NATIONAL OPEN UNIVERSITY OF NIGERIA

SCHOOL OF SCIENCE AND TECHNOLOGY

COURSE CODE: CHM 391

COURSE TITLE: PRACTICAL CHEMISTRY V- INORGANIC AND ANALYTICAL

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NATIONAL OPEN UNIVERSITY OF NIGERIA

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INTRODUCTION

CHM 391 is a practical course based on CHM 202 and CHM 303. CHM 202 titled analytical chemistry, exposes you students to the theory of useful analytical procedures involving quantitative and qualitative techniques. In the course CHM 202, theoretical concept of titrimetric

(volumetric) analysis was treated. In the course you were taught the principle of the different forms of volumetric analysis. Apart from titrimetric analysis, analytical techniques involving spectroscopic methods were dealt with as well as the concept of errors as it relates to analytical chemistry, and different statistical tools for data handling were also treated.

In CHM 303 titled Inorganic Chemistry III, you were taught the elements of the periodic table and the compounds formed from their elements with exception of those formed between carbon and hydrogen.

This course CHM 391 provides you the opportunity to apply the theoretical knowledge acquired in CHM 202 to quantitatively and qualitatively analyse 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

The course deals with analytical and inorganic practical. The analytical aspect of the practical deals with some spectroscopic technique employed in the qualitative and quantitative estimation of the composition of a substance. Spectroscopic techniques utilizes instruments known as spectrophotometers. This give rise to this technique known as instrumental methods of analysis. The inorganic part of the practical is based on the use of classical methods of analysis to obtain quantitative and qualitative data/information of an analyte 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 dealt with here. 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 needed in analyzing an analyte.

COURSE AIMS

The course aims to give you the opportunity to explore different analytical techniques viz spectroscopic and classical techniques available for quantitative and qualitative elucidation of the composition 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

- Explain the principle of UV visible spectroscopy
- Use UV visible spectroscopy to estimate the concentration of an analyte
- Explain the principle of colometric analysis
- Determine the concentration of a coloured substance by colometric 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

WORKING THROUGH THIS COURSE

The course is divided into two modules which are subdivided into 7 units. It is required that you study the units in details and carryout 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 seven units contained in this course:
of an unknown sample. In so doing, you learn to transfer your theoretical

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

Carrying out practical is very essential to understanding the theoretical concept 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 principle of the analytical techniques mentioned are explained. A practical session precedes each principle.

Module 2 deals with practical involving classical methods of analysis and instrumental method of analysis. The classical methods dealt with here are; precipitation gravimetry and qualitative inorganic analysis of cations. The instrumental method is potentiometry. The principle of precipitation gravimetry, qualitative inorganic analysis of cations and potentiometry 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. You may also need to exploit other e- reading facilities such as 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 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 CHM 202 and CHM 303. Students are expected to make use of the theoretical knowledge acquired from CHM 202 (analytical chemistry) 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

MODULE ONE (ANALYTICAL)

UNIT 1 UV- VISIBLE SPECTROSCOPY

4.0 CONCLUSION

5.0 SUMMARY

6.0 TUTOR MARKED ASSIGNMENT

7.0 REFERENCES/ FURTHER READING

1.0 INTRODUCTION

In CHM 202 you learnt that 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 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. What you need to understand from both 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 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 emission of electromagnetic radiation as a function of wavelength are called spectrometers or spectrophotometers.

2.0 OBJECTIVES

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
- Prepare 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

Recall from you study of CHM 202 that the electromagnetic radiation covers a long range of radiations which are broken down into different regions according to wavelength. The Ultraviolet (uv) region extends from about 10 to 380 nm, but the most analytical useful region is from 200 – 380nm, called the near ultraviolet region. 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 (380 nm) to about 780 nm. 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 antibonding 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 antibonding 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 antibonding, in turn, is the Lowest Unoccupied Molecular Orbital (LUMO).

When organic molecules that are capable of absorbing UV visible radiation (chromophores) 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 appear 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.

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. 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 antibonding 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 and 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.

$n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ Transitions

Unsaturated compounds containing atoms with lone pairs (non-bonding electrons) 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 antibonding orbital (π^*). 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 is based on transitions of *n* or π electrons to the π^* excited state. 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 absorptivities 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 metal ion to the ligand or vice versa. Such transitions include promotion of electrons from π levels in the ligand or from σ bonding orbitals to the unoccupied orbitals of the metal ion or promotion of σ 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 absorbtivities from charge-transfer absorption are large (greater that 10,000 L mol^{-1} cm^{-1}).

3.3 APPLICATIONS OF UV-VISIBLE SPECTROSCOPY

- 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.

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:

$$\text{Log}_{10} \frac{I_0}{I} \quad C \text{ or } \text{Log}_{10} I_0 / I = \varepsilon C$$

Where, $\text{Log}_{10} I_0 / I$ is the absorbance (A), C is the concentration and ε is a constant, I_0 = incident light, I = transmitted light

This can also be represented as: A C or $A = \varepsilon C$

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,

$Log_{10} I_0 / I \propto l$ or $Log_{10} I_0 / I = k l$
Note that : absorbance (A) = $Log_{10} I_0 / I = k l$
Where, k is a constant and l is the path length.
The two laws are combined together and called Beer-Lambert's law:

$A = Log_{10} I_0 / I \propto Cl$ or $Log_{10} I_0 / I = \varepsilon Cl$

Where, ε is a constant called molar extinction coefficient (or molar absoptivity) 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 is often expressed as a percentage called percent transmittance.

