KARPAGAM ACADEMY OF HIGHER EDUCATION

(Deemed to be University Established Under Section 3 of UGC Act 1956)

COIMBATORE-21

Syllabus-I M.Sc Chemistry

Semester - II

17CHP211 INORGANIC CHEMISTRY PRACTICAL–I 4H 2C
(QUALITATIVE ANALYSIS AND PREPARATIONS)

Instruction Hours/week:L: 0 T:0 P:4 Marks: Internal:40 External: 60 Total:100

Scope

This practical deal with the semi micro-qualitative analysis and spot tests of mixtures of familiar cations and non familiar cations and to motivate the students to understand the basic principles of lab techniques adopted in laboratories.

Programme Outcome

On successful completion of the course the students should have

1. Learnt about the qualitative analysis by semi micro-qualitative analysis method.
2. Learnt the preparation of inorganic complexes.

Contents

Thallium, Tungsten, Selenium, Tellurium, Molybdenum, Cerium, Thorium, Titanium, Zirconium, Vanadium, Beryllium, Uranium and Lithium.

Note: Each student should analyze a minimum of six inorganic mixtures.

About ten preparations involving different techniques selected from the following:

Lead tetra acetate, dipyridinium hexaplumbate, hydroxylamine hydrochloride, ortho and para-hydroxy phenyl mercuric chloride, potassium cupric chloride, chrome alum, copperI chloride, tris(thio urea) copper(I) Chloride, potassium trioxalato- aluminato(III), potassium trioxalato-chromate(III), potassium trioxalato- ferrate(III), hexammine cobalt(III)chloride, chloropentammine chromium(III), chloro aquo pentammine chromium(III) nitrate, tetrammine copper(II) sulphate, ammonium hexa chloro stanate(IV).
Note: Each student should do a minimum of ten preparations.

SUGGESTED READINGS:

Text Books:

1. Ramanujam, V. V. (2014). *Inorganic Semi-micro Qualitative Analysis* (III Edition). Chennai: The National Publishing Company.
2. Venkateswaran, V., Veeraswamy, R., & Kulandaivelu, A. R. (2014). *Basic Principles of Practical Chemistry* (II Edition). New Delhi: S. Chand Publications.
3. Siddhiqui, Z. N. (2002). *Practical Industrial Chemistry* (I Edition). New Delhi: Anmol Publications Pvt. Ltd.

Reference Books:

1. Mendham, J. R., Denney, C., Barnes, J. D., & Thomas, M. (2012). *Vogel's Textbook of Quantitative Chemical Analysis* (VI Edition). Singapore: Pearson Education Ltd.
2. Lepse, P. A., & Peter, L. B. (1986). *Lab Manual for Lingren's Essentials of Chemistry*. New Delhi: Prentice Hall.

Lab Manual on Inorganic Quantitative Analysis

Department of Chemistry

Enable | Enlighten | Enrich

KARPAGAM

ACADEMY OF HIGHER EDUCATION

(Deemed to be University)

(Established Under Section 3 of UGC Act, 1956)

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Titrimetric Analysis

Introduction

Analytical chemistry is broadly divided into two categories qualitative and quantitative analysis. The former deals with identification of chemical substances (organic or inorganic) while the latter deals with determination of the amount of a substance present, either alone or in a mixture with other substances.

Titrimetric (Volumetric) analysis is quantitative analysis carried out by determining the volume of a solution of accurately known concentration which is needed to react quantitatively with the solution of the substance to be determined. The solution whose concentration is known is called the standard solution. The amount of the substance to be determined is calculated from the volume of the standard solution used and the known laws of stoichiometry.

A reaction which is used in a quantitative titrimetric determination must meet the following criteria:

- The overall chemical reaction should be uncomplicated and easily expressed in terms of chemical equations, and the substances to be determined must react stoichiometrically with the reagent.
- The reaction must proceed quickly, although a catalyst may be used to increase the speed of a reaction.
- When stoichiometric quantities of the reagent have been consumed; there must be a definite change in some physical or chemical property which allows the end of the reaction to be easily detected. This is generally achieved either by using an indicator or potentiometrically or conductometrically.

Apparatus Used in Titrimetric Analysis

You are already familiar with the apparatus used in titrimetry as you have used them in school. You will use the following:

- Burette
- Pipette
- Measuring flask (volumetric or standard flask)
- Conical flask

- Analytical Balance
- Stoppered weighing bottle

Cleaning of apparatus

All glassware must be perfectly clean and free from grease, otherwise results will be unreliable. One test for cleanliness of glass apparatus is that on being filled with water and the water withdrawn, only an unbroken film of water (not in form of drops) remains.

A cleaning agent commonly used is chromic acid, a saturated solution of potassium dichromate in concentrated sulphuric acid. The apparatus is filled with this and allowed to stand for several hours (preferably overnight). The acid is then poured off and the apparatus is washed with tap water followed by repeated rinsing with distilled water.

The glass apparatus used is generally of two types – apparatus meant to contain a specific volume of liquid (TC) and apparatus meant to deliver definite volume of liquid (TD). Thus a standard flask comes under TC category whereas burette and pipette are under the TD category.

