indicates the changes in ion concentration, must respond rapidly. Throughout the titration, the analyte solution must **be stirred** thoroughly.

In titrimetric analysis, the titrand is titrated against the titrant, the end of the reaction is indicated by a change in colour of the indicator. In potentiometric titration as the titrant is added to the titrand, there is change in electrode potential. The principle involved in potentiometric titration is the measurement of the e.m.f. between two electrodes, an indicator electrode and a reference electrode. In these titrations, measurement of e.m.f. is made while the titration is in progress. The equivalence point of the reaction is revealed by a sudden change in potential in the plot of e.m.f. readings against the volume of the titrant. The reference electrode potential is independent of solution; the cell potential is a measure of the indicator electrode potential.
A simple arrangement for a manual potentiometric titration is given in Figure 23. A is a reference electrode (e.g a saturated calomel half-cell), B is the indicator electrode. The solution to be titrated is normally contained in a beaker fitted with a magnetic stirrer. When titrating solutions that require exclusion of air or atmospheric carbon dioxide, a three or four necked flask is used to enable nitrogen to be bubbled through the solution before and during the titration.

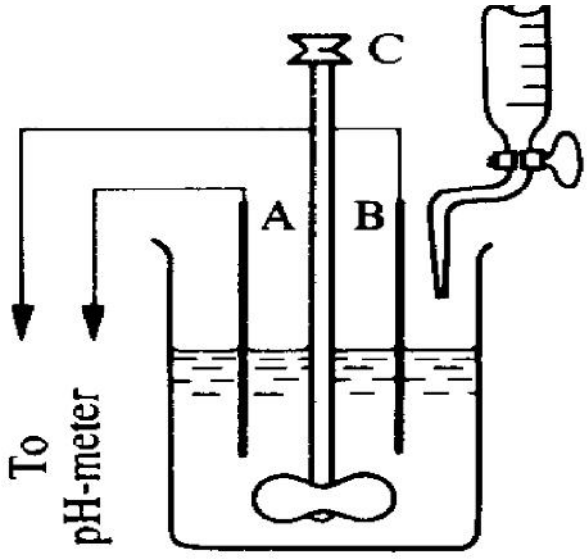


Figure 23: Arrangement for potentiometric titration

The e.m.f. of the cell containing the initial solution is determined, and relatively large increments (1-5mL) of the titrant solution are added until the equivalence point is approached; the e.m.f. is determined after each addition. The approach of the equivalence point is indicated by a somewhat more rapid change of the e.m.f. In the vicinity of the equivalence point, equal increments (e.g. 0.1 or 0.05 mL) should be added. Sufficient time should be allowed after each addition for the indicator electrode to reach a reasonably constant potential(+1, – 2 mV) before the next increment is introduced. Several points should be obtained well beyond the equivalence point. To measure the e.m.f., the electrode system is usually connected to a pH meter that can function as a millivoltmeter so that e.m.f. values are recorded. Used as a millivoltmeter, pH meters can be employed with almost any electrode assembly to record the results of many different types of potentiometric titrations, and in many cases the instruments had provision for

connection to a recorder so that a continuous record of the titration results could be obtained usually in the form of a titration curve.

In-text Question

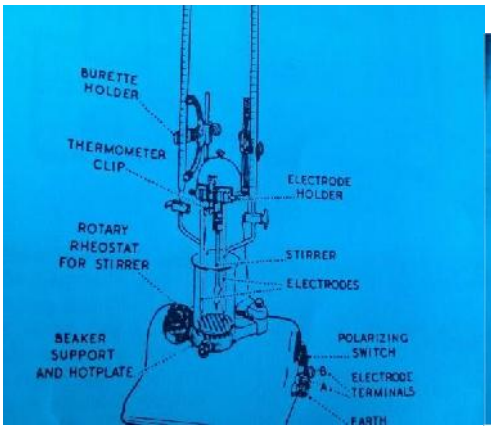
In titrimetric analysis, the — is titrated against the —, the end of the reaction is indicated by —

Answer

Titrand, titrant and a change in colour of the indicator.

3.2 Potentiometric Measurements

We use a potentiometer to determine the difference between the potential of two electrodes. The potential of one electrode- the working or indicator electrode- responds to the analyte's activity, and the other electrode- the counter or reference electrode has a known, fixed potential.



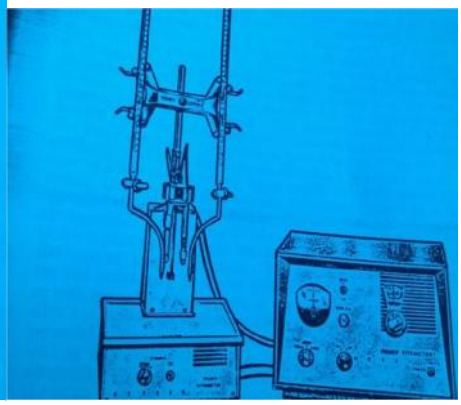


Figure 24. 1: potentiometer Figure 25.2: potentiometer

In figure 24 and 25, the titration unit comprises a strong cast aluminum stand fitted with two burette holders, electrode holders, a thermometer clip, hot plate, beaker support and motor-driven stirrer. A rheostat is fitted in the base to control the speed of stirring. Terminals are provided for connection to a potentiometer, and a third terminal for connection to earth.

3.3 Location of End Point in Potentiometric Titration

Generally speaking, the end point of a titration can be most easily fixed by examining the titration curve, including the derivative curves to which this gives rise, or by examining a Gran's plot. When a titration curve has been obtained – i.e. a plot of e.m.f. readings obtained with the normal reference electrode-indicator electrode pair against volume of titrant added, either by manual plotting of the experimental readings, or with suitable equipment, plotted automatically during the course of the titration – it will in general be of the same form as the neutralization curve for an acid, i.e. an S-shaped curve (figure 26 and 27).

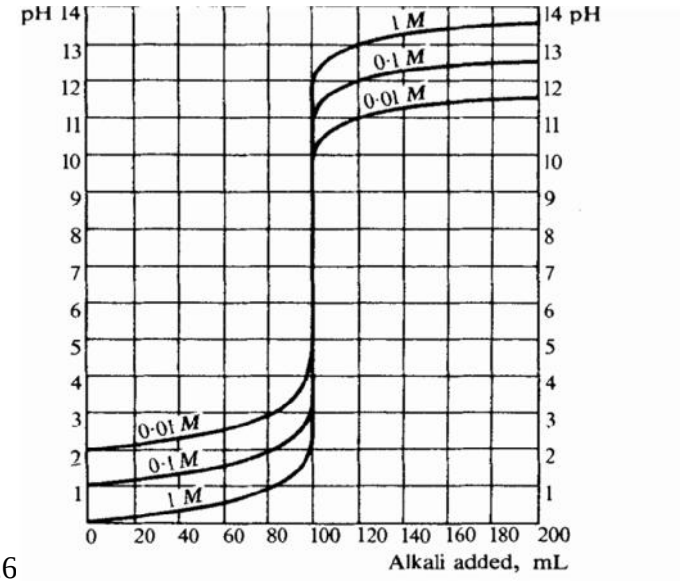


Figure 26

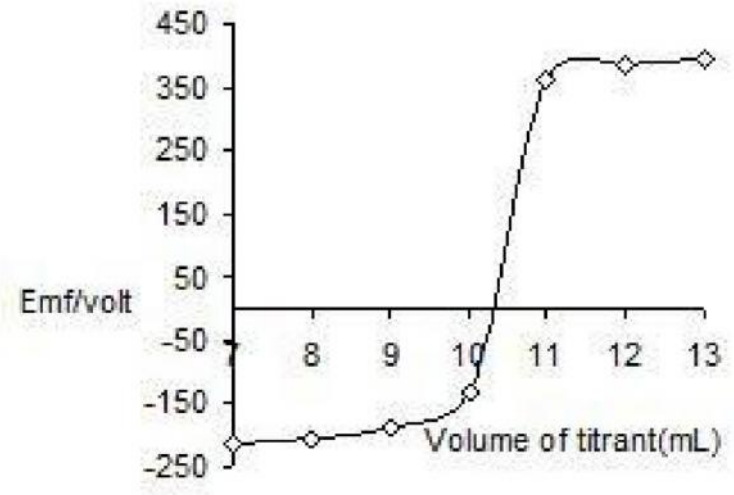


Figure 27: Titration methods of locating end point

The central portion of this curve is shown in Figure 26 and 27, and clearly the end point will be located on the steeply rising portion of the curve; it will in fact occur at the point of inflexion. When the curve shows a very clearly marked steep portion, although one can give an approximate value of the end point as being midway along the steep part of the curve, it is usually preferred to employ analytical (or derivative) methods of locating the end point. Analytical methods consist in plotting the first derivative curve ($\Delta E/\Delta V$ against V), or the second derivative curve ($\Delta^2E/\Delta V^2$ against V). The first derivative curve gives a maximum at the point of inflexion of the titration curve, i.e. at the point, whereas the second derivative curve ($\Delta^2E/\Delta V^2$) is zero at the point where the slope of the $\Delta E/\Delta V$ curve is a maximum.

The Gran's plot procedure is a relatively simple method for fixing an end point. If a series of additions of reagent are made in a potentiometric titration, and the cell e.m.f. E is read after each addition, then if antilog (EMF/2.303RT) is plotted against the volume of reagent added, a straight

line is obtained which, when extrapolated, cuts the volume axis at a point corresponding to the equivalence point volume of the reagent; plotting is simplified if the special semi-antilog Gran's plot paper is used. The particular advantage of this method is that the titration need not be pursued to the end point to permit a straight line to be drawn, and the greatest accuracy is achieved by using results over the last 20% of the equivalence point volume.

Potentiometric titrations, when performed manually, can take a considerable time. A number of commercial automatic titrators are available for potentiometric titrations. The electrical measuring unit may be coupled to a chart recorder to produce a titration curve directly. The delivery of the titrant from an automatic burette is linked to the movement of the recorder, giving an autotitrator. Instruments will also plot the first derivative curve ($\Delta E/\Delta V$) and the second derivative ($\Delta^2 E/\Delta V^2$), and will provide a Gran's plot. A most important feature is the facility to stop the delivery of the titrant when the equivalence potential has been reached.

3.4 Types of Potentiometric Titration

As with classical titrimetry, potentiometric titrations involve chemical reactions and can be classified as (a) neutralization reactions, (b) complexation reactions, (c) precipitation reactions and (d) oxidation–reduction reactions.

3.4. 1 Redox reaction: Determination using potentiometry

A redox titration is based on an oxidation–reduction reaction between analyte and titrant. Because there is generally no difficulty in finding a suitable indicator electrode, redox titrations are widely used; an inert metal such as platinum is usually satisfactory for the electrode. ↔

The determining factor for redox titration by potentiometry is the ratio of the concentrations of the oxidized and reduced forms of certain ion species. For the reaction

Oxidized form + n electrons ↔ reduced form

The potential E acquired by the indicator electrode at 25^0C is given by E

$= E^{\Theta} + 0.0591/n \log [ox]/[red]$

Where E^{Θ} is the standard potential of the system. The potential of the immersed electrode is thus controlled by the ratio of these concentrations. During the oxidation of a reducing agent or the reduction of an oxidizing agent the ratio, and therefore the potential, changes more rapidly in the vicinity of the end point of the reaction. Thus titrations involving these reactions (e.g iron (II) with potassium permanganate or potassium dichromate or cerium (IV) sulphate may be followed potentiometrically and produce titration curves characterized by a sudden change of potential at the equivalence point.

3.5 Advantages of Potentiometric Titrations over Classical Visual Indicator Methods

1. It can be used for coloured, turbid or fluorescent analyte solution.
2. It can be used if there is no suitable indicator or the colour change is difficult to ascertain.
3. It can be used in the titration of polyprotic acids, mixtures of acids, mixtures of bases or mixtures of halides.

