1: Precipitation reactions

1.1. Definition:

Reactions occurring in solution may produce substances which are insoluble in the solution and thus eventually settle to the bottom or "precipitate" out.

This is of interest to the chemists because so much of what we do occurs in some type of solution, generally in the water.

Typically precipitation reactions occur in aqueous solutions between ions (i.e., the reactants are electrolytes). Often only one pair of ions actually reacts or precipitates while the other pair remains in the solution unchanged.

These ions which remain unchanged during the reaction are called spectators and can be omitted from the final balanced equation written in net – tonic forms.

Although solubility is often related to the position of an element in the periodic table, there are enough exceptions to make for an interesting set of rules that describe which combinations are insoluble.

A precipitation reaction is one of the fundamental reaction types. In which ionic compounds may precipitate from aqueous solutions by mixing separate solutions containing the cation and anion of the ionic compound. Precipitation reactions find wide applications in analytical chemistry and many of analytical methods depend on the idea of precipitation reactions e.g. "gravimetric analysis and precipitation titration" [1].

1.2. Precipitation process:

The phenomenon of precipitation, so familiar from our experience in quality, it is in reality one of the most complicated processes we deal with, even-though the reaction is apparently very simple. We mix two solutions, containing respectively the anion and cation of insoluble substances and observe that shortly after mixing a precipitate appears. Usually this is instantaneous, but on occasion
Supersaturated solutions may remain for sometime without forming a precipitate unless a seed crystal is added, when a precipitate does appear, it may be in variety of forms: as very large single crystals, very small crystals, large cruds, or a slimy gelatinous mass.

Whatever the form, all crystals have one feature in common; the ions or molecules are packed closely together in an ordinary array that is repeated throughout the crystal. A good representation of the arrangement of the ions in a simple crystal can be by filling a box with marble; the marbles assumed the regular arrangement that gives the closest packing. If the crystals are composed of ions, such as (AgCl), the two ions are of different size but are arranged that every positive ion is surrounded by negative ions and vice versa.

It is truly remarkable that a billion billions ions (or more) which are randomly disappeared in a few hundred milliliters in solution can within a few seconds become arranged in the ordinarily planes of crystals. The process is initiated when a few ions clump together to start the nucleus of the crystal but after nuclei are formed; more ions strike the surface and adhere, always in the regular pattern characteristic of that crystal, thus causing the crystal to grow. In a given solution this growth continues until there is equilibrium between the ions in solution and the solid phase. At equilibrium the rate of the deposition of ions on the surface is just equal to the rate at which ions leave the surface to go into solution.

These two processes continue as long as the crystal remains in contact with the mother liquor [2].

1.3. Size of crystals:

The nature of the precipitate when equilibrium is attained depends on the properties of the specific crystal species present and on conditions under which the reagents containing the ions of the crystals are mixed.

1. If mixing is rapid a very large number of nuclei are formed at the start of the crystallization, each particle may be of colloidal size when equilibrium is reached. A colloidal particle is so small that gravitational forces don't overcome the Brownian
movement caused by bombardment with solvent nucleus. Thus, instead of settling out as a precipitate, the particles may remain in suspension indefinitely colloidal particles have, in general, a diameter less than 2000 Å units. They are too small by naked eye, and many are too small to be observed by an ordinary microscope.

A precipitate that remains dispersed as a colloidal is useless for analytical purposes.

ii. The colloidal precipitate first formed may coagulate to give a precipitate; some colloids are readily coagulate, to form a mass of cruds. A familiar example is silver chloride "AgCl" precipitate as ordinarily obtained. The particles observed settling out of solution are not individual crystals but are composed of a large numbers of colloids may agglomerate to form a gelatinous mass, semi-liquid state coherent enough to settle out of solution but without any fixed shape or size. Such agglomerate mass is known as a gel. It holds large amounts of liquid from which the precipitation is made. Precipitates of ferric and aluminum hydroxide known as hydrous oxide, are gels, the individual colloidal particles making up the gel are very small in deed; if there were not agglomerated as a gel it would be impossible to filter out these particles for "gravimetric analysis".

iii. The colloidal particles first formed may grow into large crystals that eventually precipitate, if precautions are taken to start precipitation slowly, so that an excessive number of nuclei is not formed, then each particle grows to relatively large size and we have a crystalline precipitate that settles out of a solution readily and returned by ordinary filters. The speed of crystallization, and consequently the number of particles formed in given system, can be controlled to some extent by the manner in which the reagent is mixed. In general, the number of nuclei formed is a function of the amount by which concentration of the ions in the solution exceed the equilibrium value at the time precipitation begins. If precipitation is made to occur very slowly, we can, in extreme case, obtain single
crystals of as in slow evaporation of salt solution. We do not seek single crystals in analysis but often we do employ the principle of slow deposition in order to obtain crystals of such size that filtration is made easy [2].