Use of the pipette

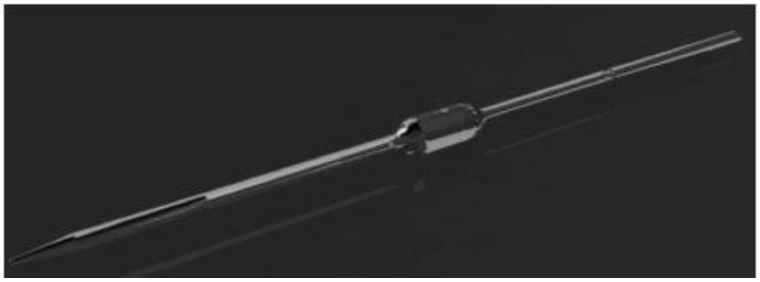


Figure 1. Pipette

- The pipette is first washed with tap water and then it is rinsed with distilled water.
- A small portion of the solution to be measured (1 to 2 cm^3 for a 10 or 20 cm^3 pipette, less for smaller ones) is drawn into the pipette. The solution is rolled around the pipette in such a manner that it comes in contact with all portions of the pipette. The solution is then allowed to drain. This procedure of rinsing is repeated once.
- The pipette is filled with the solution until above the etched mark and the forefinger of the right hand (left hand for a left hander) is quickly placed on the top of the pipette. The finger tip should be dry and the solution should be above the mark.

- The pipette is held in a vertical position and the level of the liquid is allowed to fall slowly until the bottom of the meniscus is at the top of the etched mark of the pipette (Figure 2).

- The liquid in the pipette is dispensed into the container, holding the pipette in a vertical position. The pipette is allowed to remain in contact with the container for about 10 seconds after the liquid has drained from it (Figure 3). The last drop of solution, which remains in the tip of the pipette, is not blown out as the apparatus is calibrated in such a manner that this drop does not contribute to the volume of the solution delivered.

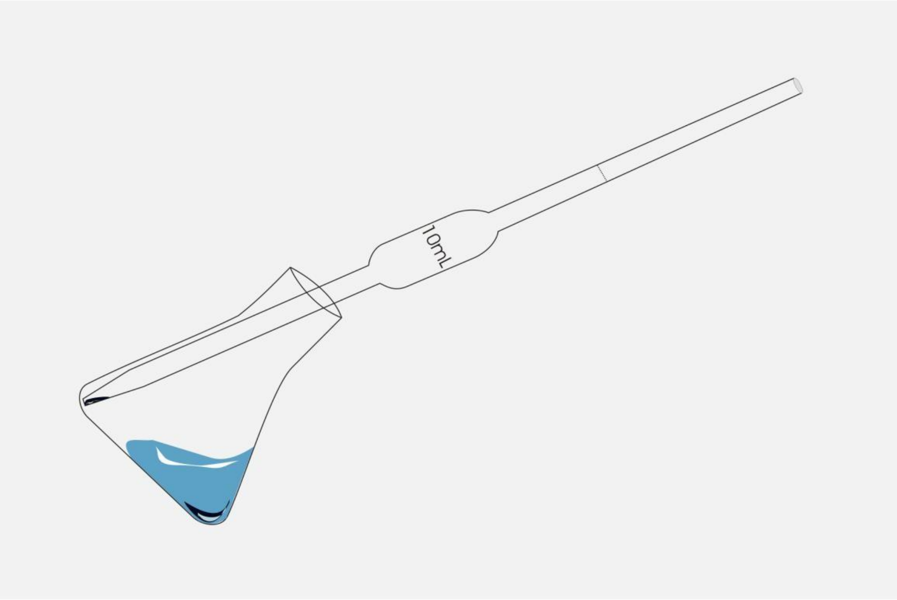


Figure 3. Last drop of the solution remains in the tip of the pipette

- Toxic or corrosive substances are not sucked with a pipette; a pipette bulb (or a dispenser) or a burette is to be used for measuring these substances.

Use of the burette

- The burette is first washed with tap water and then it is rinsed with distilled water.

It is rinsed with several small portions of the solution with which it is to be filled making sure that the solution contacts all portions of the burette. The solution is drained through the tip

- The burette is mounted in a vertical (upright) position and is filled above the zero mark by using a funnel. The solution is then allowed to flow through the tip. All air bubbles should be removed from the tip and the nozzle.

This is achieved by opening the stop cock and allowing the solution to flow out rapidly or by tapping the nozzle gently with the fingertip to dislocate the bubble.

- The funnel is removed and the level of the liquid is adjusted to eye level to minimize parallax error. A rectangular piece of white paper is folded and two horizontal slits are made in it about 5 cm apart. These slits are inserted into the burette in such a manner that the white paper provides a background for reading the scale on the burette (Figure 5.). This is called an index card and is helpful in minimizing parallax error. It is not necessary to adjust the level to the zero mark if it is too high for your eye level.

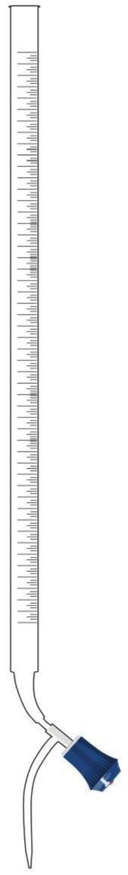


Figure 4. Burette

- The burette is first washed with tap water and then it is rinsed with distilled water.
- It is rinsed with several small portions of the solution with which it is to be filled making sure that the solution contacts all portions of the burette. The solution is drained through the tip.