4. **Potentiometric instrument merely signals the end point and thus behaves in an identical fashion to a chemical indicator.**

5. **The other advantage is that the result isanalyte concentration even though the electrode responds to activity, therefore ionic strength effects are not important in the titration procedure.**

6. **In potentiometric titration, the reference electrode potential does not need to be known accurately.**

EXPERIMENT – 1 Redox Titration of Manganese by Potentiometry

Purpose: To determine the end point of redox titration of manganese by potentiometry.

Discussion: The method is based on titrating manganese (II) ions with permanganate in neutral pyrophosphate solution:

$$4Mn^{2+} + MnO_4^- + 15H_2P_2O_7^{2-} = 5Mn(H_2P_2O_7)_3^{3-} + 4H_2O$$

The manganese (III) pyrophosphate complex has an intense reddish violet colour, so the titration must be performed potentiometrically; a combination redox electrode would be used. With relatively pure manganese solutions, a sodium pyrophosphate concentration of 0.2-0.3 M, the potential at the equivalence point can easily be measured at pH 6-7. But at pH greater than 8 the pyrophosphate complex dissociates, hence the method cannot be used.

Table 15: Reagents/Equipment / Materials:

Potassium permanganate	1 mL graduated pipette
Sodium pyrophosphate	pH Meter
Distilled water	Manganese (II) Sulphate
400 mL beaker	NaOH
Concentrated H_2SO_4	Combination redox electrode

Experimental Procedure

Place 150 mL of freshly made sodium pyrophosphate solution (about 12g in 100-150 mL water) in a 250-400 mL beaker, adjust the pH to 6 – 7 by adding concentrated sulphuric acid from a 1 mL graduated pipette (use a pH meter). Add 25 mL of the manganese (II) sulphate solution and adjust the pH again to 6 – 7 by adding 5 M sodium hydroxide solution. Place the combination redox electrode into the solution. It is now ready for autotitration with the standardized permanganate solution. The end point can be obtained either directly or using derivatives. The method can be adapted for manganese in steel or in manganese ores.

EXPERIMENT – 2 Redox Titration of Steel by Potentiometry

Purpose: To determine the end point of redox titration of steel by potentiometry.

Table 16: Equipment / Materials:

Weighing balance	Urea
Steel	
Conc. HNO_3	
HCl	
Kjeldahl flask	

Experimental Procedure

Accurately weigh 5g of steel and dissolve it in 1:1 nitric acid using the minimum volume of hydrochloric acid in a kjedahl flask. Boil the solution down to a small volume with excess concentrated nitric acid to reoxidise any vanadium present reduced by the hydrochloric acid; this step is not necessary if vanadium is absent. Dilute, boil to remove gaseous oxidation products, allow to cool, add 1 g of urea and dilute to 250 mL. Titrate 50.0 mL portions as above.

EXPERIMENT –
3 Redox Titration of Copper by Potentiometry

Purpose: To determine the end point of redox titration of copper by Potentiometry.

Table 17: Equipment / Materials:

Weighing balance	Glacial ethanoic acid
Copper	Potassium iodide
Conc. HNO_3	Combination redox electrode
Urea	Sodium thiosulphate
Conc ammonia solution	

Experimental Procedure

Following the usual methods, prepare a sample solution containing about 0.1 g copper and without interfering elements; any large excess of nitric acid and all traces of nitrous acid must be removed. Boil the solution to expel most of the acid, add about 0.5g urea (to destroy the nitrous acid) and boil again. Treat the cooled solution with concentrated ammonia solution dropwise until the deep blue cuprammonium compound is formed, and then add a further two drops. Decompose the cuprammonium complex with glacial ethanoic acid and add o.2 mL in excess .Too great a dilution of the final solution should be avoided otherwise the reaction between the copper (II) ethanoate and the potassium iodide may not be complete.

Place the prepared copper ethanoate solution in the beaker and add 10 mL of 20% potassium iodide solution. Using a combination redox electrode carry out the normal potentiometric titration procedure with a standard sodium thiosulphate solution as titrant.

4.0 SELF- ASSESSMENT EXERCISES

1. Explain why potentiometric titrations are preferred to direct potentiometry

2. State if the following statements about potentiometric titrations are true or false

a. Potentiometric instrument merely signals the end point and thus behaves in an identical fashion to a chemical indicator.

b. The other advantage is that the result is analyte concentration even though the electrode responds to activity, therefore ionic strength effects are not important in the titration procedure.

c. In potentiometric titration, the reference electrode potential does not need to be known accurately.

3. Distinguish the first derivative curve ($\Delta E/\Delta V$ against V) from the second derivative curve ($\Delta^2E/\Delta V^2$ against V).
4. Enumerate the types of chemical reactions that constitute potentiometric titration

Answers

1. Potentiometric titrations offer additional advantages over direct potentiometry, due to the fact that the measurement is based on the titrant volume which causes a rapid change in potential close to the equivalent point.

2a True (2b) True (2c) True

3 The first derivative curve gives a maximum at the point of inflexion of the titration curve, i.e. at the point, whereas the second derivative curve ($\Delta^2E/\Delta V^2$) is zero at the point where the slope of the $\Delta E/\Delta V$ curve is a maximum.
4 (a) neutralization reactions, (b) complexation reactions, (c) precipitation reactions and (d) oxidation–reduction reactions

5.0 CONCLUSION

In classical titrimetry, the end point of a titrimetric reaction/analysis can be determined by the use of indicators, but where there are no available indicator to detect the end point, potentiometric, coulometric, amperometric methods etc. can be used to determine end point of a reaction. Potentiometric titration can be used to determine the end point of a neutralization reaction, complexation reaction, precipitation reaction and redox reaction.

6.0 SUMMARY

As with classical titrimetry, potentiometric titrations involve chemical reactions which can be classified as neutralization reactions, complexation reactions, precipitation reactions and

oxidation – reduction reactions. In the potentiometric titration, the potential of an indicator electrode is measured as a function of the volume of titrant added. The value of the e.m.f. readings against the volume of the titrating solution added is plotted, this produces a titration curve. The end point of the potentiometric titration can be most easily fixed by determining the titration curve, including the derivative curves to which this gives rise, or by examining a Gran's plot.

CLASS ACTIVITY (CLASS TUTOR TO DIRECT)

1. Discuss briefly the principle of potentiometric titration.

2. How can the end point of a potentiometric titration be located?

3. State the advantages of potentiometric titration over titration using indicator.

7.0 REFERENCES/ FURTHER READING

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UNIT 4 DETERMINATION OF ACIDITY IN WATER AND WASTE WATER

UNIT 4 DETERMINATION OF ACIDITY IN WATER AND WASTE WATER

3.1 SOURCES OF ACIDITY IN WATER AND WASTE WATER
https://www.youtube.com/watch?v=1yvN3B6oafU

3.2 SIGNIFICANCE OF ACIDITY IN WATER
https://www.youtube.com/watch?v=sxicf0Fe3Bo

3.3 METHODS OF ACIDITY MEASUREMENT
https://www.youtube.com/watch?v=UL56Lr_TKTI

1.0INTRODUCTION

Acidity is a measure of the ability of a given water sample to neutralize bases. Acidity is the sum of all titrable acid present in the water sample. Strong mineral acids, weak acids such as carbonic acid, acetic acid present in water sample contributes to acidity of the water. Usually dissolved carbon dioxide (CO_2) is the major acidic component present in the unpolluted surface water. Acid waters are of concern because of their corrosive characteristics, hence, it is important to determine if a water or waste water is acidic and remove or control the corrosion producing substance.

2.0 INTENDED LEARNING OUTCOME (S)

After studying this unit, you should be able to:

- Explain acidity in water
- Discuss the sources of acidity in water and waste water
- Explain the significance of acidity in water
- State and explain the steps involved in determining acidity in a water sample
- Carry out experiments to determine acidity in a water sample

3.0 MAIN CONTENT

3.1 SOURCES OF ACIDITY IN WATER AND WASTE WATER

Combustion of fossil fuels in power plants and automobiles leads to the formation of oxides of nitrogen and sulphur which are released into the atmosphere. In the atmosphere they undergo oxidation to their corresponding acids (HNO_3 and H_2SO_4) which subsequently fall together with rain as acid rain into water bodies and on land. The interaction of water with atmospheric CO_2 leads to the formation of carbonic acid, a weak acid of about pH 5.6 which dissolves in rain and contributes to acidity in water. Carbonic species are also formed when CO_2 enters surface waters. This happens when the concentration of CO_2 in water is less than that in equilibrium with CO_2 in

the atmosphere. Through biological oxidation of organic matter particularly in polluted water, CO_2 produced can also be absorbed by water.

Ground waters and waters from the hypolimnion of stratified lakes and reservoirs often contain considerable amounts of CO_2 resulting from bacterial oxidation of organic matter with which the water has been in contact. Under these conditions, the CO_2 is not free to escape to the atmosphere. Carbon dioxide is an end product of both aerobic and anaerobic bacterial oxidation; therefore, its concentration is not limited by the amount of dissolved oxygen originally present. It is not uncommon to encounter ground waters with 30 to 50 mg/L of CO_2.

Mineral acidity is present in many industrial waste waters particularly those of the metallurgical industry and some from the production of synthetic organic materials. The drainage from abandoned mines and iron ore dumps will contain significant amounts of sulphuric acid or salts of sulphuric acid if sulphur, sulphide or iron pyrite are present. Conversion of these materials to sulphuric acid and sulphate is brought about by sulphur-oxidizing bacteria under aerobic conditions.

$$2S + 3O_2 + 2H_2O \xrightarrow{\text{bact.}} 4H^+ + 2SO_4^{2-} \; FeS_2 +$$

$$3½\ O_2 + H_2O \xrightarrow{\text{bact.}} Fe^{2+} + 2H^+ + 2SO_4^{2-}$$

Salts of trivalent heavy metals particularly e.g. Fe^{3+} and Al^{3+}hydrolyse in water to release mineral acidity.

$$FeCl_3 + 3H_2O \rightleftharpoons Fe(OH)_3 + 3H^+ + 3Cl^-$$

In-text Question

Briefly explain how acid rain is formed

Answer

Combustion of fossil fuels in power plants, automobiles and other high temperature reaction processes leads to the formation of oxides of nitrogen (NO_X) and sulphur (SO_X) which are released into the atmosphere. In the atmosphere they undergo oxidation and in combination with water or moisture form their corresponding acids (HNO_3 and H_2SO_4) which subsequently fall together with rain as acid rain into water bodies and on land.

3.2 SIGNIFICANCE OF ACIDITY IN WATER

Acidity interferes in the treatment of water. Carbon dioxide is of important considerations in determining whether removal by aeration or simple neutralization with lime/lime soda ash or NaOH will be chosen as the water treatment method. The size of the equipment, chemical requirements, storage spaces and cost of treatment all depends on the carbon dioxide present.

Aquatic life is affected by high acidity in water. The organisms present are prone to death with low pH of water. High acidity water is not used for construction purposes, especially in reinforced concrete construction due to the corrosive nature of high acidity water. Water containing mineral acid is not fit for drinking purposes. Industrial waste water containing high mineral acidity must be neutralized before they are subjected to biological treatment or direct discharge into water sources.

3.3 METHODS OF ACIDITY MEASUREMENT

Both CO_2 and mineral acidity can be measured by means of standard solutions of alkaline reagents. Mineral acids are measured by titration to a pH of about 3.7, the methyl orange end point. For this reason, mineral acidity is also called **methyl orange acidity**. Titration of a sample to the phenolphthalein end point of pH 8.3 measures both mineral acidity plus acidity due to weak acids (total acidity). This total acidity is also termed **phenolphthalein acidity.** The volume of standard alkali required to titrate a specific volume of the water sample to pH 8.3 is called phenolphthalein acidity (total acidity). The volume of standard alkali required to titrate a specific volume of the water sample (wastewater and highly polluted) to pH 3.7 is called methyl orange acidity (mineral acidity).