1.4. Solubility of precipitates:

We can define a precipitate by a substance which separates as a solid phase out of the solution. The precipitate may be crystalline or colloidal, and can be removed from the solution by filtration or by centrifugation. A precipitate is formed if the solution becomes over saturated with particular substances [3].

1.4.1 Solubility (S):

Solubility is a physical property referring to the ability for a given substance (the solute) to dissolve in solvent. It is measured in the terms of the maximum amount of solute dissolved in solvent at equilibrium.

The solubility (S) of a precipitate is by definition equal to the molar concentration of the saturated solution. Solubility depends on various circumstances like: temperature, pressure, concentration of other materials in the solution and on the composition of the solvent. These factors are detailed below [3]:

(i) Pressure

The variation of solubility with pressure has a little practical importance in qualitative inorganic analysis, as all operations are carried out in open vessels at atmospheric pressure; slight variations of latter don't have marked influence on the solubility [3].

(ii) Temperature

The variation of the solubility with temperature is the most important factor. In general it can be said, that solubilities of precipitates increase with temperature, though in exception cases (like Calcium sulphate) the opposite is true. The rate of increase of solubility with temperature varies; in some cases it is marginal, in
other cases considerable. The variation of solubility with temperature can, in some cases, serve as the basis of separation.

The separation of lead from silver and mercury (I) ions can be achieved for example by precipitating the three ions first in the form of chlorides, followed by treating the mixture with hot water. The latter will dissolve lead chloride (PbCl₂), but will leave silver and mercury (I) chlorides practically un-dissolved, after filtration of the hot solution; lead ions will be found in the filtrate and can be identified by characteristics reactions [3].

(iii) Solvents used:

The variation of solubility with the composition of the solvent has some importance in inorganic qualitative analysis. Though most of the tests are carried out in aqueous solutions, in some cases it is advantageous to apply other substances (like alcohols, ether, etc) as solvents. The separation of alkali metals can for examples be achieved by the selective extraction of their salts by various solvents. In other cases, the reagent used in the test is dissolved in a non-aqueous solvent, and the addition of the reagent to the test solution in fact changes the composition of the medium [3].

(iv) Solubility, nature & concentration of other substances:

Solubility depends also on the nature and concentration of other substances, mainly ions, in the mixture. There is marked difference between the effect of the so called common ions and of the foreign ions. A common ion is an ion which is also a constituent of the precipitate. With silver chloride (AgCl) for example, both silver and chloride ions are common ions, but all other ions are foreign. It can be said in general, that the solubility of precipitate decrease considerably if one of the common ions is present in excess though this effect might be counterbalanced by the formation of a soluble complex with excess of the common ion [3].

(v) The effect of acidity on solubility of precipitates:
The solubility of a precipitate whose anion is derived from a weak acid will be increased in the presence of added acid, because the acid will tend to combine with the anion and thus remove the anion from solution. For example, the precipitate "MA" that partially dissolves to give "M⁺" and "A⁻" ions will inhibit the following equilibria:

\[
\text{MA} \rightleftharpoons \text{M}^+ + \text{A}^- \\
+ \text{H}^+ \\
\text{HA}
\]

The anion "A⁻" can combine with protons to increase the solubility of the precipitate "MA". The combined equilibrium concentration of "A⁻" and "HA" make up the total analytical concentration, "C_{HA}" which will be equal to [M⁺] from the dissolved precipitate (if neither M⁺ or A⁻ is in excess) by suitable application of the equilibrium constants for the equilibrium involved, the solubility of the precipitate at a given acidity can be calculated.