Use of the measuring flask

- Wash the flask with tap water and rinse it with distilled water.
- If a solution is to be made from a weighed solid, then transfer the solid through a funnel into the flask and dissolve in a small amount of distilled water. Swirl the flask gently to aid in dissolution.
- If a solution is to be made by diluting a concentrated solution, then transfer it using a pipette into the flask.
- Mix the solution well when the flask is about ¾ full.

- Dilute the solution up to the mark. The bottom of the meniscus should just rest on the top of the mark. The last few drops of the solvent should be added using a dropper or pipette.

Figure 5. Standard Measuring flask

- Make the solution homogenous. Hold the stopper securely and invert the flask six to eight times. Turn the flask right side up.

Note: Never use the pipette, burette or measuring flask to deliver or contain a hot solution as this will spoil the calibration of the apparatus.

Expression of Concentration

The concentration of a solution is expressed in various ways. It is worthwhile to recapitulate a few fundamental concepts.

Mole (mol)

This is the amount of a substance that contains as many entities, as are there in 0.012 kg of ^{12}C isotope. The mole may be of atoms, ions, molecules or any other entity. The number of entities in a mole of any substance is a constant called Avogadro's number (N_A) which is equal to 6.022 x10^{23}.

Relative Molecular Mass (M_r)

This is also referred to as the molecular weight and is the mass of one molecule in atomic mass unit (a.m.u.) relative to 1/12 of the mass of ^{12}C isotope (12.000 a.m.u.) the relative molecular mass is calculated from knowledge of the formula of the compound and atomic mass of the constituent atom.

For example, one molecule of H_2SO_4 has the relative molecular mass of 98 which may be calculated as:
(2 x 1) + 32 + (4 x 16) = 98
If does not have any units as it relative in nature.

Molar mass (M_m)
This is the mass of one mole of a substance. It is equal to the relative molecular mass, but is expressed in the units of g mol^{-1}.
For example, the molar mass of H_2SO_4 is 98 g mol^{-1}.

The amount of a substance having mass equal to molar mass is called a mole.
In titrimetic analysis, concentration is generally expressed in terms of molarity, which is equal to the amount of solute present in 1 dm^3 of the solution.

$$\text{Molarity (M)} = \frac{\text{Amount of solute (in moles)}}{\text{Volume of solution (in dm}^3\text{)}}$$

Standard Solution

A standard solution is one, which contains a known weight of the solute in a known volume of the solution. It is prepared by dissolving an accurately weighed pure solute in an appropriate solvent. Preparation of the standard solution is the first step in titrimetry. The substances used to make standard solutions are called primary standards.

Primary Standard Substances

A primary standard is a substance of sufficient purity from which a standard solution may be prepared by weighing a fixed amount and dissolving it in a definite volume of distilled water. It must satisfy the following conditions:

- It must be easy to obtain and to preserve in a pure state.
- It should be unaltered in air during weighing, i.e., it should not be hygroscopic, oxidized by air or affected by carbon dioxide.
- It should be easily soluble in the given solvent.
- The solution should maintain its composition during storage.
- The reaction with the standard solution should be stoichiometric, instantaneous and have minimum titration error.
- To minimize weighing errors, it is preferable if the molecular weight of the substance is high.

Some substances used as primary standards are given in Table 1. Table 1. List of

Name of the substance	**Formula**	**Relative molecular mass**
Oxalic acid	$H_2C_2O_4.2H_2O$	$M_r = 126.00$
Sodium oxalate	$Na_2C_2O_4$	$M_r = 134.00$
Anhydrous sodium carbonate	Na_2CO_3	$M_r = 106.00$
Ferrous ammonium sulphate	$FeSO_4.(NH_4)_2SO_4.6H_2O$	$M_r = 392.00$
Potassium dichromate	$K_2Cr_2O_7$	$M_r = 294.20$

Substances not satisfying the above conditions are called **secondary standards** (for example, NaOH, HCl, $KMnO_4$). The concentrations of these can be determined by titrating them against a standard solution. This process is called standardization.

Titration

The process is carried out to find the volume of one solution required to react completely with a certain known volume of solution of some other substance.

For this purpose, one of the solutions (either the standard solution or the substance to be determined) is taken in a burette and an accurately measured volume of the other is pipetted out in a conical flask. The solution from the burette is added slowly and the conical flask is continuously shaken to enable the two solutions to mix. The solution from the burette is added till both solutions react quantitatively.

The solution in the conical flask is called the **titrand**, while the one in the burette is the **titrant**. The stage at which quantities of titrant and titrand are in stoichiometric proportion is called the **equivalence point**. The completion of the titration should be detectable by change in some property like colour. A substance used to indicate equivalence point of a titration through a colour change is called the indicator and the equivalence point so obtained is called the **end point**.

Notes:

- The titrant should be added drop wise at the vicinity of the end point, till addition of one drop gives a sharp colour change.
- The correctness of the end point may be checked by adding one drop of the titrand with a pipette. Restoration of the original colour confirms correctness of the end point.

- The titration should be repeated to get three concordant readings.

Types of Titrations

There are four types of titrations:

Acid – Base titration

- These titrations involve the reaction of an acid with a base to give salt and water. The reaction involved is a neutralization reaction.