3.3.1 DETERMINATION OF ACIDITY IN NATURAL AND WASTE WATERS

(a) Methyl Orange Acidity: While methyl orange was formerly used for this purpose, bromophenol blue is now recommended as it has a sharper colour change at pH 3.7. The titration is carried out using 0.02M NaOH. Results are reported in terms of methyl orange acidity expressed as $CaCO_3$. That is,

$$\text{Acidity (as mg/L CaCO3)} = \frac{V \times M \times 100000}{\textit{Vol (mL) of water sample}}$$

Where V = mL sodium hydroxide titrant.
M = molarity of sodium hydroxide
The molecular weight of $CaCO_3$ = 100g (=100,000mg)

(b) Phenolphthalein Acidity: This measures the total acidity resulting from both mineral acids and weak acids in the sample. Either phenolphthalein or metacresol purple indicator can be used for this titration. When heavy-metal salts are present, it is usually desirable to heat the sample to boiling and then carry out the titration. The heat speeds the hydrolysis of the metal salts allowing the titration to be completed more readily. Again, 0.02M NaOH is used as the titrating agent. Result are reported in terms of phenolphthalein acidity expressed as $CaCO_3$ as before.

Determination of Total Acidity by Mixed Indicators Method The mixed indicator is prepared by mixing 10mL of 0.1percent thymol blue (in 50percent ethanol) with 30mL of 0.1percent phenolphthalein (in 50 percent ethanol).

Measure accurately 50 or 100mL of water sample into a titration flask. Add one drop of the mixed indicator. Titrate with 0.0125M barium hydroxide solution to the end point yellow (acid) to violet detected with a pH meter rather than by indicator.

$$\text{Acidity (as mg/L } CaCO_3) = \frac{V \times M \times 100000}{\text{Vol (mL) of water sample}}$$

Where V = mL Barium hydroxide
M = molarity of barium hydroxide
The molecular weight of $CaCO_3$ = 100g (=100,000mg)

3.3.2 EXAMPLE OF EXPERIMENT ON DETERMINATION OF ACIDITY IN A WATER SAMPLE

Study the procedure chart below to understand the steps taken in determining the acidity of a water sample.

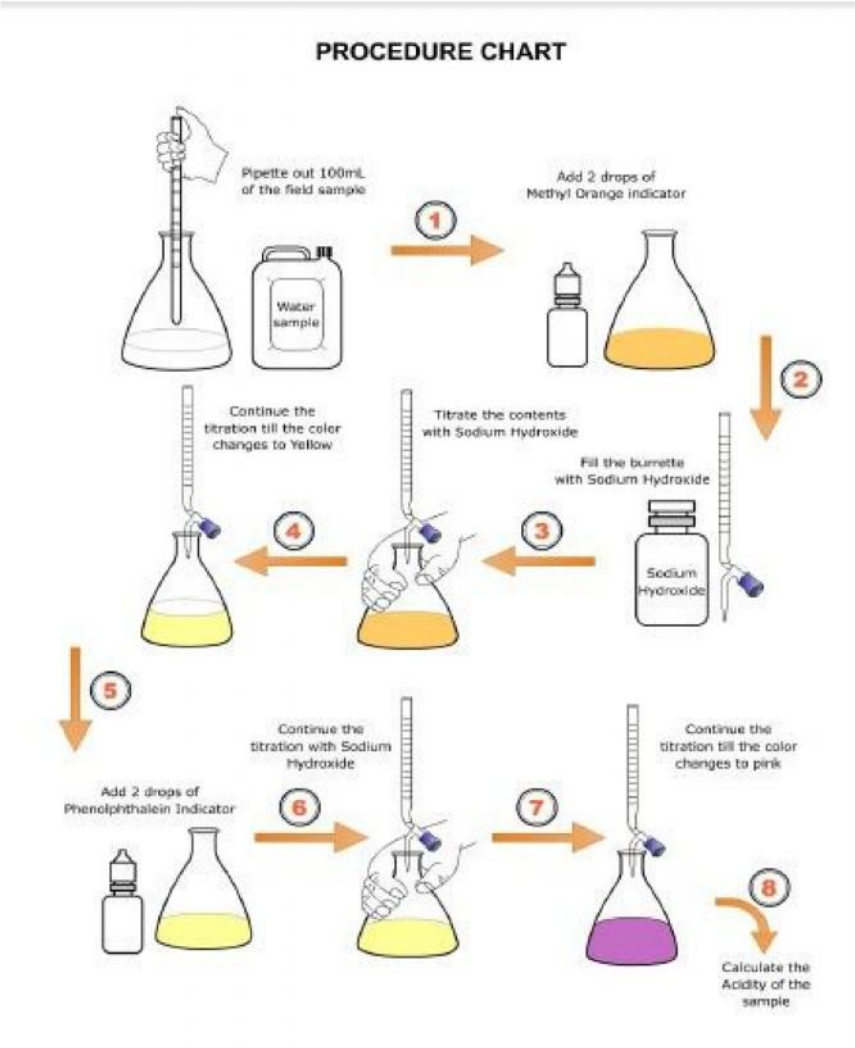

Fig 28: Procedure diagram for determining the acidity of water

Example: In an experiment to determine the acidity of a water sample, the burette was filled with 0.02M NaOH, 100 ml of the water sample was transferred to a conical flask using pipette and few drops of methyl orange indicator was added to the content in the conical flask. The sample was titrated against the 0.02M NaOH solution until the orange colour became faint. The volume V_1 consumed for this titration was noted. This volume is used for calculating the mineral acidity. To the same solution in the conical flask few drops of phenolphthalein indicator was added and the titration continued until the colour changed to faint pink colour. The total volume V_2 consumed for this titration was noted. This volume is used for calculating the total acidity. The experiment was repeated three times to get concordant values; the average was calculated and used.

Calculation of mineral acidity

Table 18 for Mineral Acidity

NO of titration	Volume sample of (mL)	Initial burette reading	Final burette reading	Volume of NaOH (mL)
1	100	0.00	0.50	0.50
2	100	0.00	0.40	0.40
3	100	0.00	0.40	0.40

Average titre value = 0.40 mL
Therefore volume of NaOH consumed = 0.40 mL
Molarity of NaOH = 0.02M
Volume of water sample = 100mg

Mineral acidity (as mg/L $CaCO_3$) = $\frac{V \times M \times 100000}{Vol\ (mL)\ of\ sample}$

Where V = Volume (mL) of sodium hydroxide titrant.
M = Molarity of NaOH
The molecular weight of $CaCO_3$ = 100g (=100,000mg)

Mineral acidity (as mg/L$CaCO_3$) = $\frac{0.40 \times 0.02 \times 100000}{100}$ = 8 mg/L
Calculation for total acidity

Table 19 for Total Acidity

NO of titration	Volume sample of (mL)	Initial burette reading	Final burette reading	Volume of NaOH (mL)
1	100	0.00	2.20	2.20
2	100	0.00	2.30	2.30
3	100	0.00	2.30	2.30

Average titre value = 2.30 mL
Therefore volume of NaOH consumed = 2.30 mL
Molarity of NaOH = 0.02M
Volume of water sample = 100mg
Total acidity (as mg/L $CaCO_3$) = $\frac{V\ x\ M\ x 100000}{ML\ sample}$
Where V = mL sodium hydroxide titrant.

The molecular weight of $CaCO_3$ = 100g (=100,000mg)

Total acidity (as mg/L$CaCO_3$) $= \frac{2.30 \, x \, 0.02 x 100000}{100} = 46$ mg/L

Over view of the experiment above for mineral acidity:

- The burette is filled with the NaOH
- For the first titration the volume of water sample taken is 100 mL. The initial reading is 0.00, the final reading is 0.50 mL.
- The volume of NaOH consumed to get the end point is 0.50 mL.
- For the second titration the volume of water sample taken is 100 ml. The initial reading is 0.00, the final reading is 0.40 mL.
- The volume of NaOH consumed to get the end point is 0.40 mL.
- For the third titration the volume of water sample taken is 100 mL. The initial reading is 0.00, the final reading is 0.4mL.
- The volume of NaOH consumed to get the end point is 0.40 mL.

For total acidity:

- The burette is filled with the NaOH
- For the first titration the volume of water sample taken is 100 mL. The initial reading is 0.00; the final reading is 2.20 mL.
- The volume of NaOH consumed to get the end point is 2.20 mL.
- For the second titration the volume of water sample taken is 100 ml. The initial reading is 0.00, the final reading is 2.30 mL.
- The volume of NaOH consumed to get the end point is 2.30 mL.
- For the third titration the volume of water sample taken is 100 mL. The initial reading is 0.00, the final reading is 2.30 M.
- The volume of NaOH consumed to get the end point is 2.30 mL.

EXPERIMENT 1 – Determination of Acidity in Water

Purpose: To determine the acidity of a given water sample.

Principle: Hydrogen ions present in a sample as a result of dissociation or hydrolysis of solutes reacts with additions of standard alkali (NaOH). Acidity thus depends on end point of the indicator used.

The colour change of phenolphthlein indicator is close to pH 8.3 at 25^0C corresponds to stoichiometric neutralization of carbonic acid to bicarbonate.

Table 20: Equipment / Materials:

Burette	Pipette	Wash bottle	Methyl orange
Burette stand	Pipette bulb	Beakers	Ethyl alcohol
Porcelain tile	Conical flask	Sodium hydroxide	Distilled water
500 ml conical flask	Measuring cylinders	Phenolphthalein	

Sample handling and preservation

- Preservation of sample is very important, because biological activity will continue after a sample has been taken, changes may occur during handling and storage
- To reduce the change in samples, keep all samples at 4^0C. Do not allow samples to freeze
- Analysis should begin as soon as possible
- Do not open sample bottle before analysis

Precautions

- Coloured and turbid samples may interfere in end point. These samples may be analyzed electrometrically using pH meter.
- Do not keep the indicator solution open since it contains the alcohol which tends to evaporate.
- Presence of residual chlorine may interfere in the colour response, which can be nullified by addition of small amount of sodium thiosulphate or destroy it with ultraviolet radiation.
- Presence of iron and aluminumsulphate may interfere in the colour response while titrating at room temperature, which can be nullified by titrating the sample at boiling temperature.
- Dissolved gases contributing to acidity such as CO_2, H_2S may interfere in the titration, hence avoid vigorous shaking.
- Samples suspected to have hydrolysable metal ions or reduced forms of polyvalent cat ions need hydrogen perioxide treatment.

Experimental Procedure

- Rinse the burette with 0.02 M sodium hydroxide and then discard the solution.
- Fill the burette with 0.02 M sodium hydroxide and adjust the burette.
- Fix the burette to the stand.
- Measure 100 ml of a given water sample in a conical flask using measuring cylinder (for highly concentrated samples, dilute the sample before taking 100 ml).
- Add few drops of methyl orange indicator in the conical flask.
- The colour changes to orange. Now titrate the sample against the 0.02 M sodium hydroxide solution until the orange colour faints.
- Note down the volume (V_1) consumed for titration. This volume is used for calculating the mineral acidity.
- To the same solution in the conical flask add few drops of phenolphthalein indicator.

- Continue the titration until the colour changes to faint pink colour.
- Note down the total volume (V_2) consumed for titration. This volume is used for calculating the total acidity.
- Repeat the titration two times to get three concordant values, determine the average titre value to obtain the volume of NaOH consumed for mineral acidity and total acidity.
- Calculate the mineral acidity and total acidity of the water sample.