Percentage transmittance (T) = I/I_0 X 100

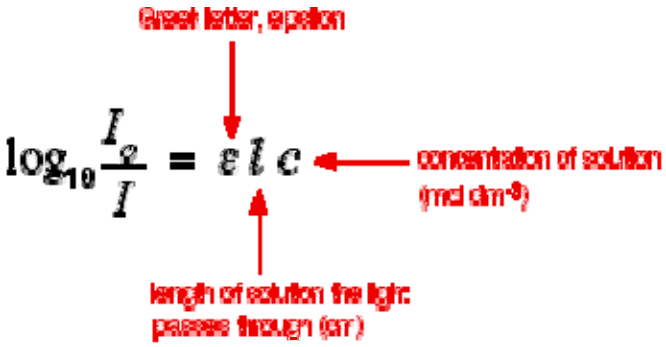
But, absorbance is related to transmittance as follows:

$A = Log_{10} 100/T$
Note that as the absorbance of a solution increases, the transmittance decreases.

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

$A = \varepsilon LC$

The absorbance $Log_{10} I_0 / I$ is measured by a spectrometer or spectrophotometer.



3.4.1.1 Finding 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:

$$A = \varepsilon l c$$
$$1.92 = 19400 \times 1 \times c$$
$$c = \frac{1.92}{19400}$$
$$= 9.90 \times 10^{-5} \text{ mol dm}^{-3}$$

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 determine is to be carried out is to prepare a standard solution of the sample, afterwhich you measure the absorbance and percentage transmittance over a series of wavelengths e.g wavelengths covering the range 360nm –640 nm at for instance 10nm intervals i.e. 360nm, 370nm, 380nm e.t.c. Plot the graph of absorbance against the wavelength or percentage transmittance. You would obtain a graph as shown in Figure 1

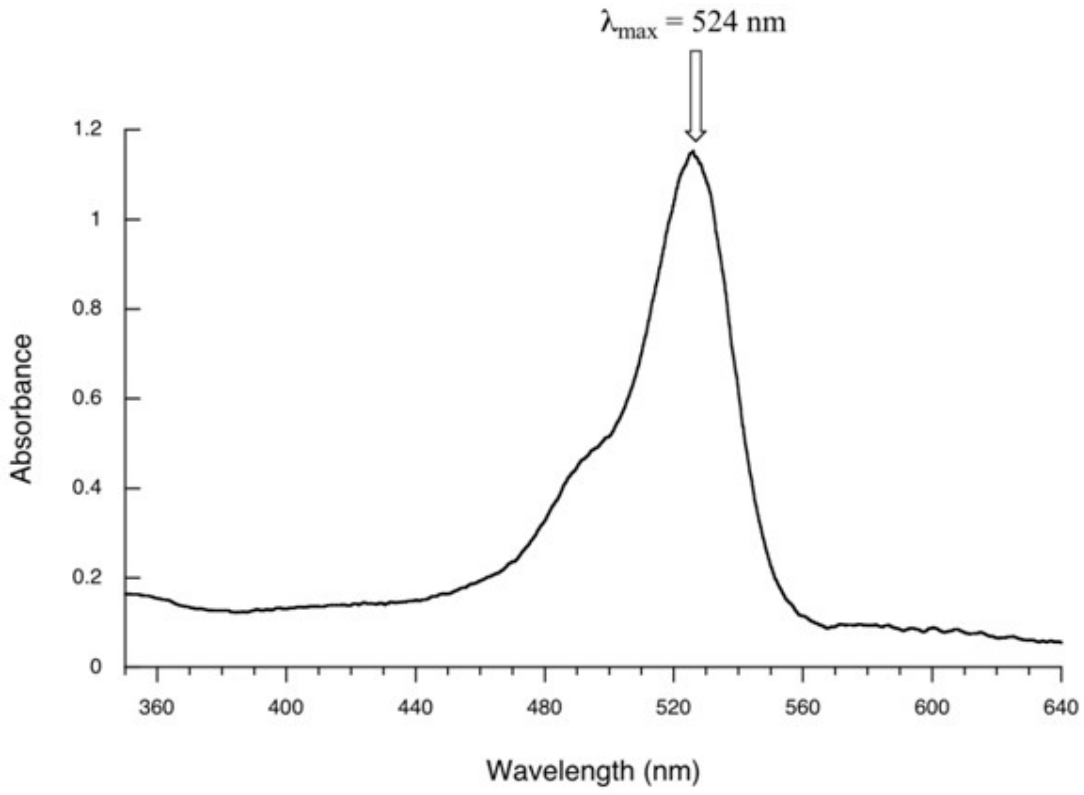


Figure 1

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 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.

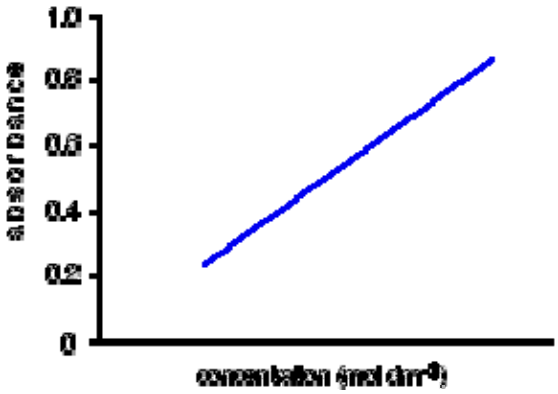


Figure 2

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).