Example - titration involving NaOH and HCl, NaOH and oxalic acid, Na_2CO_3 and HCl etc.

- The choice of indicator is governed by change in pH at the end point; common examples are methyl orange and phenolphthalein.

Oxidation – Reduction (Redox) Titration

- In these titrations, there is change in oxidation number or transfer of electrons between reactants. One component gets oxidized while the other gets reduced. Example - titration involving $KMnO_4$ with oxalic acid or Fe(II), $K_2Cr_2O_7$ with Fe(II) or Sn(II), titrations involving iodine.
- Indicators used in such titrations are diphenylamine, starch (in titrations involving iodine) and $KMnO_4$ itself (self indicator).

Precipitation Titration

- These titrations involve the combination of ions to form a precipitate. Example - titration between potassium chloride and silver nitrate.
- Indicators used include potassium chromate and eosin.

Steps in titrimetric analysis

The main steps in a titrimetric analysis are:

1) Preparation of standard solution.
2) Standardization of secondary standard by titration with a standard solution.

Determination of concentration of unknown sample by titration with secondary standard

Recording of experiment

The aim of the experiment, instructions given by the teacher and observations are initially noted in the auxiliary note book.

The experiment is then recorded in the record book in the following way:

Left – hand page	**Right – hand page**
Observations	Date & experiment number
Preparation of standard solution	Aim
Recording of titration in tabular form.	Theory
Calculation	Procedure (Past tense, passive voice)
Result	Result (up to 4 decimal places)

Complex Metric Titration

The technique involves titrating metal ions with a complexing agent or chelating agent (Ligand) and is commonly referred to as complexometric titration. This method represents the analytical application of a complexation reaction. In this method, a simple ion is transformed into a complex ion and the equivalence point is determined by using metal indicators or electrometrically. Various other names such as **chilometric titrations**, chilometry, chilatometric titrations and EDTA titrations have been used to describe this method. All these terms refer to same analytical method and they have resulted from the use of EDTA (Ethylene diamine tetra acetic acid) and other chilons. These chilons react with metal ions to form a special type of complex known as **chelate**.

Objective

1. To perform water analysis regarding the presence of chloride, sulphate, and ammonium ions.
2. To measure water hardness caused by dissolved calcium and magnesium ions by complexometric titration

Equipment

- Beaker
- Test tube

- pH paper
- Erlenmeyer flask
- Burette
- Stands
- Pipette

Chemicals and Materials

- Aquadest
- Tap water
- $AgNO_3$ (silver nitrate)
- $BaCl_2$ (barium chloride)
- NaOH (sodium hydroxide)
- 1 M Ammonium buffer (1M NH_4OH)+ 1 M NH_4Cl)
- $5x10^{-3}$ M EDTA solution (ethylenediaminetetraacetic acid)
- Eriochrome Black T

Procedure

2 beakers were prepared and filled with the following fluid:

- Beaker 1: 20 ml distilled water
- Beaker 2: 20 ml tap water

The appearance and smell of each sample were checked and the pH values were measured using pH paper.

A few drops of 1 n $AgNO_3$ were put into each beaker.

observation was done to see whetherprecipitation occurred. When precipitation occurred, chloride ions were present.

Some crystals of $BaCl_2$ were dissolved in 5 ml of distilled water.

Another set of beakers were prepared and filled with appropriate fluids

A few drops of $BaCl_2$ solution were put into each beaker.

Observation was done to see whether precipitation occurred. When precipitation occurred, sulphate ions were present.

2 test tubes were prepared and filled with the following fluid:

- Test tube 1: distilled water
- Test tube 2: tap water

One flake of NaOH was put inside each test tube.

The appearance and smell (pungent smell of ammonia) were observed for presence of ammonium chloride.

Measurement of water hardness with EDTA titration:

1. The 1500 ml of 5 x 10^{-4} EDTA solution was prepared by mixed the 50 ml of 5 x 10^{-3} M EDTA with solution of 50 ml NH_4OH 1 M and 50 ml NH_4Cl.
2. The 25 ml tap water was put into an Erlenmeyer flask and it was added with 20 drops of ammonia buffer and 10 drops of Eriochrome Black T indicator. This solution color was red purplish.
3. The burette was clamped to the ring stand and the EDTA solution was put into the burette until it reached 50 ml.
4. Then, the solution in the Erlenmeyer flask was titrated with EDTA solution until its color reached blue color.
5. The total volume of EDTA solution that being used to titrate the solution in the Erlenmeyer flask was recorded.
6. The second procedure until fifth procedure was repeated once.

Observation and Measurement Result

CHARACTERISTIC	DISTILLED WATER	TAP WATER
Appearance	Transparent	Transparent
Smell	No smell	No smell
pH	5.5	6.5

CONDITION	DISTILLED WATER	TAP WATER
Addition of $AgNO_3$	Colorless, no precipitation	Turbid
Addition of $BaCl_2$	Colorless, no	Colorless, no

Measurement of water hardness with EDTA titration:

Distilled water

After it was added with the Eriochrome Black T Indicator, the solution color turned to dark blue.

Tap water

After it was added with the Eriochrome Black T Indicator, the solution color turned to purplish red. After it was titrated with EDTA, the solution color turned to blue.

The volume of EDTA used in the first titration = 16.6 ml. The volume of EDTA used in the second titration = 15.7 ml.