TITRIMETRY

Titrimetry, is a measure of volume of a reagent reacting stoichiometrically with the analyte of known concentration, first appeared as an analytical method in the early eighteenth century. Unlike gravimetry, titrimetry initially did not receive wide acceptance as an analytical technique. Many prominent late-nineteenth century analytical chemists preferred gravimetry to titrimetry and few of the standard texts from that era include titrimetric methods. By the early twentieth century, however, titrimetry began to replace gravimetry as the most commonly used analytical method.

Overview of Titrimetry

Titrimetric methods are classified into four groups based on the type of reaction involved. These groups are acid–base titrations, in which an acidic or basic titrant reacts with an analyte that is a base or an acid; complexometric titrations involving a metal–ligand complexation reaction; redox titrations, where the titrant is an oxidizing or reducing agent; and precipitation titrations, in which the analyte and titrant react to form a precipitate. Despite the difference in chemistry, all titrations share several common features, providing the focus for this section.

Terminologies in Titrimetry

- Titrant: The reagent added to a solution containing the analyte and whose volume is the signal.
- Equivalence point: The point in a titration where stoichiometrically equivalent amounts of analyte and titrant react.
- End-point: The point in a titration where we stop adding titrant.
- Indicator: A coloured compound whose change in colour signals the end-point of a titration.

- Titration error: The determinate error in a titration due to the difference between the end - point and the equivalence point.
- Back titration: A titration in which a reagent is added to a solution containing the analyte, and the excess reagent remaining after its reaction with the analyte is determined by a titration.
- Displacement titration: A titration in which the analyte displaces a species, usually from a complex, and the amount of the displaced species is determined by a titration.
- Titration curve: A graph showing the progress of a titration as a function of the volume of titrant added.

Classification of Titrimetric Analysis

The reactions employed in titrimetric analysis are divided into four main clases:

1. NeutralisationTitrimetry (or acid and base titrimetry): this involves the titration of acid and base solution, which reacts to form salts by hydrolysis with standard acid (acidimetry) or base (alkalimetry). The reaction involves the combination of hydrogen and hydroxyl ion to form water as part of end product.
2. Complexometric Titration: These depends on the combination of ions other than hydrogen or hydroxyl ions to form a solution, slightly dissociated ion or compound, as in the titration of solution containing cyanide with silver nitrate or of chloride ion with mercury (II) nitrate solution. EDTA (Ethylene-diamine tetra-acetic acid) is largely used in complexometric titration as metal ion indicator.
3. Precipitation Titration: these depends upon the combination of ions to form a simple precipitate as in titration of silver ion with solution of chloride. No change in oxidation state occurs.
4. Oxidation-Reduction Titration: This involves the change in oxidation number or transfer of electrons among the reacting substances. The standard solutions are either oxidising or reducing agents.

NEUTRALIZATION TITRATIONS BASED ON ACID – BASE REACTIONS

The earliest acid–base titrations involved the determination of the acidity or alkalinity of solutions, and the purity of carbonates and alkaline earth oxides. Before 1800, acid–base titrations were conducted using H_2SO_4, HCl, and HNO_3 as acidic titrants, and K_2CO_3 and Na_2CO_3 as basic titrants. End points were determined using visual indicators such as litmus, which is red in acidic solutions and blue in basic solutions, or by observing the cessation of CO_2 effervescence when neutralizing CO_3^{2-}. The accuracy of an acid–base titration was limited by the usefulness of the indicator and by the lack of a strong base titrant for the analysis of weak acids. The utility of acid–basetitrimetry improved when NaOH was first introduced as a strong base titrant in 1846. In addition, progress in synthesizing organic dyes led to the development of many new indicators. Phenolphthalein was first synthesized by Bayer in 1871 and used as a visual indicator for acid–base titrations in 1877. Other indicators, such as methyl orange, soon followed. Despite the increasing availability of indicators, the absence of a theory of acid–base reactivity made selecting a proper indicator difficult.

Developments in equilibrium theory in the late nineteenth century led to significant improvements in the theoretical understanding of acid–base chemistry and, in turn, of acid–basetitrimetry. Sørenson's establishment of the pH scale in 1909 provided a rigorous means for comparing visual indicators. The determination of acid–base dissociation constants made the calculation of theoretical titration curves possible, as outlined by Bjerrum in 1914. For the first time a rational method existed for selecting visual indicators, establishing acid–basetitrimetry as a useful alternative to gravimetry.

Neutralization Curves

For an acid–base titration, the equivalence point is characterized by a pH level that is a function of the acid–base strengths and concentrations of the analyte and titrant. The pH at the end point, however, may or may not correspond to the pH at the equivalence point. To understand the relationship between end points and equivalence points we must know how the pH changes during a titration.

1. Titrating Strong Acids and Strong Bases

For our first titration curve, let's consider the titration of 50.0 mL of 0.100 M HCl with 0.200 M NaOH. For the reaction of a strong base with a strong acid the only equilibrium reaction of importance is

$$H_3O^+_{(aq)} + OH^-_{(aq)} \leftrightarrow 2H_2O_{(l)}$$

The first task in constructing the titration curve is to calculate the volume of NaOH needed to reach the equivalence point. At the equivalence point we know from above that

$$\text{Moles HCl} = \text{moles NaOH or } M_aV_a = M_bV_b$$

where the subscript 'a' indicates the acid, HCl, and the subscript 'b' indicates the base, NaOH. The volume of NaOH needed to reach the equivalence point, therefore, is

$$V_{eq} = V_b = \frac{M_aV_a}{M_b} = \left(\frac{(0.100M)(50.0ml)}{(0.200M)}\right) = 25.0ml$$

Before the equivalence point, HCl is present in excess and the pH is determined by the concentration of excess HCl. Initially the solution is 0.100 M in HCl, which, since HCl is a strong acid, means that the pH is

$$\text{pH} = -\log[H_3O^+] = -\log[\text{HCl}] = -\log(0.100) = 1.00$$

The equilibrium constant is $(K_w)^{-1}$, or 1.00×10^{14}. Since this is such a large value we can treat reaction 9.1 as though it goes to completion. After adding 10.0 mL of NaOH, therefore, the concentration of excess HCl is giving a pH of 1.30.

$$[HCl] = \left(\frac{moles\ excess\ HCl}{total\ volume}\right) = \frac{M_aV_a - M_bV_b}{V_a + V_b}$$

$$= \left(\frac{(0.100M)(50.0mL) - (0.200M)(10.0mL)}{50.0mL + 10mL}\right) = 0.050M$$

At the equivalence point the moles of HCl and the moles of NaOH are equal. Since neither the acid nor the base is in excess, the pH is determined by the dissociation of water.

$$(K_w)^{-1} = 1.00 \times 10^{14} = [H_3O^+][OH^-] = [H_3O^+]^2$$

$[H_3O^+] = 1.00 \times 10^{-7}$ M. Thus, the pH at the equivalence point is 7.00.

Finally, for volumes of NaOH greater than the equivalence point volume, the pH is determined by the concentration of excess OH–. For example, after adding 30.0 mL of titrant the concentration of OH– is

$$[OH^-] = \left(\frac{moles\ excess\ NaOH}{total\ volume}\right) = \frac{M_b V_b - M_a V_a}{V_a + V_b}$$

$$= \left(\frac{(0.200M)(10.0mL) - (0.100M)(50.0mL)}{50.0mL + 10mL}\right) = 0.0125M$$

To find the concentration of H_3O^+, we use the K_w expression giving a pH of 12.10.

2. Titrating a Weak Acid with a Strong Base.

Let's consider the titration of 50.0 mL of 0.100 M acetic acid, CH_3COOH, with 0.100 M NaOH. Again, we start by calculating the volume of NaOH needed to reach the equivalence point; thus

Moles CH_3COOH = moles NaOH or $M_aV_a = M_bV_b$

$$V_{eq} = V_b = \frac{M_a V_a}{M_b} = \left(\frac{(0.100M)(50.0ml)}{(0.100M)}\right) = 50.0ml$$

Before adding any NaOH, the pH is that for a solution of 0.100M acetic acid. Since acetic acid is a weak acid, we calculate the pH using the method in previous method

$$CH_3COOH(aq) + H_2O_{(l)} \leftrightarrow H_3O^+_{(aq)} + CH_3COO^-_{(aq)}$$

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = \left(\frac{(x)(x)}{(0.100 - x)}\right) = 1.75 \times 10^{-5}$$

$$x = [H_3O^+] = 1.32 \times 10^{-3}\text{M}$$

At the beginning of the titration the pH is 2.88. Adding NaOH converts a portion of the acetic acid to its conjugate

$$CH_3COOH(aq) + OH^-_{(aq)} \leftrightarrow H_2O_{(l)} + CH_3COO^-_{(aq)}$$

Any solution containing comparable amounts of a weak acid, HA, and its conjugate weak base, A–, is a buffer. We can calculate the pH of a buffer using the Henderson–Hasselbalch equation.

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

The equilibrium constant for reaction 9.2 is large ($K = K_a/K_w = 1.75 \times 109$), so we can treat the reaction as one that goes to completion. Before the equivalence point, the concentration of unreacted acetic acid is

$$[CH_3COOH] = \left(\frac{moles\ excess\ CH_3COOH}{total\ volume}\right) = \frac{M_aV_a - M_bV_b}{V_a + V_b}$$

and the concentration of acetate is

$$[CH_3COO^-] = \left(\frac{moles\ excess\ NaOH}{total\ volume}\right) = \frac{M_bV_b}{V_a + V_b}$$

For example, after adding 10.0 mL of NaOH the concentrations of CH_3COOH and CH_3COO^- are giving a pH of

$$P^H = 4.76 + log\frac{0.0167}{0.0667} = 4.16$$

A similar calculation shows that the pH after adding 20.0 mL of NaOH is 4.58.

At the equivalence point, the moles of acetic acid initially present and the moles of NaOH added are identical. Since their reaction effectively proceeds to completion, the predominant ion in solution is CH3COO–, which is a weak base. To calculate the pH we first determine the concentration of CH_3COO

$$[CH_3COO^-] = \left(\frac{moles\ excess\ CH_3COOH}{total\ volume}\right) = \frac{(0.100M)(50.0mL)}{50.0mL + 50.0mL} = 0.0500M$$

$$CH_3COO^-_{(aq)} + H_2O_{(l} \leftrightarrow) OH^-_{(aq)} + CH_3COOH(aq)$$

$$K_a = \frac{[OH^-][CH_3COOH]}{[CH_3COO^-]} = \left(\frac{(x)(x)}{(0.500 - x)}\right) = 5.71 \times 10^{-10}$$

$$x = [OH^-] = 5.34 \times 10^{-6}M$$

The concentration of H_3O^+, therefore, is 1.87×10^{-9}, or a pH of 8.73.

After the equivalence, point NaOH is present in excess, and the pH is determined in the same manner as in the titration of a strong acid with a strong base. For example, after adding 60.0 mL of NaOH, the concentration of OH^-

$$[OH^-] = \left(\frac{(0.100M)(60.0mL) - (0.100M)(50.0mL)}{50.0mL + 60mL}\right) = 0.00909M$$

is giving a pH of 11.96

Indicators used in Neutralization Titration

One interesting thing about titration is dependent on pH and colour change due to organic indicators and category of acid-base combination. This change in colour can serve as a useful means for determining the end point of a titration, provided that it occurs at the titration's equivalence point. The pH at which an acid–base indicator changes colour is determined by its acid dissociation constant.

There are several indicators which laboratory analyst use to observe a change in colour and are dependent on pH range.