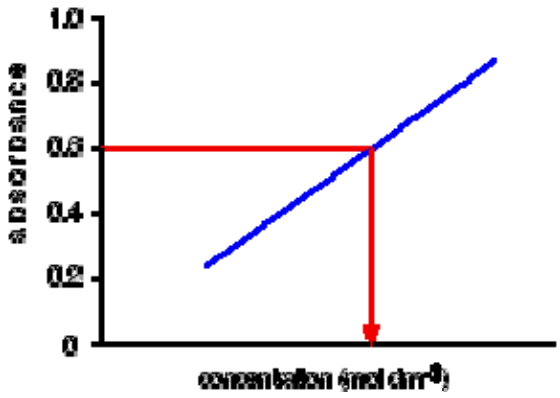


Figure 3

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 more sure. 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 A Spectrophotometer

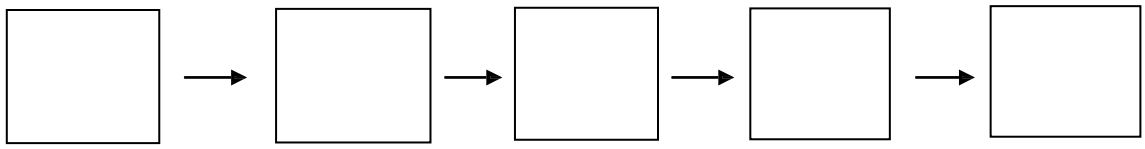


Figure 4: A schematic representation of a spectrophotometer
The schematic diagram above gives brief description of the basic components of a spectrophotometer.

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 240-360nm at 5nm 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 nanometres). 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 0.01-0.001M solution is sufficiently concentrated for the highest absorbances, 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 305nm 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 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.

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 240-350nm. Plot the data in three different ways:

(a) absorbance against wavelength

(b) percentage transmittance against wavelength

(c) log ε (molar absorptivity, or extinction coefficient (ε)) 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.

Determination of Absorption Curve and Concentration of Potassium Nitrate

REPORT SHEET

Name _____

Instructor _____ **Date** _____

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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 [$Fe(C_{12}H_sN_2)_3^{2+}$], 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. $4Fe^{3+} + 2NH_2OH \longrightarrow 4Fe^{2+} + N_2O + 4H^+ + H_2O$

Equipment / Materials:

1 litre volumetric flask	Ferrous ammonium sulphate	UV – Visible spectrophotometer
Beakers	Conc sulphuric 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 2.5ml of concentrated sulphuric acid, dilute exactly to the mark with distilled water, and mix thoroughly. This solution contains 10.0mg of iron per litre (10ppm); 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 100ml of water
3. Hydroxylammonium chloride solution. Dissolve 10 g of hydroxylammonium chloride in 100ml of water.
4. Sodium acetate solution. Dissolve 10 g of sodium acetate in 100ml of water.

Into a series of 100ml volumetric flasks, add with pipettes 1.00, 5.00, 10.00, and 25.00ml of the

standard iron solution. Into another 100ml volumetric flask, place 50ml 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 5.0ml of the 1, 10-phenanthroline solution. Buffer each solution by the addition of 8.0ml 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 100ml. The standards will correspond to 0.1, 0.5; 1, and 2.5ppm of iron, respectively. Obtain the absorption spectrum of the 2.5-ppm solution by measuring the absorbance from about 400nm to 700nm (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 10nm 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.

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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.

Equipment / Materials:

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.

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

3. 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.

4. 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 water to 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 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

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

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4.0 CONCLUSION

UV-Visible spectroscopy refers to absorption spectroscopy. It involves the absorption of radiation at the near ultraviolet region 200nm to 780nm. 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.

5.0 SUMMARY

UV-Visible spectroscopy is an analytical technique which involves the absorption of electromagnetic radiation at the near ultraviolet (200nm) 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.

6. 0 TUTOR MARKED ASSIGNMENT

1. What type of electrons in a molecule are 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.

7.0 REFERENCES/ FURTHER READING

1. 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.

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

UNIT 2 - COLORIMETRY

1.0 INTRODUCTION

2.0 OBJECTIVES

3.0 MAIN CONTENT

3.1 Principle of colorimetry

3.2 Colorimetric determinations

3.3 Mode of operation of a colorimeter

3.4 Experimentals

4.0 CONCLUSION

5.0 SUMMARY

6.0 TUTOR MARKED ASSIGNMENT

7.0 REFERENCES/ FURTHER READING

1.0 INTRODUCTION

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 OBJECTIVES

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

3.1 Principle of colorimetry

Colorimetric analysis is based on Beer- Lambert law. 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. Remember 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, so, in colorimetry the complimentary colour absorbed by a coloured solution occurs at particular wavelength.

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.

3.2 Colorimetric determinations

The determination is similar to spectrophotometric determination. It will normally require

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 strenght.

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

The colorimeter consist of light source, monchromator, 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 1

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

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.