Consider the example, the solubility of CaC₂O₄ in the presence of strong acid. The equilibria are:

\[
\text{CaC}_2\text{O}_4 \rightleftharpoons \text{Ca}^{+2} + \text{C}_2\text{O}_4^{-2} \quad \text{K}_{sp} = [\text{Ca}^{+2}][\text{C}_2\text{O}_4^{-2}] = 2.6 \times 10^{-9}
\]

\[
\text{C}_2\text{O}_4^{-2} + \text{H}^+ \rightleftharpoons \text{HC}_2\text{O}_4^- \quad \text{K}_{a2} = [\text{H}^+][\text{C}_2\text{O}_4^{-2}] / [\text{HC}_2\text{O}_4^-]
\]

Kₚₛₚ ≡ solubility product

\[
\text{HC}_2\text{O}_4^- + \text{H}^+ \quad \text{H}_2\text{C}_2\text{O}_4 \quad \text{K}_{a1} = [\text{H}^+][\text{HC}_2\text{O}_4^-] / [\text{H}_2\text{C}_2\text{O}_4] = 6.5 \times 10^{-2}
\]
The solubility "S" of CaC₂O₄ is equal to [Ca²⁺] = CH₂C₂O₄ represents the concentration of all oxalate species in equilibrium (=[H₂C₂O₄] + [HC₂O₄⁻] + [C₂O₄²⁻])[^4].

**(vi) Effect of complexation on solubility:**

Complexing agents can compete for the metal ions in a precipitate. Just as acids compete for the anion. A precipitate "MA" that dissociate to give "M⁺" and "A⁻" and whose metal complex with ligand "L" to form "ML⁺" would have the following equilibria:

\[
\begin{align*}
\text{MA} & \rightleftharpoons \text{M}^+ + \text{A}^- \\
& + \\
\text{L}^+ & \\
& \rightleftharpoons \\
\text{ML}^+ &
\end{align*}
\]

The sum of [M⁺] and [ML⁺] is the analytical concentration "Cₘ" in equilibrium, which is equal to [A⁻].

Calculations for such situation are handled in a manner completely analogous to those for the effects of acids on the solubility.

Consider the solubility of AgBr in presence of NH₃.

The equilibria are:

\[
\begin{align*}
\text{AgBr} & \quad \text{Ag}^+ + \text{Br}^- \\
\text{Ag}^+ + \text{NH}_3 & \quad \text{Ag (NH}_3)^+ \\
\text{Ag (NH}_3)^+ + \text{NH}_3 & \quad \text{Ag (NH}_3)_2^+
\end{align*}
\]

The solubility (S) of AgBr is equal to [Br⁻] = Cₜₐᵦ

Where Cₜₐᵦ represents the concentrations of all the silver species in equilibrium (= [Ag⁺] + [Ag(NH₃)⁺] + [Ag (NH₃)₂⁺])[^4].

**1.5. Solubility product (Kₚₛ):**
When substances have a limited solubility and their solubility is exceeded, the ions of the dissolved portions exist in equilibrium with a solid material. So-called "insoluble" compounds generally exhibit this property.

When a compound is referred to as insoluble, its not completely insoluble but is slightly soluble. For example, if solid AgCl is added to water, a small portion of it will dissolve:

\[
\text{AgCl} \rightarrow (\text{AgCl})_{\text{aq}} \rightarrow \text{Ag}^{+} + \text{Cl}^{-}
\]

The precipitate will have a definite solubility (i.e., a definite amount that will dissolve) in g/dm\(^3\) or mol/dm\(^3\) at a given temperature (a saturated solution). A small amount of un-dissolved compound usually exists in equilibrium in the aqueous phase (e.g., on the order of 0.1%) and its concentration is constant. It is difficult to measure the un-dissociated molecule, and we are interested in the ionized form, presence of any un-dissociated species can generally be neglected.

An overall equilibrium constant can be written for the above stepwise equilibrium, called solubility product \(K_{\text{sp}}\), \((\text{AgCl})_{\text{aq}}\) cancels when the two stepwise equilibrium constants are multiplied together.

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

The "concentration" of any solid such as AgCl is constant and is combined in the equilibrium constant to give \(K_{\text{sp}}\). The above relationship holds regardless of the presence of any un-dissociated intermediate; that is, the concentration of free ions are rigorously defined by the equation above. And we will take these as a measure of a compound's solubility. From knowledge of the value of the solubility product at specific temperature, the equilibrium solubility of the compounds can be calculated. (The solubility product is determined in the reverse order, by measuring the solubility).

The amount of a slightly soluble salt that dissolves doesn't depend on the amount of the solid in equilibrium with the solution. So long as there is enough to saturate the solution. Instead, the amount that
dissolves depends on the volume of the solvent. A non-symmetric salt such as Ag₂CrO₄ would have a Ksp as follows:

\[
\text{Ag}_2\text{CrO}_4 \rightarrow 2\text{Ag}^+ + \text{CrO}_4^{2-}
\]

\[
K_{sp} = [\text{Ag}^+]^2 [\text{CrO}_4^{2-}]
\]

Such electrolytes don’t dissolve or dissociate in steps because they are really strong electrolytes. The portion that dissolves ionizes completely. Therefore, we don’t get stepwise Ksp values. As with any equilibrium constant, the Ksp product holds under all equilibrium conditions at a specific temperature. Since we are dealing with heterogeneous equilibrium the equilibrium state will be achieved more slowly than will homogenous solutions equilibria \[4\].