Table 21: Shows different indicators, colour in acid and base media and pH range

Indicator	**Acid Colour**	**Base Colour**	**pH Range**	**pK_a**
Cresol Red	Red	Yellow	0.2–1.8	—
Thymol Blue	Red	Yellow	1.2–2.8	1.7
Bromophenol Blue	Yellow	Blue	3.0–4.6	4.1
Methyl Orange	Red	Orange	3.1–4.4	3.7
Congo Red	Blue	Red	3.0–5.0	—
Bromocresol Green	Yellow	Blue	3.8–5.4	4.7
Methyl Red	Red	Yellow	4.2–6.3	5.0
Bromocresol Purple	Yellow	Purple	5.2–6.8	6.1
Litmus	Red	Blue	5.0–8.0	—
Bromothymol Blue	Yellow	Blue	6.0–7.6	7.1
Phenol Red	Yellow	Red	6.8–8.4	7.8
Cresol Red	Yellow	Red	7.2–8.8	8.2
Thymol Blue	Yellow	Blue	8.0–9.6	8.9
Phenolphthalein	Colourless	Red	8.3–10.0	9.6
Alizarin Yellow R	Yellow	Orange/Red	10.1–12.0	—

Quantitative Applications

1. Selecting and Standardizing a Titrant: Most common acid–base titrants are not readily available as primary standards and must be standardized before they can be used in a quantitative analysis. Standardization is accomplished by titrating a known amount of an appropriate acidic or basic primary standard.

2. Inorganic Analysis: Acid–basetitrimetry is a standard method for the quantitative analysis of many inorganic acids and bases. Standard solutions of NaOH can be used in the analysis of inorganic acids such as H_3PO_4 or H_3AsO_4, whereas standard solutions of HCl can be used for the analysis of inorganic bases such as Na_2CO_3.

3. Acidity is determined by titrating with a standard solution of NaOH to fixed end points at pH 3.7 and pH 8.3. These end points are located potentiometrically, using a pH meter, or

by using an appropriate indicator (bromophenol blue for pH 3.7, and metacresol purple or phenolphthalein for pH 8.3).

4. Alkalinity is determined with a standard solution of HCl or H_2SO_4 solution to fixed point at a pH of 4.5, or to the bromocresol green end point. Alkalinity is reported as milligrams $CaCO_3$ per liter.

5. Acid–Base titrimetry continues to be listed as the standard method for the determination of free CO_2, OH^-, and HCO_3^- in water and wastewater analysis.

6. Organic Analysis The use of acid–basedtitrimetry for the analysis of organic compounds continues to play an important role in pharmaceutical, biochemical, agricultural, and environmental laboratories. Perhaps the most widely employed acid–base titration is the Kjeldahl analysis for organic nitrogen

PRECIPITATION TITRATION

A reaction in which the analyte and titrant form an insoluble precipitate also can form the basis for a titration, which is referred as precipitation titration. One of the earliest precipitation titrations, developed at the end of the eighteenth century, was for the analysis of K_2CO_3 and K_2SO_4 in potash. Calcium nitrate, $Ca(NO_3)_2$, was used as a titrant, forming a precipitate of $CaCO_3$ and $CaSO_4$. The end point was signaled by noting when the addition of titrant ceased to generate additional precipitate. The importance of precipitation titrimetry as an analytical method reached its zenith in the nineteenth century when several methods were developed for determining Ag+ and halide ions.

The most utilized precipitation process is the silver nitrate used as reagent (argentometric process).

Principle of Precipitation Reactions in titrimetry

For the sake of precipitation titration, we will confine to argentometric precipitation. The titration curve for a precipitation titration follows the change in either the analyte's or the

titrant's concentration as a function of the volume of titrant. For example, in an analysis for I– using Ag+ as a titrant

$$Ag^{+}_{(aq)} + I^{-}_{(aq)} \leftrightarrow AgI_{(s)}$$

the titration curve may be a plot of pAg or pI as a function of the titrant's volume. As we have done with previous titrations, we first show how to calculate the titration curve and then demonstrate how to quickly sketch the titration curve.

Calculating the Titration Curve As an example, let's calculate the titration curve for the titration of 50.0 mL of 0.0500 M Cl– with 0.100 M Ag+. The reaction in this case is

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

The equilibrium constant for the reaction is

$$K = (Ksp)^{-1} = (1.8 \times 10^{-10})^{-1} = 5.6 \times 10^{9}$$

Since the equilibrium constant is large, we may assume that Ag+ and Cl– react completely.

The first task is to calculate the volume of Ag+ needed to reach the equivalence point. The stoichiometry of the reaction requires that

$$\text{Moles } Ag^{+} = \text{moles } Cl^{-} \text{ or} M_{Ag}V_{Ag} = M_{Cl}V_{Cl}$$

Solving for the volume of Ag^{+}

$$V_{Ag} = \frac{M_{Cl}V_{Cl}}{M_{Ag}} = \frac{(0.0500M)(50.0mL)}{(0.100M)} = 25.0mL$$

shows that we need 25.0 mL of Ag^{+} to reach the equivalence point.

Before the equivalence point Cl^{-} is in excess. The concentration of unreacted Cl^{-} after adding 10.0 mL of Ag+, for example, is

$$[Cl^{-}] = \left(\frac{moles\ excess\ Cl^{-}}{total\ volume}\right) = \frac{M_{Cl}V_{Cl} - M_{Ag}V_{Ag}}{V_{Cl} + V_{Ag}}$$

$$= \frac{(0.0500M)(50.0mL) - (0.100M)(10.0mL)}{50.0mL + 10.0mL} = 2.50 \times 10^{-2}M$$

If the titration curve follows the change in concentration for Cl^-, then we calculate pCl as

$$pCl = -log[Cl^-] = -log(2.50 \times 10^{-2}M) = 1.60$$

However, if we wish to follow the change in concentration for Ag+ then we must first calculate its concentration. To do so we use the K_{sp} expression for AgCl

$$K_{sp} = [Ag^+][Cl^-] = 1.80 \times 10^{-10}$$

Solving for the concentration of Ag+

$$[Ag^+] = \frac{K_{sp}}{[Cl^-]} = \frac{1.80 \times 10^{-10}}{2.50 \times 10^{-2}} = 7.2 \times 10^{-9}M$$

Will give a p^{Ag} of 8.14.

At the equivalence point, we know that the concentrations of Ag^+ and Cl^- are equal. Using the solubility product expression

$$K_{sp} = [Ag^+][Cl^-] = [Ag^+]^2 = 1.80 \times 10^{-10} \; gives$$

$$[Ag^+] = [Cl^-] = 1.3 \times 10^{-5} \, M$$

At the equivalence point, therefore, p^{Ag} and p^{Cl} are both 4.89.

After the equivalence point, the titration mixture contains excess Ag^+. The concentration of Ag^+ after adding 35.0 mL of titrant is

$$[Ag^+] = \left(\frac{moles\ excess\ Ag^+}{total\ volume}\right) = \frac{M_{Ag}V_{Ag} - M_{Cl}V_{Cl}}{V_{Cl} + V_{Ag}}$$

$$= \frac{(0.100M)(35.0mL) - (0.0500M)(50.0mL)}{50.0mL + 35.0mL} = 1.18 \times 10^{-2}\ M \text{ or a } p^{Ag} \text{ of } 1.93.$$

The concentration of Cl– is

$$[Cl^-] = \frac{K_{sp}}{[Ag^+]} = \frac{1.80 \times 10^{-10}}{1.18 \times 10^{-2}} = 1.5 \times 10^{-8} M$$

or a pCl of 7.82.

Indicator used in Precipitation Titration

- The first important visual indicator to be developed was the Mohr method for Cl^- using Ag^+ as a titrant. By adding a small amount of K_2CrO_4 to the solution containing the analyte, the formation of a precipitate of reddish-brown Ag_2CrO_4 signals the end point. Because K_2CrO_4 imparts a yellow colour to the solution, obscuring the end point, the amount of CrO_4^{2-} added is small enough that the end point is always later than the equivalence point. To compensate for this positive determinate error an analyte-free reagent blank is analyzed to determine the volume of titrant needed to effect a change in the indicator's color. The volume for the reagent blank is subsequently subtracted from the experimental end point to give the true end point. Because $CrO4^{2-}$ is a weak base, the solution usually is maintained at a slightly alkaline pH. If the pH is too acidic, chromate is present as $HCrO_4^-$, and the Ag_2CrO_4 end point will be in significant error. The pH also must be kept below a level of 10 to avoid precipitating silver hydroxide.

- A second end point is the Volhard method in which Ag+ is titrated with SCN^- in the presence of Fe_3^+. The end point for the titration reaction

$$Ag^+_{(aq)} + SCN^-(aq) \leftrightarrow AgSCN_{(s)}$$

is the formation of the reddish colored Fe(SCN)2+ complex.

$$SCN^-_{(aq)} + Fe^{3+}_{(aq)} \leftrightarrow Fe(SCN)^{2+}_{(aq)}$$

The titration must be carried out in a strongly acidic solution to achieve the desired end point.

➢ A third end point is evaluated with Fajans' method, which uses an adsorption indicator whose colour when adsorbed to the precipitate is different from that when it is in solution. For example, when titrating Cl^- with Ag^+ the anionic dye dichloro-fluoroscein is used as the indicator. Before the end-point, the precipitate of AgCl has a negative surface charge due to the adsorption of excess Cl^-. The anionic indicator is repelled by the precipitate and remains in solution where it has a greenish yellow colour. After the end-point, the precipitate has a positive surface charge due to the adsorption of excess Ag^+. The anionic indicator now adsorbs to the precipitate's surface where its colour is pink. This change in colour signals the end-point.

Quantitative Applications

1. Precipitation titrimetry is rarely listed as a standard method of analysis, but may still be useful as a secondary analytical method for verifying results obtained by other methods. Most precipitation titrations involve Ag^+ as either an analyte or titrant. Those titrations in which Ag^+ is the titrant are called argentometric titrations.

In-text Question

Explain the following terms: Indicator, End-point, Titration error and Titrant.

Answers

Indicator: A coloured compound whose change in colour signals the end-point of a titration.

End-point: The point in a titration where we stop adding titrant.

Titration error: The determinate error in a titration due to the difference between the end -point and the equivalence point.

Titrant: The reagent added to a solution containing the analyte and whose volume is the signal.

4.0 SELF-ASSESSMENT EXERCISES

1. Define the term pH of any given solution
2. Explain how combustion of fossil and automobiles contribute to acid rain
3. In an experiment to determine the acidity of a given water sample, vigorous shaking should be avoided because?

Answers

1. The pH of any given solution is defined as the negative logarithm of the hydrogen ion concentration, mathematically expressed as
   $-\log [H^+]$

2. Combustion of fossil fuels in power plants and automobiles causes the formation of oxides of nitrogen and sulphur which in the atmosphere undergo oxidation to their corresponding acids (HNO_3 and H_2SO_4) which subsequently fall together with rain as acid rain into water bodies and on land.
3. Dissolved gases contributing to acidity such as CO_2, H_2S may interfere in the titration,

5.0 CONCLUSION

The measurement of acidity in a water sample is very important because acidic water contributes to corrosiveness and influence chemical reaction rates, it affects aquatic life in natural water; high acidity in water decreases biota, notably fisheries, and it is not good for consumption. The determination of acidity in water is important so as to remove or control the substances causing acidity in water. Strong mineral acids such as H_2SO_4 and HNO_3 contribute to mineral acidity and its pH is about 3.7, total acidity is caused by both mineral acids and weak acids, its pH is about 8.3

6.0 SUMMARY

Acidity is a measure of the ability of a given sample to neutralize bases. Sources of acidity in water include dissolved H_2SO_4, HNO_3 and H_2CO_3 falling down in rain as acid rain, dissolved CO_2 in water produced from biological oxidation of organic matter particularly in polluted water, mineral acids from metallurgical industry, industries and abandoned mines and iron ore dumps.
It is important to determine the acidity of water because of its corrosive characteristic and effects on aquatic life. Acidity in a water sample can be determined by mineral acidity and total acidity measurements.