Equipment / Materials:

Measuring cylinders (50cm^3 and 10 $cm^{3)}$	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 l^{-1} nitric acid		

CAUTION

Wear eye protection and if any chemical splashes on your skin wash it off immediately. The acidified 0.0010 mol l^{-1} potassium permanganate is harmful if ingested and irritates the eyes and skin. Wear gloves.
Both 2 mol 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 mol l^{-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 deionised 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 formular 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' – add 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 deionised 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 a permanganate concentration and then calculate the percentage by mass of manganese in the steel paper clip.

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4.0 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 radiatio n absorbed by the coloured compound is related to the concentration of the analyte in the solution.

5.0 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 light at 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 it s concentratio n. 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.

6. 0 TUTOR MARKED ASSIGNMENT

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 analysed

3.0 Describe the mode of operation of a colorimeter

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

7.0 REFERENCES/ FURTHER READING

1. 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.

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

3. Colorimetry, http://www.docbrown.info/page07/appendixtrans09.htm.

UNIT 3 - INFRARED SPECTROSCOPY

1.0 INTRODUCTION

2.0 OBJECTIVES

3.0 MAIN CONTENT

- **3.1 Principle of Infrared (IR) spectroscopy**
- **3.2 Types of vibrations**
- **3.3 Group frequencies**
- **3.4 Correlation of structure and frequency**
- **3.5 IR Spectroscopy Experimental Procedure**
- **3.6 Experiments**

4.0 CONCLUSION

5.0 SUMMARY

6.0 TUTOR MARKED ASSIGNMENT

7.0 REFERENCES/ FURTHER READING

1.0 INTRODUCTION

Infrared spectroscopy is a spectroscopic method of analysis used qualitatively to identify and study chemicals and quantitavely to measure concentration. 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) occur 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-vibrational_structure. 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** (or spectrophotometer) to produce an infrared spectru**m**. 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 OBJECTIVES

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 practicals

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 vibrational energy. The energy absorbed appear 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.

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 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 are used to detect the functional groups in molecules.

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 3300cm^{-1} and 1050cm^{-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 1 summaries some of the correlations for various types of vibrations.

Table 2: 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

3.5 IR Spectroscopy Experimental Procedure

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 appear as absorption peaks at the wavelenght 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/wavelenghts it corresponds to, is/are matched with the wavelenght 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 pathlength to compensate for the diluteness. The pathlength 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 analysed 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 light-absorption 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.

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, well-resolved 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

$A_{calc} = \log 1/T = I_0/I$

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,

$A = \varepsilon cl = \log 1/T = \log I_0 / I$ 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

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:

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 nondispersive 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 spectometer. 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 atmosphers; 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 Kim-wipe 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 deciccator.

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

Identification of Functional Groups of an Unknown Substance

REPORT SHEET

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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 nitromethane. 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.

Determination of the Concentration of Cyclohexane by IR Spectroscopy

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4.0 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 wavelengths, with intensities proportional to the concentration of absorbing species. Infrared spectroscopy exploits the fact that molecules absorb specific frequencies that are characteteristic 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.

5.0 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 is 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.

6. 0 TUTOR MARKED ASSIGNMENT

1. State two criteria necessary for a molecule to absorb infrared radiation

2. Explain briefly infrared spectroscopy

3. What are group frequencies

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

5. State the uses of infrared spectroscopy.

7.0 REFERENCES/ FURTHER READING

1. 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.

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

3. Infrared Spectroscopy, http:people.uwplatt.edu/~sundin/351/351h-ir.htm

UNIT 4 – ATOMIC ABSORPTION SPECTROSCOPY

1.0 INTRODUCTION

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 unexpected 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 OBJECTIVES

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 analysed). The wavelength of radiation given off by the source is the same t hat this sample elements 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.

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 (deionised) 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 analysed 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 digestio n, 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 suppied 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 furnance 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 solutions 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.

3.3 Uses of Atomic Absorption Spectroscopy

Atomic Absorption Spectroscopy is used particularly for determining the concentrations of metal ions in solutions.

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.

Equipment / Materials:

Magnesium metal	Deionised 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 ($1000 mgL^{-1}$) 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 $50 mgL^{-1}$ 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, remember to aspirate deionised 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.

Determination of The Concentration of Magnesium in Tap Water

REPORT SHEET

Name _____

Instructor _____ **Date** _____

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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.

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.

Determination of The Concentration of Vanadium in Lubricating Oil

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4.0 CONCLUSION

Atomic Absorption Spectroscopy (FAAS) 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.

5.0 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.

6. 0 TUTOR MARKED ASSIGNMENT

1. What is Atomic Absorption Spectroscopy (AAS)

2. Discuss the principle of AAS

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

4. Distinguish between wet ashing and dry ashing

7.0 REFERENCES/ FURTHER READING

1. 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.

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

MODULE TWO (INORGANIC)

UNIT 1 - PRECIPITATION GRAVIMETRY

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 CHM 202 where 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 as pure a 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 a knowledge of the formular 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 OBJECTIVES

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 an insoluble compound forms when we add a precipitating reagent, 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. 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.

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 nonaqueous solvent. A precipitate's solubility is generally greater in aqueous solutions because of the ability of water molecu les to stabilize ions through solvation. The poorer solvating ability of nonaqueous 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. Because 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 1). The presence of these partial charges makes the precipitate's surface an active site for the chemical and physical interactions that produce impurities.