Figure: end point of titration

I. Evaluation and Calculation

Measurement of water hardness with EDTA titration:

Water hardness is an expression for the sum of the calcium and magnesium cation concentration in a water sample. An excellent way to determine water hardness is to perform a complexometric titration using a standard ethylenediaminetetraacetic acid (EDTA) solution. EDTA is a chelating agent that can donate electrons (Lewis base) thereby forming a complex with metal ions (Lewis acid). The

EDTA will complex first with the Ca^{2+} and then with the Mg^{2+} in a one-to-one molar ratio. But, in this experiment, it was assumed that only Ca ions contribute to the water hardness.

In this experiment, 20 drops of ammonia buffer and 10 drops of Eriochrome Black T indicator were added into 25 ml of tap water in Erlenmeyer flask. Then the tap water was titrated with EDTA solution two times to get the average volume of EDTA solution used. Ammonia buffer was used to adjust and keep the pH to 9.9-10.1. It is necessary to keep the pH at about 10 for two reasons. First, all reactions between metal ions and EDTA are pH dependent, and for divalent ions, solutions must be kept basic (and buffered) for the reaction to go to completion. Second, the Eriochrome black T indicator requires a pH of 8 to 10 for the desired color change.

Since both of EDTA solution and Ca ions are colorless, it is necessary to use Eriochrome black T indicator to detect the end point of titration. Eriochrome black T indicator (denoted as In) is a metal ion indicator whose color changes when it binds to a metal ion. When the indicator was added into tap water, the solution color changed from colorless into purplish red. It means the tap water which used in the experiment contained Ca ions. The reaction occurred:

$$Ca^{2+} \quad + \quad In^{2-} \quad \rightarrow \quad CaIn$$

(blue) (wine red)……………………equation 1

Then the solution in Erlenmeyer flask was titrated with the EDTA solution. When EDTA solution was added drops by drops into Erlenmeyer flask, the indicator must give up its metal ions, Ca^{2+} to the EDTA because EDTA can bind to the metal ions stronger than the indicator. When all metal ions bind with EDTA, the indicator is in its free form and it doesn't bind to any metal. Then the solution color will turn to blue color which meant the end point was reached. The reaction occurred:

$$CaIn + EDTA^{4-} \rightarrow CaEDTA^{2-} + In^{2-}$$

(wine red) (blue)………………….equation 2

<u>The calculation of the concentration of water hardness from tap water</u>

$$\text{The average volume of EDTA} = \frac{16.6\text{ ml} + 15.7\text{ ml}}{2}$$

= 16.15 ml

= 16.15 x 10-3 l n EDTA = M EDTA x V EDTA

= 5 x 10-3 M x 16.15 x 10-3 l

= 80.75 x 10-7 mol

1 mol EDTA = 1 mol Ca

80.75 x 10-7 mol EDTA = 80.75 x 10-7 mol Ca n Ca = 80.75 x 10-7 mol

gr Ca = n Ca x Ar Ca

= 80.75 x 10-7 mol x 40.078

= 3.24 x 10-4 gr

= 0.324 mg [Ca] = <u>0.324 mg</u>

25.10-3 l

= 12.96 mg/l

= 12.96 ppm

In this experiment, the sample water was not given so there are no much comparison could be made with the tap water. The distilled water did not need to be titrated with EDTA because when it was added with Eriochrome Black T Indicator the solution colour was dark blue. It means there were no metal ions in distilled water such as Ca2+ and Mg2+ which can bind to the indicator to give red color The [Ca] in tap water in this experiment were 12.96 ppm.

Conclusion

- The distilled water sample did not contain Cl^{-} and SO $^{-}{}_{4}$ions and may also contain ammonium chloride.
- The tap water sample did contain Cl^{-} ions but did not contain SO $^{-}$ ions. $_{4}$

Ammonium chloride may be present.

- Distilled water did not contain any ions and can be considered as soft water.
- The concentrations of Ca ions in tap water were 12.96 ppm.
- Tap water used in this experiment is considered to be soft water.

BASIC CONCEPT OF NON –AQUEOUS TITRATIONS

The Bronsted Lowery theory of acid and bases can be applied equally well to reactions occurring during acid base titrations in non-aqueous solvents. This is because this approach considers an acid as any substance, which will tend to donate a proton, and a base as any substance, which will accept a proton. Substances which give poor end points due to being weak acids or bases in aqueous solution will frequently give far more satisfactory end point when titrations are carried out in non-aqueous media. An additional advantage is that many substances, which are insoluble in water, are sufficiently soluble in organic solvents to permit their titrations in these non-aqueous media. In the Bronsted Lowery theory, any acid, (HB) is considered to dissociate in solution to give a proton
(H_+) and a conjugate base (B_-):- where as any base (B) will combine with a proton to produce a conjugate acid (HB_+):

$$HB \leftrightarrow H+ + B_- \; B+H_+ \leftrightarrow HB+$$

The ability of substances to act as acids or bases will very much depend on the choice of solvent system

ADVANTAGES OF NON AQUEOUS SOLVENT OVER AQUEOUS SOLVENT:

1. Organic acids and bases that are insoluble in water are soluble in non-aqueous solvent.
2. Organic acid, which is of comparable strength to water, can be titrated easily in non- aqueous solvent. Bases also follow the same rules.
3. A non-aqueous solvent may help two are more acids in mixture. The individual acid can give separate end point in different solvent.
4. By the proper choice of the solvents or indicator, the biological ingredients of a substance whether acidic or basic can be selectively titrated.
5. Non aqueous titrations are simple and accurate, examples of non aqueous titration are: Ephedrine preparations, codeine phosphate in APC, tetracycline, teramycin, Antihistamines and various piprazine preparations.