CLASS ACTIVITY (THE TUTOR TO DIRECT)

1. Why is the determination of acidity in water important?

2. Discuss the sources of acidity in water.

3. Calculate the mineral acidity and total acidity of a water sample which was titrated with standard solution of 0.02 M NaOH solution. The volume of NaOH consumed for the mineral acidity determination is 0.7 ml and 2.5 ml for total acidity determination. What inferences can be drawn from the results obtained?

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UNIT 5 DETERMINATION OF ALKALINITY IN WATER

UNIT 5 DETERMINATION OF ALKALINITY IN WATER

3.1 SOURCES OF ALKALINITY IN WATER
https://www.youtube.com/watch?v=uRw8wUmBDNc

3.3 METHODS OF ALKALINITY DETERMINATION
https://www.youtube.com/watch?v=K16rQDo3cKI

1.0INTRODUCTION

The alkalinity of a water sample is a measure of its capacity, to neutralize acids. Alkalinity in water results from hydroxyl (OH^-), carbonate (CO_3^{2-}), bicarbonate (HCO_3^{-}) ions E.T.C present in water. The ability of natural water to act as a buffer is controlled in part by the amount of calcium and carbonate ions in solution. Carbonate ion and calcium ion both come from calcium carbonate or limestone. So water that comes in contact with limestone will contain high levels of both Ca^{2+} and CO_3^{2-} ions and have elevated hardness and alkalinity. Determination of alkalinity in water is important because alkaline water reacts with certain cations in water to form precipitates. The resultant precipitate can foul pipes and other water-system appurtenances. Alkalinity is an important consideration in calculating the lime and soda-ash requirements in softening of water by precipitation methods. It is also a means of evaluating the buffering capacity of natural water, waste waters and sludge.

2.0 INTENDED LEARNING OUTCOME (S)

After studying this unit, you should be able to:

- Explain alkalinity in water
- Discuss the sources of alkalinity in water
- Explain the significance of alkalinity in water
- State and explain the steps involved in determining alkalinity in a water sample
- Carry out experiments to determine alkalinity in a water sample

3.0 MAIN CONTENT

3.1 SOURCES OF ALKALINITY IN WATER

Constituents of alkalinity in natural water systems include CO_3^{2-}, HCO_3^-, OH^-, $HSiO_3^-$, $H_2BO_3^-$, HPO_4^-, $HS^-$and NH_3.These compounds result from the dissolution of mineral substances in the soil and atmosphere. Phosphates may also originate from detergents in waste water discharges and from fertilizers and insecticides from agricultural land. Hydrogen sulphide and ammonia may be products of microbial decomposition of organic material. By far, the most common

constituents of alkalinity are bicarbonate (HCO_3^-), carbonate (CO_3^{2-}) and hydroxide (OH^-). In addition to their mineral origin, these substances can originate from CO_2, a constituent of the atmosphere and a product of microbial decomposition of organic material, according to the following reactions.

$CO_2 + H_2OH_2 \rightleftharpoons CO_3$ (dissolved CO_2 and carbonic acid)

$H2CO3 \rightleftharpoons H^+ + HCO3^-$ (bicarbonate)

$HCO_3- \rightleftharpoons H^+ + CO3^{2-}$ (carbonate)

$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$ (hydroxyl)

The last reaction is a weak reaction chemically. However, **utilization** of the bicarbonate ion as a carbon source by algae can drive the reaction to the right and result in substantial accumulation of OH-. Water with heavy algal growths often has pH values as high as 9 to 10.

In-text Question

State the scientific reason for determination of alkalinity in water

Answer

Determination of alkalinity in water is important because alkaline water reacts with certain cations in water to form precipitates (solid substances)

3.2 SIGNIFICANCE AND APPLICATION OF ALKALINITY DATA

The principal objection to alkaline water is the reactions that can occur between alkalinity and certain cations in the water. The resultant precipitate can corrode pipes and other accessories of water distribution systems. Alkalinity is an important consideration in calculating the lime and soda-ash requirements in softening of water by precipitation methods. It is also a means of evaluating the buffering capacity of water, waste waters and sludge.

Alkalinity is important for fish and aquatic life because it protects or buffers against rapid pH changes. Higher alkalinity levels in surface waters will buffer acid rain and other acid wastes and prevent pH changes that are harmful to aquatic life. Large amount of alkalinity imparts bitter taste in water.

3.3 METHODS OF ALKALINITY DETERMINATION

In the natural and treated waters alkalinity determination, four quantities are commonly reported. These are phenolphthalein alkalinity, total alkalinity, carbonate alkalinity and total carbon dioxide.

3.3.1 DETERMINATION OF ALKALINITY IN WATER

Determination of Phenolphthalein alkalinity (PA): Phenolphthalein alkalinity is used for determining alkalinity due to hydroxyl ions in the water sample. Put 100 mL of water sample into a clean conical flask. Add one drop of 0.05M sodium thiosulphate solution to remove free residual chlorine if present. Add 2 drops of phenolphthalein indicator. The colour of the solution will turn to pink. This colour change is due to alkalinity of hydroxyl ions in the water sample. If hydroxyl ions are absent, the colour will remain unchanged. If the solution turns pink, then titrate the solution with 0.02M HCl or H_2S0_4 until the colour disappears. This indicates that all the hydroxyl ions have been removed from the water sample. The volume of acid consumed for this titration is noted and used for calculation of phenolphthalein alkalinity.

The conversion obtained in this titration corresponds to:

$OH^- + CO_3^{2-} + 2H^- + \longrightarrow H_2O + HCO_3^-$

Now,

Phenolphthalein alkalinity (PA) (as mg/L $CaCO_3$) = $\frac{VP \times M \times 100000}{Vol\ (mL)\ of\ water\ sample}$

Where V_p= volume (mL) of the acid used M
= molarity of the acid ml = volume of water sample
The molecular weight of $CaCO_3$ = 100g (=100,000mg)

Determination of Total Alkalinity (TA): Add two drops of mixed indicator (bromocresol green + methyl red solution) or of methyl orange indicator into 50 or 100 mL of water sample in a clean conical flask. Shake and titrate with 0.02M HCl or H_2S0_4 acid until, at pH 4.6, the colour changes to pink or red (for mixed indicator) or from yellow to orange (for methyl orange indicator). When few drops of mixed indicator is added to the water sample, the colour of the solution turns to blue. This colour change is due to CO_3^{2-} and HCO_3^- ions in the water sample.

The conversion for this titration corresponds to

$OH^- + CO_3^{2-} + HCO_3^- + 4H^+ \longrightarrow 3H_2O + 2CO_2$

Now,

Total Alkalinity (TA) (as mg/L $CaCO_3$) = $\frac{V_T x\ M\ x\ 100000}{Vol\ (mL)\ of\ water\ sample}$

Where V_T = volume (mL) of acid used
M = molarity of acid used.
ml = volume of water sample

The molecular weight of $CaCO_3$ = 100g (=100,000mg)

Determination of Hydroxide, Hydrogen Carbonate and Carbonate

To 50 or 100 mL of the water sample in a clean volumetric flask, add a slight excess of $BaCl_2$ solution to precipitate the carbonate. The HCO_3^- and OH^- are not affected; the HCO_3^- is not also affected by phenolphthalein indicator. Add two drops of phenolphthalein indicator and titrate the OH^- in the water sample against 0.02M HCl until the solution is colourless. Let the volume of the acid used be V_HmL. Add two drops of the mixed indicator or methyl orange to the solution of the hydroxide/ acid titration. Shake and titrate the HCO_3^- to the end point with 0.02M HCl. Let the volume of acid used be V_{HC}mL. To a fresh 50 or 100 mL water sample, add 2 drops of mixed indicator or methyl orange and shake. Titrate to the end point with 0.02M HCl. The volume of the acid used, V_T, is for the three species OH^-, HCO_3^- and CO_3^{2-}. Hence, the volume of acid used for CO_3^{2-} only, $V_C = [V_T - (V_H + V_{HC})]$ mL. The alkalinities can now be calculated as usual.

Determination of Total CO_2: Collect the water sample into a 500 mL flask leaving no air space. Taketo the laboratory as soon as possible and siphon into a 100 mL graduated cylinder allowing overflow to occur. Add five to ten drops of phenolphthalein indicator. If the water sample turns red, the free-CO_2 is absent, but if the water remains colourless, titrate rapidly with a standardNa_2CO_3 or NaOH solution until pink colour persists for about 30seconds.

$$\text{Alkalinity as mg/L } CO_2 = \frac{V \times M \times 44000}{\text{Vol (mL) of water sample}}$$

Where V = volume (mL) of Na_2CO_3 OR NaOH used M = molarity of the alkali (Na_2CO_3 or NaOH) 44000 = molar weight of CO_2 in mg.

3.3.2 EXAMPLE OF EXPERIMENT ON DETERMINATION OF ALKALINITY IN A WATER SAMPLE

Study the procedure chart below to understand the steps taken in determining alkalinity in a water sample.

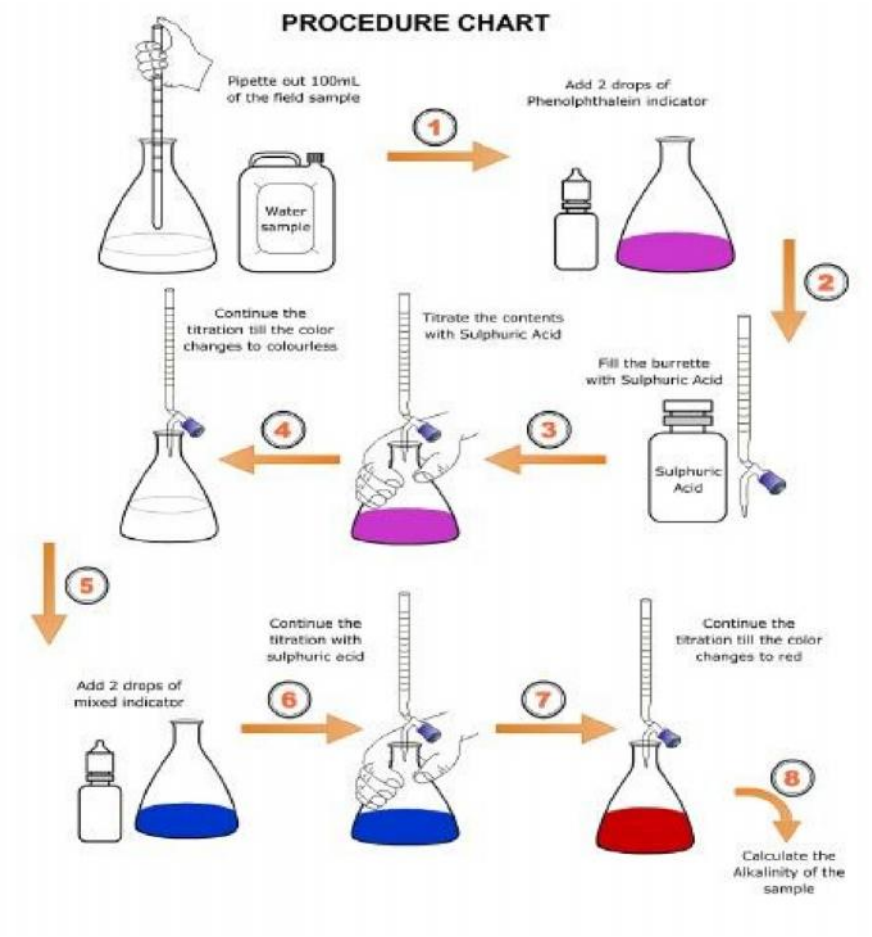

Fig 29: Procedure chart for the determination of alkalinity in water

Example: 100 ml of a water sample contained in a 250 ml conical flask was added few drops of phenolphthalein indicator, the colour of the solution turned pink. The solution was then titrated against 0.02M H_2SO_4 till the pink colour disappeared. The volume V_1 of sulphuric acid consumed was noted and used to calculate the phenolphthalein alkalinity. To the same solution in the conical flask few drops of mixed indicator was added, the colour of the solution turned blue, the titration was continued from the point where the phenolphthalein alkalinity was stopped till the solution became red. The entire volume V_2 of sulphuric acid was noted and used to calculate the total alkalinity. The experiment was repeated two times to obtain three concordant values.