In order to explain many of the precipitation reactions in qualitative inorganic analysis, values of solubility products are useful, some of the most important values are collected in appendix A.

The values of solubility products are determined by various means and many of these constant values are obtained by indirect means such as measurement of electrical conductivity, the e.m.f of cells, or from thermodynamic calculations, using data obtained by calorimetry. The various methods however don’t always give constant results, and this may be attributed to various causes including the following: the physical structure and hence the solubility of precipitate at the time of precipitation is not the same as that of an old or stabilized precipitate; this may be due to the process known as `ripening`, which is a sort of recrystallization, or it may be due to a real change of crystal structure. Thus, for nickel sulfide three forms (α, β and γ) have been reported with solubility products of 3x10⁻²¹, 1x10⁻²⁶ and 2x10⁻²⁸\[3\].

The α-form is said to be that of the freshly precipitate substance. The other forms are produced on standing. For Cadmium Sulphide a value of 1.4x10⁻²⁸ has been computed from thermal and other data. Direct determination leads to a solubility product of 5.5x10⁻²⁵.

Because the solubility product constant Ksp always holds precipitations will not take place unless the product of [Ag⁺] and [Cl⁻]
exceeds the $K_{sp}$ (here we talk about AgCl precipitate), if the product is just equal to $K_{sp}$ all the $Ag^+$ and $Cl^-$ remains in solution. (i.e., the solubility product must be exceeded for precipitation to occur)\cite{3}.

2: Fractional precipitation:

We have so far considered the solubility product principle in connection with precipitation of one spraingly soluble salt; we shall now extend our study to the case where two slightly soluble salts may be formed.

For simplicity we shall study the situation which arises when a precipitating agent is added to a solution containing two anions, both of which form slightly soluble salts with the same cation, e.g., when silver nitrate solution is added to a solution containing both chloride and iodide ions. The questions which arise are: which salt will be precipitated first, and how completely will the first salt be precipitated before the second ion begins to react with the reagent?

The solubility products of silver chloride and silver iodide are respectively $1.2 \times 10^{-10}$ mol$^2$.dm$^{-6}$ and $1.7 \times 10^{-16}$ mol$^2$.dm$^{-6}$. i.e.,

\begin{align*}
[Ag^+] [Cl^-] &= 1.2 \times 10^{-10} \quad (A) \\
[AgCl] &= 0 \\
[Ag^+] [I^-] &= 1.7 \times 10^{-16} \quad (B) \\
[AgI] &= 0
\end{align*}

It is evident that silver iodide, being less soluble, will be precipitated first, since it's solubility product will be first exceeded, silver chloride will precipitate when the $Ag^+$ ions concentration is greater than:

\begin{align*}
K_{sp} (AgCl) &= 1.2 \times 10^{-10} \\
[Cl^-] [Cl^-] &= \sqrt{K_{sp} (AgCl)}
\end{align*}

Then both salts will be precipitated simultaneously when silver chloride commences to precipitate, silver ions will be in equilibrium with both salts and equation A and B will be simultaneously satisfied, or
\[ [\text{Ag}^+] = K_{sp} [\text{Ag}] = K_s [\text{AgCl}] \]

\[ [\Gamma] [\text{Cl}] \]

And

\[ [\Gamma] = K_{sp} (\text{AgI}) = 1.7 \times 10^{-16} = 1.4 \times 10^{-6} \]

\[ [\text{Cl}] K_{sp} (\text{AgCl}) 1.2 \times 10^{-10} \]

Hence when the concentration of the iodide ion is about one millionth part of the chloride ion concentration, silver chloride will be precipitated if the initial concentration of both chloride and iodide ions is 0.1 M, then silver chloride will be precipitated when:

\[ [\Gamma] = 0.1 \times 1.4 \times 10^{-6} = 1.4 \times 10^{-7} \text{ M} \]

Thus almost complete separation is theoretically possible; the separation is feasible in practice, if the point at which the iodide precipitation is complete can be detected.

This may be done:

(a) By the use of an absorption indicator.