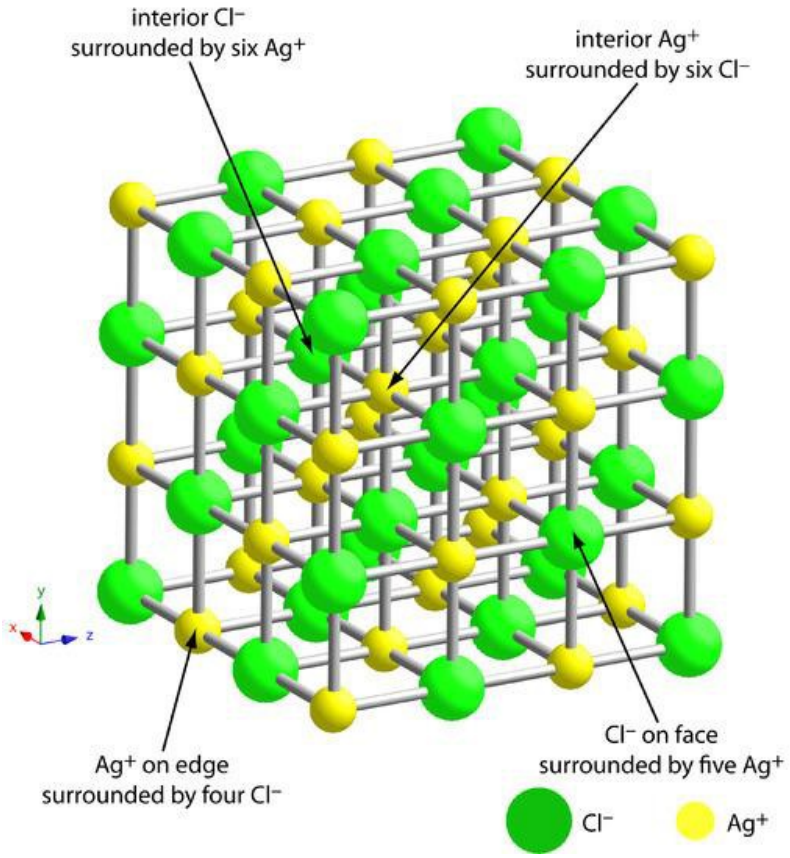

Figure 1

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.

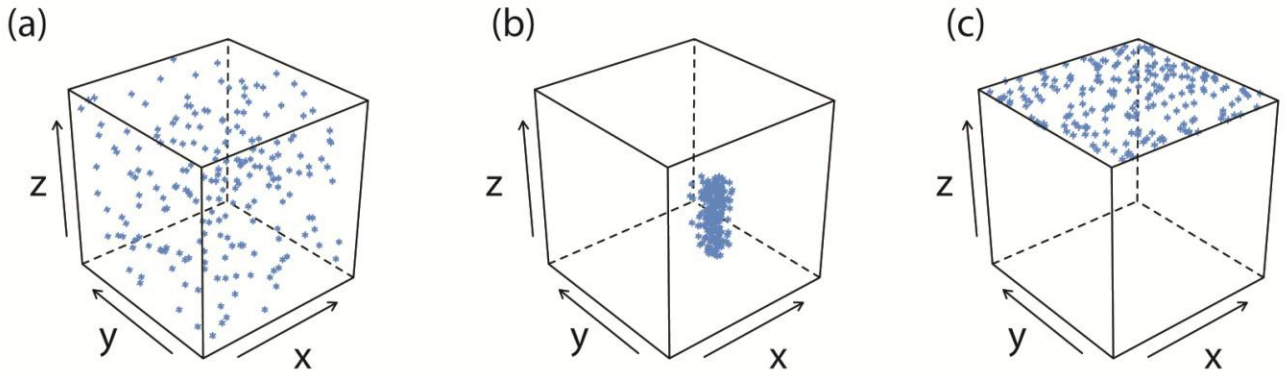

Figure 2 Three examples of impurities that may form during precipitation. The cubic frame represents the precipitate and the blue marks are impurities: (a) inclusions, (b) occlusions, and (c) surface adsorbates. Inclusions are randomly distributed throughout the precipitate. Occlusions are localized 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 2b). 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

$$RSS=Q-S/S \quad (1.0)$$

where *Q* is the concentration of the mixed reagents before precipitation occurs and is the degree of supersaturation, 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 1.0 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 reprecipitate 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 long-stem 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.