Calculation of phenolphthalein alkalinity

Table 22 for Phenolphthalein Alkalinity

NO of titration	Volume of sample (mL)	Initial burette reading	Final burette reading	Volume of Sulphuric acid (mL)
1	100	0.00	0.60	0.60
2	100	0.00	0.50	0.50
3	100	0.00	0.50	0.50

Average titre value = 0.50 mL
Therefore volume of sulphuric consumed = 0.50 mL

Phenolphthalein Alkalinity mg/L $CaCO_3$) = $\frac{\text{Volume of } H_2SO_4 \ (V_1) \text{ X Molarity of acid x } 100000 \text{ (PA) (as}}{\text{Volume of sample taken}}$

Calculation for total alkalinity $= \frac{0.50 \times 0.02 \times 100000}{100} = 10$ mg/L

Table 23 for Total Alkalinity

NO of titration	Volume of sample (mL)	Initial burette reading	Final burette reading	Volume of Sulphuric (mL)
1	100	0.00	8.50	8.50
2	100	0.00	8.30	8.30
3	100	0.00	8.30	8.30

Average titre value = 8.30 mL

Therefore volume (V_2) of H_2SO_4 consumed = 8.30 mL
Molarity of sulphuric acid = 0.02M
Volume of sample = 100 ml

Total Alkalinity mg/L $CaCO_3$) = $\frac{\text{Volume of } H_2SO_4 \ (V_2) \text{ x Molarity of acid x } 100000 \text{ (TA) (as}}{\text{Volume of sample taken}}$

$= \frac{8.30 \times 0.02 \times 100000}{100} = 166$ mL

EXPERIMENT 1 – Determination of Alkalinity in Water

Purpose: To determine the alkalinity of a given water sample.

Principle: The alkalinity of water can be determined by titrating the water sample with sulphuric acid of known value of pH volume and concentrations. Based on stoichiometry of the reaction and number of moles of sulphuric acid needed to reach the end point, the concentration of alkalinity in water is calculated.

When a water sample that has a pH of greater than 4.5 is titrated with acid to a pH 4.5 end point all OH^- and CO_3^{2-} and HCO_3^- will be neutralized.

For the pH more than 8.3, add phenolphthalein indicator, the colour changes to pink. This pink colour is due to presence of hydroxyl ions. If sulphuric acid is added to it, the pink colour disappears i.e. OH^- ions are neutralized. Then add mixed indicator, the presence of $CO_3$2- and HCO_3^- ions in the solution changes the colour to blue. While adding sulphuric acid, the colour changes to red, this colour change indicate that the CO_3^{2-} and HCO_3^- ions have been neutralized. This is the end point.

Table 24: Equipment / Materials:

Burette	Pipette	Wash bottle	Mixed indicator
Burette stand	Pipette bulb	Beakers	Ethyl alcohol
Porcelain tile	standard flask	Standard sulphuric acid	Distilled water
500 ml conical flask	Measuring cylinders	Phenolphthalein	Bromocresol green
			Methyl red

Sample handling and preservation

- Preservation of sample is very important, because biological activity will continue after a sample has been taken, changes may occur during handling and storage
- To reduce the change in samples, keep all samples at 4^0C. Do not allow samples to freeze
- Analysis should begin as soon as possible
- Do not open sample bottle before analysis

Precautions

- Do not keep the indicator solution open since it contains the alcohol which tends to evaporate.
- The mixed indicator solution is containing dye in it; Care should be taken so that it is not spilled on your skin.

Experimental Procedure

- Rinse the burette with 0.02 M sulphuric acid and then discard the solution.
- Fill the burette with 0.02 M sulphuric acid and adjust to zero.
- Fix the burette to the stand.
- Using a measuring cylinder measure exactly 100 mL of sample and pour it into a 250 mL conical flask.
- Add few drops of phenolphthalein indicator to the contents of conical flask. The colour of the solution will turn to pink. This colour change is due to alkalinity of hydroxyl ions in the water sample.
- Titrate it against 0.02M sulphuric acid till the pink colour disappears. This indicates that all the hydroxyl ions are removed from the water sample. Note down the titre value (V_1). This value is used in calculating the phenolphthalein alkalinity.
- To the same solution in the conical flask add few drops of mixed indicator, the colour of the solutions turns to blue. This colour change is due to CO_3^{2-} and HCO_3- ions in water.
- Continue the titration from the point where stopped for the phenolphthalein alkalinity. Titrate till the solution becomes red. The entire volume (V_2) of sulphuric acid is noted down and it is accountable in calculating the total alkalinity
- Repeat the titration two times to get three concordant values, determine the average titre value to obtain the volume of sulphuric acid consumed for phenolphthalein alkalinity and total alkalinity.
  Calculate the phenolphthalein alkalinity and total alkalinity of the water sample.
- If the recommended standard by relevant regulatory authorities is that alkalinity should not exceed 200mg/L for potable water and 100mg/L for fresh water, what inference can you draw from the result of the water sample tested.

In-text Question
State the reason for addition of 2 drops of phenolphthalein indicator into 100 mL of water sample in a clean conical flask.

Answer

It is to remove free residual chlorine if present.

Question

State the colour change and why on addition of 2 drops of phenolphthalein indicator to the above reaction.

Answer

The colour of the solution will turn to pink. This colour change is due to alkalinity of hydroxyl ions in the water sample.

4.0 SELF- ASSESSMENT EXERCISE(S)

1. Define alkalinity of a sample of water
2. Enumerate the four quantities that are reported in the natural and treated waters alkalinity determination

Answer

1. The alkalinity of a water sample is a measure of its capacity to neutralize acids.
2. They are phenolphthalein alkalinity, total alkalinity, carbonate alkalinity and total carbon dioxide.

5.0 CONCLUSION

Alkalinity is an important parameter to be considered in water analysis because it corrodes pipes and other accessories of water distribution systems, it is important for fish and aquatic life as it buffers against rapid pH changes in natural waters, large amount of alkalinity imparts bitter taste in water and it is an important consideration in calculating the lime and soda-ash requirements in softening of water precipitation methods.

The most common constituents of alkalinity are bicarbonate ($HC0_3^-$), carbonate (CO_3^{2-}) and hydroxyl (OH^-) ions which result from the dissolution of mineral substances in the soil and atmosphere.

Alkalinity in water is measured by the methods; phenolphthalein alkalinity, total alkalinity, carbonates alkalinity and total carbon dioxide.

6.0 SUMMARY

Alkalinity is a measure of the capacity of water to neutralize acids. The predominant chemical constituents causing alkalinity in water are bicarbonate ($HC0_3^-$), carbonate (CO_3^{2-}) and hydroxyl (OH^-) ions. The sources of alkalinity in water include dissolution of mineral substances in the soil e.g. calcium carbonate or limestone that dissolves to form Ca^{2+} and $C0_3^{2-}$ ions and dissolution of atmospheric CO_2 and CO_2 formed from microbial decomposition of organic matter

Determination of alkalinity in water is important because alkaline water reacts with certain cat ions in water to form precipitates. The resultant precipitate can foul pipes and other watersystem appurtenances. Alkalinity is an important consideration in calculating the lime and sodaash requirements in softening of water by precipitation methods. It is also a means of evaluating the buffering capacity of natural water, waste waters and sludges.

CLASS ACTIVITY (THE TUTOR TO DIRECT)

1. Why is the determination of alkalinity in water important?

2. Discuss the sources of alkalinity in water.

3. State and discuss the methods of determining alkalinity in water.

7.0 REFERENCES/FURTHER READING

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UNIT 6 DETERMINATION OF HARDNESS IN WATER

1.0 INTRODUCTION

2.0 INTENDED LEARNING OUTCOME (S)

3.0 MAIN CONTENT

3.1 SOURCES OF HARDNESS IN WATER

In-text Question

3.2 SIGNIFICANCE OF HARDNESS IN WATER

3.3 DETERMINTION OF HARDNESS IN WATER

3.3.1 EXAMPLE OF EXPERIMENT ON DETERMINATION OF HARDNESS IN A WATER SAMPLE

3.4EXPERIMENTALS

In-text Question

4.0 SELF ASSESSMENT EXERCISE (S)

5.0 CONCLUSION

6.0 SUMMARY

7.0 REFERENCES/ FURTHER READING

UNIT 6 DETERMINATION OF HARDNESS IN WATER

3.1 SOURCES OF HARDNESS IN WATER
https://www.youtube.com/watch?v=4cNlBXd0xNU

3.3 DETERMINATION OF HARDNESS IN WATER
https://www.youtube.com/watch?v=Sa0WfA9UGG0

2.0INTRODUCTION

Hardness is defined as the concentration of multivalent metallic cations in water which determine the capacity of the water to precipitate soap. Hard water contains bicarbonate, chlorides and sulphates of calcium and magnesium, thus hardness of water can also be defined as a measure of the total concentration of calcium and magnesium ions. Depending on the anion with which it associates, hardness is classified as calcium and magnesium hardness, carbonate hardness and noncarbonate hardness and pseudo-hardness.
There are two types of hardness; temporary hardness and permanent hardness. Temporary hardness is due to the presence of bicarbonates of calcium and magnesium. It is sensitive to heat and precipitates readily at high temperatures, e.g.

$$Ca(HCO3)2 \longrightarrow CaCO3 + CO2 + H2O$$

Permanent hardness is due to the presence of chlorides and sulphates of calcium and magnesium. This type of hardness cannot be removed by boiling.

2.0 Intended Learning Outcome (s)

After studying this unit, you should be able to:

- Explain water hardness
- Discuss the sources of hardness in water
- Explain the significance of hardness in water
- State and explain the steps involved in determining hardness in a water sample
- Carry out experiments to determine hardness in a water sample

3.0 MAIN CONTENT

3.1 SOURCES OF HARDNESS IN WATER

Water hardness is due mainly to the presence of Ca^{2+} and Mg^{2+} in water. Other ions that may cause hardness include Fe^{2+}, Mn^{2+}, Sr^{2+} and Al^{3+}. The latter are found in much smaller quantities than Ca^{2+} and Mg^{2+}, and for all practical purposes, hardness may be represented by the sum of the Ca^{2+} and Mg^{2+} ions in a given water sample. Ca^{2+} and Mg^{2+} ions enter a water supply by leaching from minerals within an aquifer. Common calcium-containing minerals are calcite ($CaCO_3$) and gypsum ($CaSO_4$. $2H_2O$). A common magnesium mineral is dolomite ($CaMg(CO_3)_2$ which also contains calcium.

In-text Question

Define hard water and state its components

Answer

Hardness is defined as the concentration of multivalent metallic cations in water which determine the capacity of the water to precipitate soap. Hardness of water can also be defined as a measure of the total concentration of calcium and magnesium ions.

Hard water contains bicarbonate, chlorides and sulphates of calcium and magnesium

3.2 SIGNIFICANCE AND APPLICATION OF HARDNESS DATA

Soap consumption by hard waters represents an economic loss to the water user. Sodium soaps react with multivalent metallic cations to form insoluble precipitate e.g. insoluble precipitates of salts of calcium and magnesium, thereby losing their surfactant properties.