SOME EXAMPLES OF NON-AQUEOUS SOLVENTS

***Glacial Ethanoic Acid*:** Glacial ethanoic acid is the most frequently used non-aqueous solvent. Before it is used it is advisable to check the water content. This may be between 0.1% and 1.0%.

Dimethylformamide: Dimethylformamide (DMF) is a protophillic solvent, which is frequently employed for titrations between, for instance, benzoic acid and amides, although end points may sometimes be difficult to obtain.

Acetonitrile: Acetonitrile (methyl cyanide, cyanomethane) is frequently used with other solvents such as chloroform and phenol and especially with ethanoic acid. It enables very sharp end points to be obtained in the titration of metal ethanoates when titrated with perchloric acid.

***Dioxane*:** Dioxane is another popular solvent, which is often used in place of glacial ethanoic acid when mixtures of substances are to be quantified. Unlike ethanoic acid, dioxane is not a levelling solvent and separate end points are normally possible, corresponding to the individual components in the mixtures.

Alcohol: Salts of organic acids, especially of soaps are best determined in mixtures of glycols and alcohols or mixtures of glycols and hydrocarbons. The most common combinations are ethylene glycol (dihydroxyethane) with propan-2-ol or butan-1-ol. The combinations provide admirable solvents for both the polar and non-polar ends of the molecules.

APPLICATIONS OF NON –AQUEOUS TITRATIONS

Although indicators may be used to establish individual end points, as in traditional acid-base titrations, potentiometric methods of end point detection are also used extensively, especially for highly coloured solutions. Non aqueous titration have been used to quantify the mixtures of primary, secondary and tertiary amines, for studying sulphonamides, mixture of purines and for many other organic amino compounds and salts of organic acid. And also it is used for the titration of Halogen acid salts of weak bases.

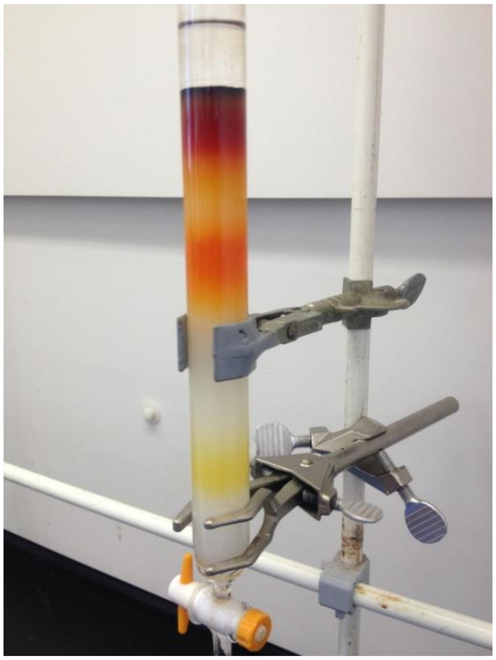
CHROMATOGRAPHY

Introduction

Chromatography in all its variations is one of the most widely used and most potent of all the laboratory purification methods in the chemist’s armamentarium. First demonstrated by Michael Tswett, a Russian botanist who report the separation of plant pigments (coloring agents) by this method in 1903, chromatography has since been applied to every conceivable type of compound in a wide variety of uses. The name chromatography stems from the early application to mixtures of colored compounds; the separation amounted to graphing the color (Greek: chroma = color).

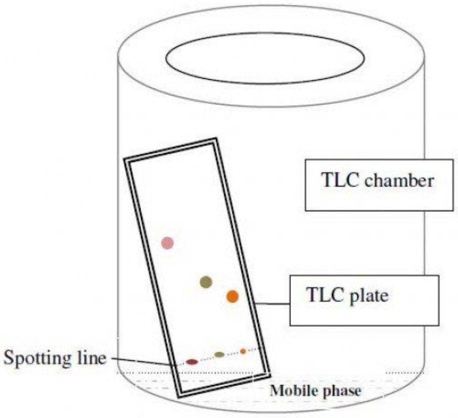
Chromatography involves an analogous principle. A mixture of two or more compounds is placed on a section of stationary material over which a fluid is slowly passed. The various compounds will be attracted to (adsorbed on or dissolved in) the stationary material, but will also have a competing tendency to dissolve in the fluid and pass slowly through the stationary material and out. This competition will cause some compounds of mixture to move through relatively quickly (they will be very soluble in the fluid and only weakly absorbed – the thin people) and some to move through very slowly (much less soluble in the fluid, strongly absorbed –the wider people). By collecting and analyzing the fluids leaving the stationary material in small batches, one can separate compounds that can never be purified of each other by other by any other technique. Alternatively, for analytical purposes, one could stop the fluid flow at some point before the compounds leave the stationary material and inspect their relative positions to see how many compounds are present and what their chromatographic properties are. Both approaches have been widely used,