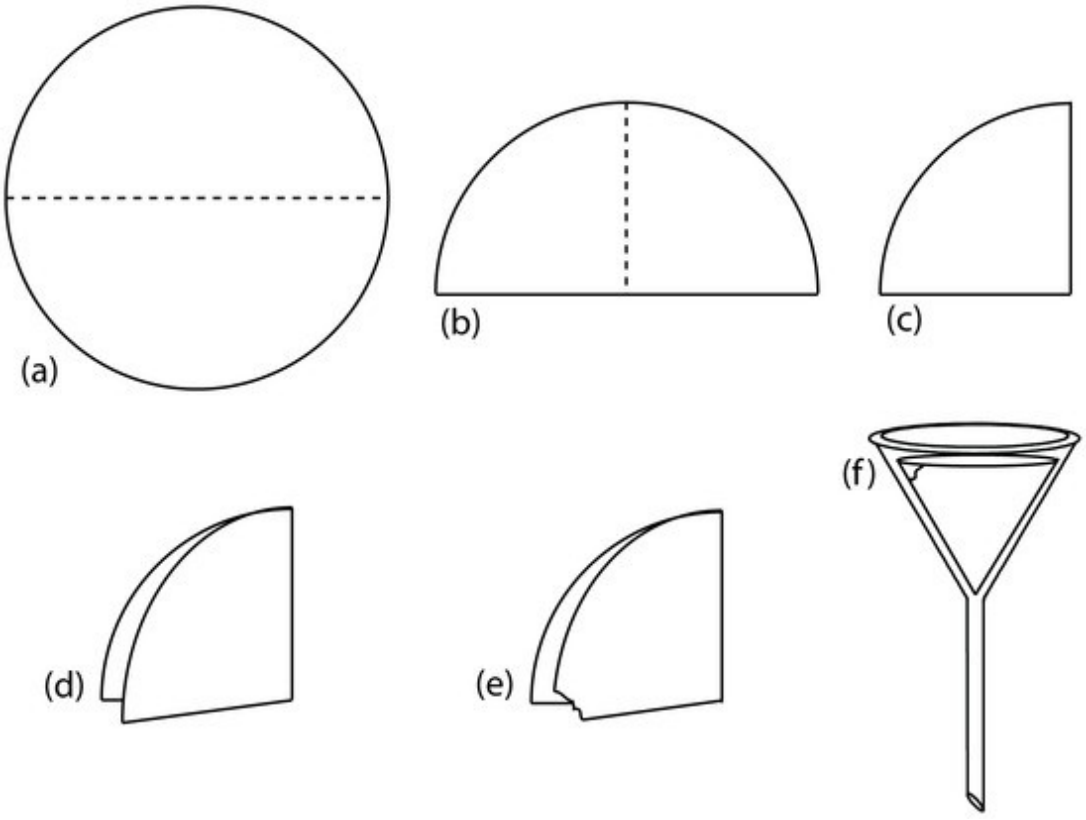

Figure 3 Preparing a filter paper cone. The filter paper circle in (a) is folded in half (b), and folded in half again (c). The folded filter paper is parted (d) and a small corner is torn off (e). The filter paper is opened up into a cone and placed in the funnel (f).

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).

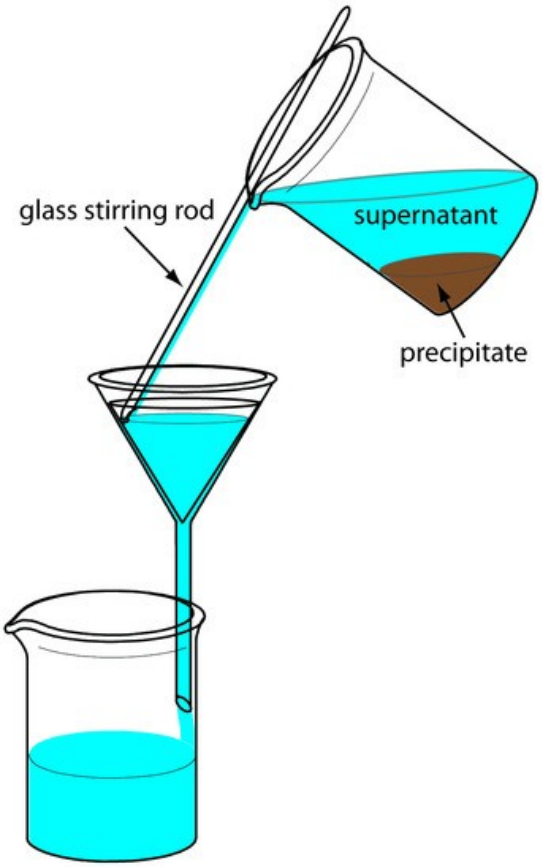

Figure 4 Proper procedure for transferring the supernatant to the filter paper cone.

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 4).