$2NaCO_2\ C_{17}H_{35} + Ca2+ \longrightarrow Ca\ 2+(CO_2\ C_{17}H_{35})_2 + 2Na+$

Soap precipitate

Lathering does not occur until all of the hardness ions are precipitated. The precipitate formed adheres to surfaces of tubs, sinks, dishwashers and may stain clothing, dishes and other items. Residues of the precipitate may remain in the pores so that skin may feel rough and uncomfortable. Boiler scale, resulting from carbonate hardness, may cause considerable economic loss through fouling of water heaters and hot-water pipes. Changes in pH of the water distribution systems may also result in deposits of precipitates. Bicarbonates begin to convert to the less soluble carbonates at pH values above 9.0.

Magnesium hardness, particularly associated with the sulphate ion, has a laxative effect on persons unaccustomed to it. Magnesium concentrations of less than 50 mg/L are desirable in potable waters although many public water supplies exceed this amount.

Hardness of water is an important consideration in determining the suitability of a given water source for domestic and industrial uses. The environmental engineer uses it as a basis for recommending the need for softening processes and design types. Hardness may range from Practically zero to several hundred or thousand parts per million. Although acceptability levels vary according to a consumer's acclimation to hardness, a generally accepted classification is as follows:

Soft water < 50 mg/L as CaCO3
Moderately hard water 50 – 150 mg/L as CaCO3
Hard water 150 – 300 mg/L as CaCO3
Very hard water > 300 mg/L as CaCO3
The Public Health Service Standards recommend a maximum of 500 mg/L of hardness in drinking water.

3.3 DETERMINATION OF HARDNESS IN WATER

Hardness can be measured by using spectrophotometric techniques or chemical titration to determine the quantity of calcium and magnesium ions in a given water sample. Hardness can be measured directly by titration with ethylenediaminetetraacetic acid (EDTA) using Eriochrome Black T (EBT) as an indicator. The EBT reacts with the divalent metallic cations, forming a complex that is red in colour. The EDTA replaces the EBT in the complex, and when the replacement is complete, the solution changes from red to blue.

M^{n+} + EBT $\longrightarrow$ M – EBT

M – EBT + EDTA $\longrightarrow$ M – EDTA + EBT
red blue

If 0.01M EDTA is used, 1.0 mL of the titrant measures 1.0 mg of hardness as $CaCO_3$.

3.3.1 EXAMPLE OF EXPERIMENT ON DETERMINATION OF HARDNESS IN A WATER SAMPLE

Study the procedure chart below to understand the steps taken in determining hardness in a water sample.

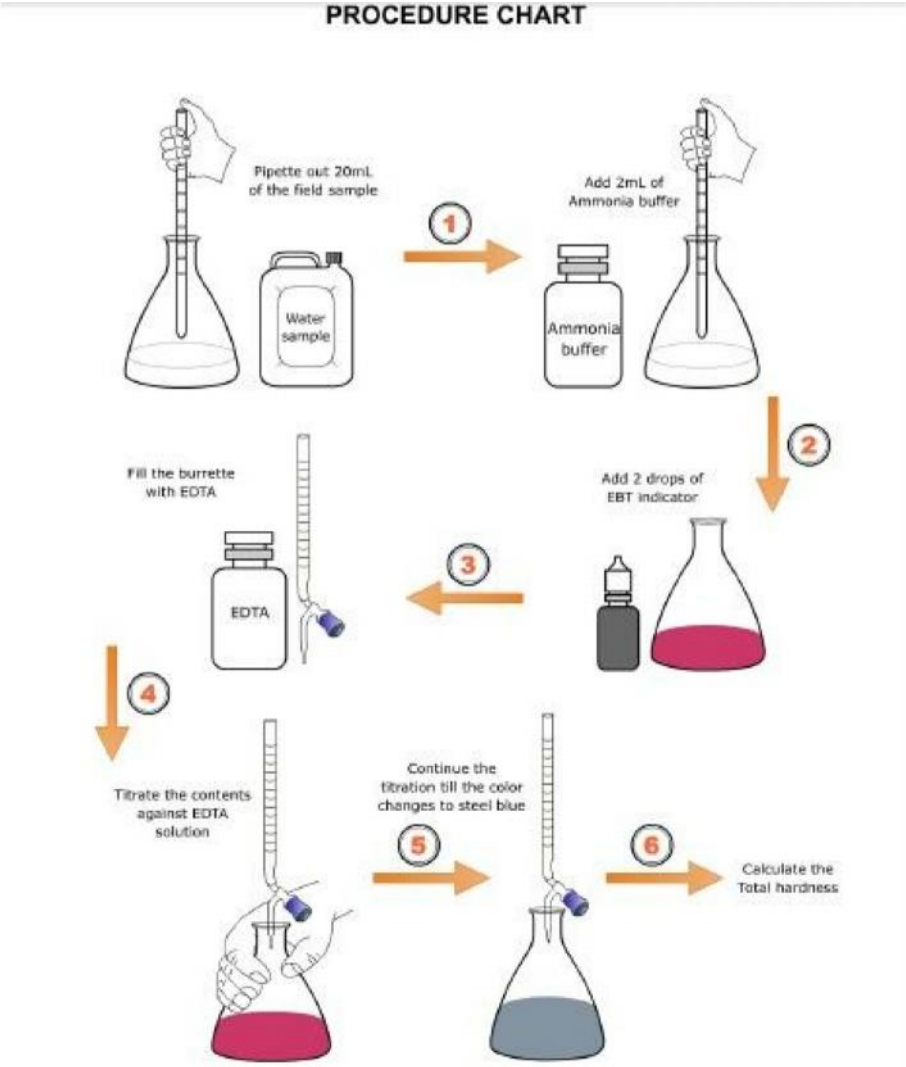

Table 30: Procedure chart for the determination of hardness in water

Example:

In an experiment to determine the amount of hardness in a water sample, 20 ml of the water sample was added 2 ml of ammonia buffer and 2 drops of EBT (eriochrome black T) indicator, the colour of the water sample turned red. This was titrated against EDTA (ethylenediaminetetraacetic acid) filled in a burette. The titration was continued till the solution turned blue. The experiment was repeated two times to get three concormittant results. Calculate the total hardness of the water sample.

Solution:

Table 25: Data obtained for determination of total hardness in water

NO of titration	Volume of sample (mL)	Initial burette reading	Final burette reading	Volume of EDTA (mL)
1	20	0.00	29.30	29.30
2	20	0.00	29.80	29.80
3	20	0.00	29.80	29.80

Average titre value = 29.60 mL
Therefore volume of EDTA consumed = 29.60 mL

Total hardness: $CaCO_3$) = $\frac{\text{Volume of EDTA x Molarity of EDTA x 100,000 (as mg/L}}{\text{Volume of sample taken}}$

$$= \frac{29.60 \times 0.02 \times 100000}{20} = 2960 \text{ mg/L}$$

NOTE:
The molecular weight of $CaCO_3$ = 100g (=100,000mg)

EXPERIMENT 1 – Determination of Total Hardness in Water

Purpose: To determine the total hardness in a given water sample.

Principle: A water sample is buffered to pH 10.1 and taken into a conical flask, if an indicator dye like EBT is added to a solution containing calcium and magnesium ions, the colour of the solution turns to wine red. EDTA the titrant complexes with magnesium and calcium ions, removing them from association with the indicator.

Table 26: Equipment / Materials:

Burette	Pipette	Beakers
Burette stand	Pipette bulb	Ammonium chloride hydroxide
Porcelain tile	standard flask	EDTA (disodium salt of EDTA)
Conical flask (Erlenmeyer)	Measuring cylinders	Erichrome Black T
250 mL graduated cylinders	Wash bottle	Magnesium sulphate

Sample handling and preservation

- Preservation of sample is not practical, because biological activity will continue after a sample has been taken, changes may occur during handling and storage.
- If analysis is to be carried out within two hours of collection, cool storage is not necessary, if analysis cannot be started within the two hours of sample collection to reduce the change in sample, keep all samples at 4^0C.
- Do not allow samples to freeze.
- Do not open sample bottle before analysis.
- Begin analysis within six hours of sample collection.

Precautions

- Here we are handling ammonia solution so necessary precaution should be taken for preventing the inhalation. It causes irritation if inhaled.
- Do not pipette out the buffer solution using measuring cylinder, automatic pipette or pipette with a sucker.
- Always store EDTA solution and buffer solution in a plastic or resistant glass container.• Discard the buffer solution if it is turbid or if it is stored for a very long period of time.

Experimental Procedure

- Pipette 20 mL of water sample and transfer it to a clean 250 mL conical flask.
- Add 2 mL of ammonia buffer solution to the water sample so that the pH will be maintained between 9 and 10.
- Add few drops of EBT indicator to the conical flask and the sample turns to wine red in colour.
- Before starting the titration rinse the burette with few mL of EDTA. Fill the burette with 0.02M EDTA solution and adjust to zero, then fix it in burette stand.
- Titrate the sample against the EDTA solution in the burette till all calcium and magnesium ions present in the sample reacts with the EDTA. The appearance of blue colour indicates that all Ca^{2+} and Mg^{2+} ions are complexed i.e, the end point of the titration.
- Note down the burette reading.
- Repeat the titration two times to get three concordant values.
- Calculate the total hardness of the water sample.
- Is the water sample safe for drinking?
- If the water sample is not safe for drinking, suggest ways to make it safe for drinking.

In-text Question

Explain the fate of the precipitates formed before lathering

Answer

The precipitate formed adheres to surfaces of tubs, sinks, dishwashers and may stain clothing, dishes and other items.

4.0 SELF-ASSESSMENT EXERCISES

1. Explain why necessary precaution should be taken for preventing the inhalation of ammonia.
2. What is EDTA and its function?
3. State the advantage of metallic salts that cause hardness in water

Answers

1. It causes irritation when inhaled
2. EDTA is ethylenediaminetetraacetic acid, it is a chelating agent.
3. They increase the alkalinity of the water, hence has buffering effect on acidity of water.

5.0 CONCLUSION

Hardness is the property which makes water to form an insoluble precipitate with soap and is primarily due to the presence of calcium and magnesium ions. Hard water is primarily of concern because it requires more soap for effective cleaning, stains clothes, dishes and other items, causes boiler scale, makes skin rough etc.

Hardness of water is an important consideration in determining the suitability of a given water source for domestic and industrial uses.

6.0 SUMMARY

Hardness is the concentration of multivalent metallic cations in water which determine the capacity of the water to precipitate soap. The predominant chemical constituents causing hardness in water are calcium and magnesium ions.

The source of calcium and magnesium ions is leaching from minerals within an aquifer. These minerals include calcite, gypsum and dolomite.

Determination of hardness in water is important because water containing hardness requires more soap for effective cleaning, stains clothes, dishes and other items, causes boiler scale, makes skin rough. The environmental engineer uses it as a basis for recommending the need for softening processes and design types. The Public Health Service Standards recommend a maximum of 500 mg/L of hardness in drinking water.

CLASS ACTIVITY (THE TUTOR TO DIRECT)

1. What is water hardness?

2. State the sources of hardness in water.

3. Discuss the significance of hardness in water.

4. 22.3 mL of 0.02 M EDTA was used to titrate 20 mL of a water sample, calculate the total hardness of the water sample.

7.0 REFERENCES/FURTHER READING

1. Sawyer, C.; McCarty P. &Parkin, G. (2006). *Chemistry for Environmental Engineering and Science* (5th Ed.). New Delhi:
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3. Ademoroti, C. (1996). *Standard Methods for Water and Effluents Analysis*. Ibadan: Foludex Press Ltd.
4. Mendie, U. (2005). *The Theory and Practice of Clean Water Production for Domestic and Industrial Use*. Lagos: Lacto-MedalsPublishers.
5. Experiment on Determination of Total Hardness, http://www.nittrc.ac.in/Four%20quadrant/eel/Quadrant%20_%201/exp5_pdf.