Numerous forms of chromatography have been developed:



a. Column chromatography--The stationary material is often crushed mineral (silica gel, for instance) and the moving phase a solvent (acetone, benzene, etc.). The stationary material is packed in a vertical glass tube (column) and a sample to be separated is placed at the top of a column. Then solvent is added to the top of the column and passed through the sample and column of stationary material. The emerging liquid from the bottom of the column is collected in portions to isolate the individual compounds composing the sample. The method is useful as an analytical (identification) and preparative technique (10 mg – 1 kg of sample). A variation, high speed liquid chromatography (HSLC), has recently been developed where the above process is automated. The solvent is rapidly forced through the column under high pressure, the emerging liquid is analyzed continuously, and its content is indicated in a strip of chart paper. This method is used both for analytical (1 ug-100 mg) and preparative work.

b. **Gas chromatography**- (variously known as GC, GLC – gas liquid chromatography or VPC – vapor phase chromatography) – The stationary material is an oily liquid coated thinly on a crushed mineral and the moving liquid is a gas (He, N_2). The sample is injected into the column at an elevated temperature (50^0 – 250^0C) and the compounds in the gas emerging from the end of the column are continuously analyzed and record on a chart as in HSLC above. This method is used predominantly for analytical work and is capable of difficult separations (e.g. mixtures of structural alkali isomers).



c.Thin layer chromatography – (TLC) – both stationary and moving materials are as in column chromatography. However, the adsorbent is coated on a glass plate in a thin layer, the mixture is deposited neat one edge of the layer as a spot or a streak and the plate then dipped in a shallow bath of a solvent. The solvent rises up the layer through capillary action (this is called developing the plate). When it reaches to the top, the positions of the spots of the various compounds in the mixture are observed, or, in the preparative mode, the adsorbent holding the spot of each is scraped off separately for recovery of the substance. This technique is useful for analytical or preparative (up to 1 g) applications.

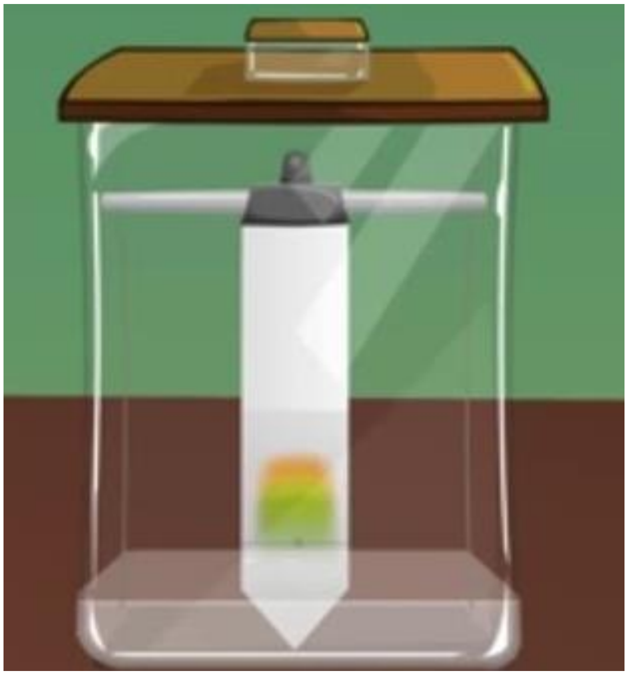
d. Paper chromatography – This is a variation of (TLC) where the stationary substance is a strip of paper. It is useful for analytical purposes only, in situations where the compounds to be identified are suitably adsorbed not on silica gel but on paper.

In this experiment paper chromatography will be applied to different samples and the components of the mixture characterized. The experimenter controls three variables in paper chromatography: solvent, paper, and distance solvent moves. The latter is difficult to repeat precisely and to compare experiments the ratio called the representative fraction, R_f, is calculated. The representative fraction, R_f, is defined by the equation:

R_f = Distance from center of spot to starting point/ Distance from solvent front to starting point.

Figure is a sample chromatogram and shows how the quantities in the equation are determined from the experiment. The R_f is independent of the distance the solvent was allowed to move and can be easily repeated.

Figure also shows how paper chromatography can be used to determine whether a sample is a mixture and to identify the components of a sample. For example, the chromatogram in Figure supports the idea that spot 2 and spot 4 are identical because both have the same R_f. For spot 5, we see the result of chromatographing a mixture of compounds. This mixture is clearly separated into two components and the identify of each component established. Sometimes when a mixture consisting of two compounds of similar R_f is chromatographed the components of the mixture will not be clearly separated or “resolved”. The resolution of a chromatograph can be changed by using a different solvent, using a different stationary phase or by letting the solvent move farther along the chromatogram.



TRIS-(THOPUREA)-COPPER(II) SULPHATE DIHYDRATE $[Cu(NH_2\text{-}CS\text{-}NH_2)_3]_2.SO_4.2H_2O$

AIM

To prepare a pure sample of tris-(thio urea)-copper(II) sulphate dehydrate $[Cu(NH_2.CS\text{-}NH_2)_3]_2SO_4.2H_2O$.