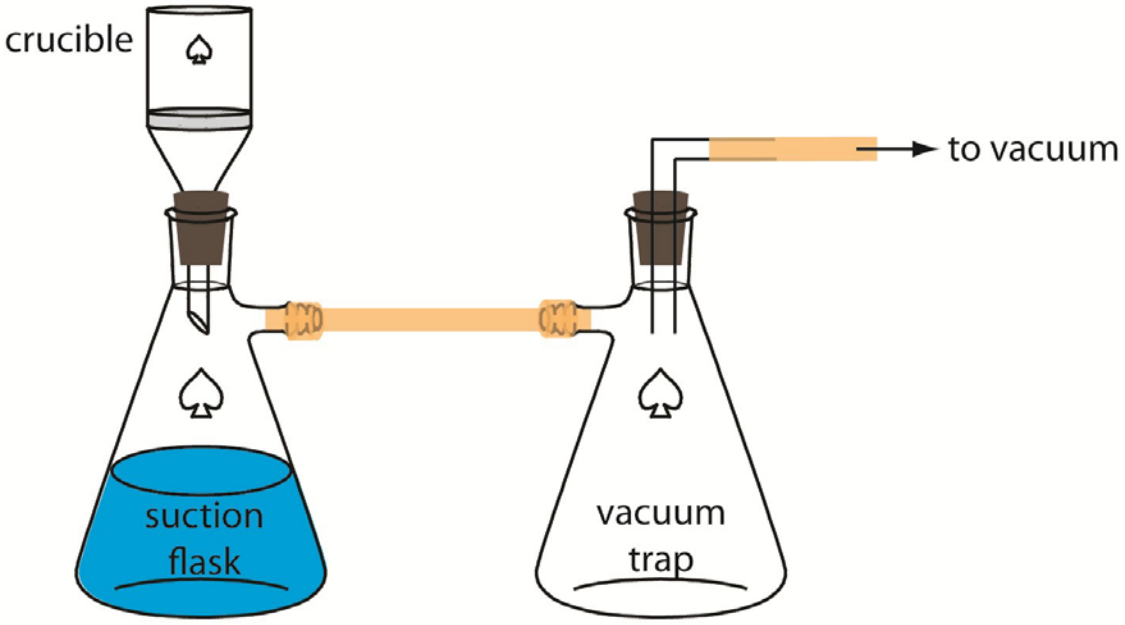

Figure 5 Procedure for filtering a precipitate through a filtering crucible. The trap prevents water from an aspirator from back-washing into the suction flask.

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 ignit ion, 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^{o}C. The glass fiber mats used in Gooch crucibles can be heated to a maximum temperature of approximately 500^{o}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

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

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

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 well-established 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 ma y 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.

EXPERIMENT 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.

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.

Gravimetric Determination of Chloride as Silver Chloride

REPORT SHEET

Name _____

Instructor _____ **Date** _____

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EXPERIMENT 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.

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 clockglass 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.

Determination of Nickel as the dimethylglyoximate

REPORT SHEET

Name _____

Instructor _____ **Date** _____

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EXPERIMENT 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.

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. Neutralise 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.

Gravimetric Determination of Lead as Chromate

REPORT SHEET

Name _____

Instructor _____ **Date** _____

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4.0 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.

5.0 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 equilibra 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 nonaqueous solvent.

To obtain a precipitate of high purity;

- The precipitate should be reprecipitated
- 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

6.0 TUTOR MARKED ASSIGNMENT

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 us.
4. Why must a wash liquid generally contain an electrolyte.

7.0 REFERENCES/ FURTHER READING

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UNIT 2 – QUALITATIVE ANALYSIS OF CATIONS

1.0 INTRODUCTION

2.0 OBJECTIVES

3.0 MAIN CONTENT

3.1 Principles of Qualitative Inorganic Analysis

3.2 Detecting Cations

3.4 Experimentals

4.0 CONCLUSION

5.0 SUMMARY

6.0 TUTOR MARKED ASSIGNMENT

7.0 REFERENCES/ FURTHER READING

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 equilibria, precipitation reactions and complex ion formation.

2.0 OBJECTIVES

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.

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^+.

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

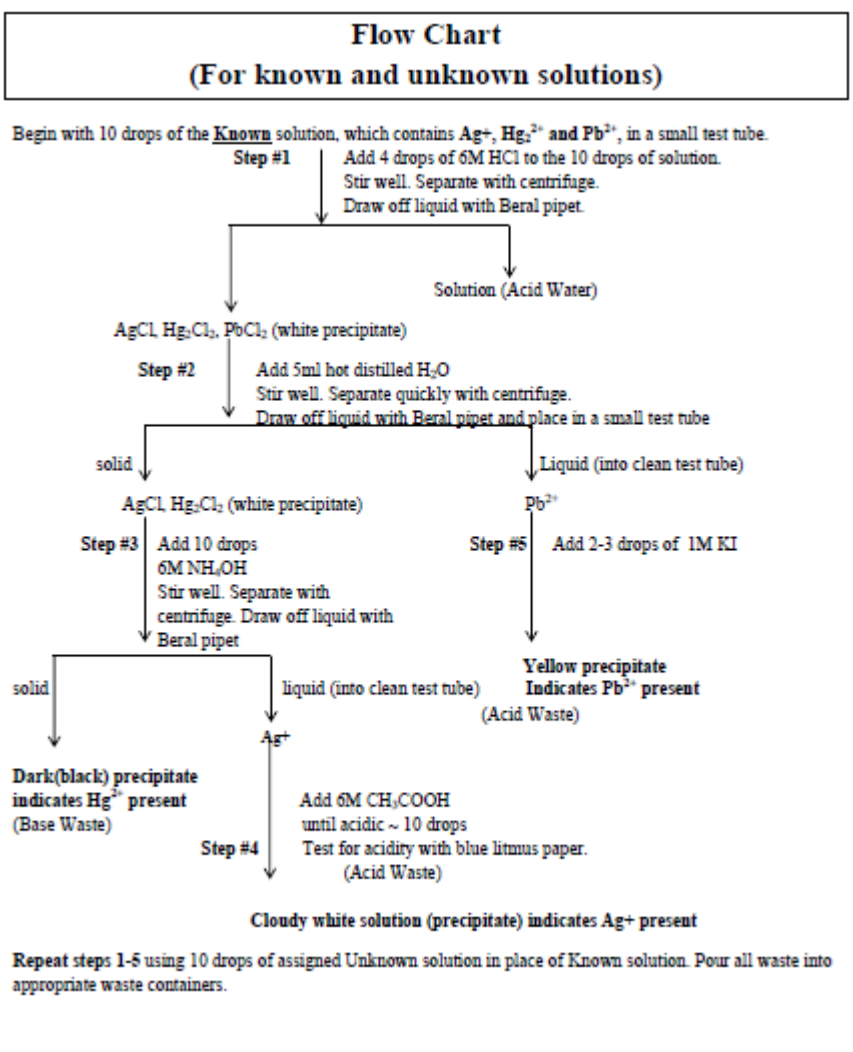
It is now necessary to consider the precipitate which may be comprised of AgCl or Hg_2Cl_2 or a mixture of the two. By adding NH_4OH to the solution, the AgCl and Hg_2Cl_2 can be separated.

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

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.



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^{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 disproportionation occurs 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 is present, 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.

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

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

$$Cu^{2+} + 4NH_4OH \longrightarrow Cu(NH_3)_4^{2+}\,(blue) + 4H_2O$$

Or

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

$$Cu^{2+} + Na_2S_2O_4 \longrightarrow Cu_{(s)} + SO_3^{2-} + 2Na^+$$

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

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+}; 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 include 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+}, $\underline{Li^{+}}$, 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>
<tr><td colspan="6">Scheme for separation of cations</td></tr>
<tr><td colspan="6">HCI or a soluble chloride, preferably NH4Cl, added to unknown; filtered</td></tr>
<tr><td rowspan="4">precipitate: contains chlorides of lead (Pb), silver (Ag), and mercurous mercury (Hg)

PbCl2 (white)
AgCI (white)
Hg2Cl2 (white)

Group I</td><td colspan="5">solution: H2S passed into the acid solution; filtered</td></tr>
<tr><td colspan="2">precipitate: treated with NH40H; ammonium polysulfide (NH4hSx; and (NH4hS; filtered</td><td colspan="3">solution: neutralized with NH40H and NH4Cl; filtered</td></tr>
<tr><td rowspan="2">precipitate: contains cupric, lead, cadmium, bismuth, and mercurie sulfides

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

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

Al(OH)s (white)
Cr(OH)s (gray-green)
Fe(OH)s (brown)

Group Ilia</td><td colspan="2">solution: H2S 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 Illb</td><td colspan="2">solution: evaporated and NH40H and (NH4hCOs added; filtered

precipitate: barium, strontium, and calcium carbonates (all white)

Group IV

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.

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.

Identification of Cations in an Unknown Mixture

REPORT SHEET

Name _____

Instructor _____ **Date** _____

Observations For Unknown Solution

Step 1:_____

Step 2:_____

Step 3:_____

Step 4:_____

Step 5: _____

Unknown Identification

Unknown Number: _____Ions Present in Unknown: _____

Confirmatory test for your identified ion(s)

.

4.0 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.

5.0 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.

6. 0 TUTOR MARKED ASSIGNMENT

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

1. Qualitative Analysis of Cations, http://classes.uleth.ca/200801/chem20001/1237%20Expt1_Qual2008.pdf .

2. Qualitative Inorganic Analysis, http://en.wikipedia.org/wiki/Qualitative_inorganic_analysis .

3. Experiment11: Qualitative Analysis of Cations, http://swc2.hccs.edu/pahlavan/…/Exp_11_Qualitative_Analysis_of_Cations .pdf

UNIT 3 – POTENTIOMETRIC TITRATION

1.0 INTRODUCTION

2.0 OBJECTIVES

3.0 MAIN CONTENT

3.1 Principles of Potentiometric Titration

3.2 Location of End Point in Potentiometric Titration

3.3 Types of Potentiometric Titration

3.3.1 Redox reaction: determination using potentiometry

3.4 Experiments

3.0 CONCLUSION

4.0 SUMMARY

6.0 TUTOR MARKED ASSIGNMENT

7.0 REFERENCES/ FURTHER READING

1.0 INTRODUCTION

In CHM 202 you were taught that an indicator is used to define 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 e.t.c.

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 OBJECTIVES

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. 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 thoroughly stirred.

A simple arrangement for a manual potentiometric titration is given in Figure . 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.

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.

3.2 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 (check CHM 202, acid-base titration). The central portion of this curve is shown in Figure , 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 (EnF/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 ($\Delta^2E/\Delta V^2$), 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.

3.3 Types of Potentiometric Titration

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

3.3 1 Redox reaction: determination using potentiometry

Redox titration has been dealt with in CHM 202. 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 concemtrations 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.

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.

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.

Redox Titration of Manganese by potentiometry

REPORT SHEET

Name _____

Instructor _____ **Date** _____

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EXPERIMENT 2 – Redox Titration of Steel by Potentiometry

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

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.

REPORT SHEET

Name _____

Instructor _____ **Date** _____

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EXPERIMENT 3 – Redox Titration of Copper by Potentiometry

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

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.

Redox Titration of Copper by potentiometry

REPORT SHEET

Name _____

Instructor _____ **Date** _____

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4.0 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 e.t.c. 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.

5.0 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.

6. 0 TUTOR MARKED ASSIGNMENT

1. Discuss briefly the principle of potentiometric titration.

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

7.0 REFERENCES/ FURTHER READING

1. 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.

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

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