PRINCIPLE

When a solution of copper sulphate and thiourea are shaken together they readily yield the complex .In the first step ,thiourea reduces Cu^{+2} to Cu^{+1} and then forms the complex as follows:

$$2CuSO_4 + 6NH_2\text{-}CS\text{-}NH_2 \rightarrow \underset{\text{Cuprous Sulphate}}{Cu_2SO_4} + NH_2\text{-}Cs\text{-}NH\text{-}HSO_4$$

$$2Cu_2SO_4 + 6NH_2\text{-}CS\text{-}NH_2 \rightarrow Cu(NH_2\text{-}CS\text{-}NH_2)_3]_2SO_4.2H_2O$$

$$2CUSO_4 + 7NH_2\text{-}CS\text{-}NH_2 \rightarrow \underset{\text{White crystalline precipitate}}{Cu(NH_2\text{-}CS\text{-}NH_2)_3]_2SO_4.2H_2O}$$

$$+NH_2\text{-}CS\text{-}NH\text{-}HSO_4$$

CHEMICALS REQUIRED:

(i) Copper sulphate,($CuSO_4.5H_2O$) =10g

(ii) Thiourea ,($NH_2\text{-}CS\text{-}NH_2$) =10g

PROCEDURE:

10g of thiourea crystals are dissolved in 50-60ml of hot water in a round bottom flask and cooled the flask to room temperature. A solution of copper sulphate is prepared by dissolving 10g of it in 50ml of water. The flask is stoppered well and thoroughly shaken after each addition. When the addition of copper sulphate solution is completed,the flask is again shaken well for another ten minutes. At this stage, triscomplex wil begin to appear. The contents of the R.B. flask are heated on a water bath to about 70◦C-80◦C for 15-20minutes. The flask is cooled to room temperature under tap water.

The mother liquor is decanted off. The oily liquid or the crystals formed at the sides of the flask are thoroughly shaken with 10% solution of thiourea. Well defined white crystals are formed now. The crystals are filtered at the pump, washed with distilled water and dried in a desiccators. The yield is recorded.

REPORT:

The weight of tris-(thiourea)-copper(II) sulphate dihydratye =…g.

PREPRATION OF POTASSIUM TRI OXALATO FERRATE (III)

AIM:

To prepare potassium trioxalato ferrate (III) from Ferrous ammounium sulphate and oxalic acid.

PRINCIPLE:

Ferrous oxalate is obtained by mixing ferrous ammonium sulphate and oxalic acid, to which potassium oxalate and hydrogen peroxide are added to get the complex potassium trioxalato ferrate (III).

CHEMICALS REQUIRED:

Ferrous ammonium sulphate - 5g

Oxalic acid - 3g

Potassium oxalate - 3.5g

Hydrogen peroxide (6%) - 9ml

Ethyl alcohol - 15ml

PROCEDURE:

5ml of ferrous ammonium sulphate are dissolved in 50ml of water containing 1ml of 3M H_2SO_4. It is mixed with a solution containing 3.5g of oxalic acid dissolved in 25ml of water. The mixture which now contains a yellow precipitate of ferrous oxalate is carefully heated to boiling point, allowed to settled and cooled to room temperature. The supernatant liquid is decanted and the solid is washed again by decantation with 20ml of hot water. The hydrated ferrous oxalate is then suspended in a solution of 3.5g of potassium oxalate monohydrate in 100ml of H_2O and the mixture is warmed to 40°C. About 9ml of 6% hydrogen peroxide is then added dropwise from a burette with continuous agitation. The greenish liquid with red brown precipitate of ferric hydroxide is heated to boiling, While a solution of 0.8g of oxalic acid is added slowly with stirring. The hot liquid is filtered, if necessary, and cooled in ice while 30ml of 95% alcohol are added. The product is filtered and dried.

RESULT:

The amount of potassium trioxalato ferrate (III)=…..g

PREPARATION OF HEXAMMINE COBALT(III) CHLORIDE

AIM:

To prepare hexamine cobalt(III)chloride from ammonium chloride and cobaltous chloride.

PRINCIPLE:

Preparation of Hexammine cobalt(III) chloride involves the mixing of ammonium chloride and cobaltous chloride followed by the addition of conc.ammonia and hydrogen peroxide.

$$2CoCl_2+2NH_4Cl+IONH_3+H_2O_2\rightarrow 2[CO(NH_3)_6Cl_3+2H_2O$$

CHEMICALS REQUIRED:

Ammonium chloride	=	12g
Cobaltous chloride	=	18g
20 volume hydrogen peroxide	=	35 ml

PROCEDURE:

18g of cobaltous chloride is dissolved in a boiling solution of 12g of ammonium chloride in 25 ml of water. Add one gram of animal charcoal and cool the contents in the running water. Wash out the vessel in which the solution was first made with 40ml of conc.NH_3 and then ammonical liquid to the flask. Cool the whole content of the preparation in the ice bath to 10◦C . 35 ml of 20 volume hydrogen peroxide is added slowly in portions while briskly shaking the flask and its contents. All the oxidizing agent having been added, heat the mixture gradually to 60◦C with mixing by shaking until the pinkish tint in the liquid is removed. Crystals began to separate at the close of heating and deposit in quantity on cooling in an ice bath.

Filter off the crude solid and without washing it, transfer it to a beaker containing a boiling mixture of 150 ml of water and 5 ml of conc.HCl. When all solid except the charcoal has dissolved, filtered the liquid while hot. Add 20 ml of conc.HCl to the filtrate and then cool the liquid in an ice bath. Golden brown crystals separate out.

RESULT:

The amount of hexamine cobalt(III) chloride = ---------- g.