(b) By potentiometric method with a silver electrode \[^5\].

3. Precipitation titrations:

3.1 Titration:
Titration is a common laboratory method of quantitative chemical analysis that is used to determine the unknown concentration of known reactant. Because volume measurements play a key role in titration, it is also known as a volumetric analysis. A reagent, called the titrant or titrator, of a known concentration and volume is used to react with a solution of the analyte or titrand, whose concentration is not known using calibrated burette to add the titrant. It is possible to determine the exact amount that has been consumed when the end point is reached. The end point is the point at which the titration is complete, as determined by an indicator.

Many methods can be used to indicate the end point of a reaction; titrations often use visual indicators (the reactant mixture change color). In simple acid/base titrations a pH indicator may be used, such as phenolnaphthalene, which becomes pink when a certain pH is reached or exceed (about 8.2). Another example is methyl orange which is red in acids and yellow in alkali solutions.

Not every titration requires an indicator. In some cases, either the reactants or the products are strongly colored and can serve as the indicator. For example, an oxidation/reduction titration using potassium permanganate (pink purple) as the titrant doesn't require an indicator. When the titrant is reduced, it turns colorless. After the equivalence point, there is excess titrant present. The equivalence point is identified from first faint pink color that persists in the solution being titrated [6].

3.2 Argentimetric titrations:

Titrimetric methods in which silver nitrate is used as the titrant, are called "argentimetric" methods. Two types of methods for determination of halides are available; direct methods, in which the titrant is added to the test solution until the end point is reached and indirect method in which a known excess of silver nitrate is added and the excess is back titrated with another standard solution. Argentimetric methods are the most important of those based on precipitation process. These are used for determination of halides, cyanates, thiocyanate and less frequently, for the arsenate,
phosphate, sulphide and certain other anions. Silver maybe
determined by using some of these methods in reverse.

It is usual to group a further argentimetric with those just
mentioned, the Liebig-Deniges method for cyanides, although the
principle involved in detecting the end point is quite different. This
method is not wide spread.

There are three general methods of argentimetry:

1. Mohr's method (1856)\[^8\]: This is a direct method using
   potassium chromate as an indicator, based on fractional
   precipitation.

2. Fajan's method: it is an adsorption indicator method, which is
   also a direct method with certain organic dyestuffs used as
   indicators, based on adsorption of certain dyestuffs.

3. Volhard's method\[^9\]: This is an indirect method. A known
   excess of silver nitrate is added to the halide solution and the
   amount unconsumed in the reaction is back titrated with
   standard thiocynate solution using ferric aluminum as
   indicator.

One of the oldest methods for the detection of the end point depends
on the solution (obtained after filtering or settling of the precipitate)
remaining clear when a further addition of silver nitrate is made.
This is Gay-Lucsac's method (1832)\[^10\]. The empirical end-point
occurs a little after the equivalence point. In the modification of
Mulder\[^11\], the equal turbidity method is used. When a solution of
silver nitrate is titrated with a solution of sodium chloride, the
solution is saturated with silver chloride as the equivalence point.
When a small amount of either silver or chloride ion is added to
apportion of the clear supernatant liquid, the latter becomes turbid
owing to precipitation of silver chloride (common ion effect).

Hence, at equivalence point (which in this case coincides with the end
point) at a small sample of the supernatant liquid yields the same
turbidity with a slight excess of silver nitrate, as a similar sample
titrated with an equal excess of chloride. This method is still used in
some laboratories for determining silver.
Anion which produce precipitates less soluble than silver chloride provide so little dissolved salt as the equivalence point that no turbidity can be detected with either common ion. In this case, a small sample of supernatant liquid is tested with a solution of silver nitrate. So long as the anion (bromide, iodide or thiocynate) is in excess. Turbidity will be produced, but at equivalence point of the solution will remain clear \(^7\).

3.2.1 Types of argentimetric titrations:

3.2.1.1 Mohr's titrations:

The principle of this method depends on the fractional precipitation of silver chloride and silver chromate. Since the former is considerably less soluble. Silver chromate doesn't precipitate until (for practical purposes) the solution is free from chloride ions. Red silver chromate then precipitates and imparts a faint (pink-red) color to the precipitate of silver chloride.

Levol (1853) \(^{12}\) was the first to suggest the use of colored silver salts to mark the end-point. He used sodium carbonate and phosphate as indicators. Mohr examined sodium arsenate and potassium chromate as indicators and recommended the latter which gives a more distinct end-point \(^7\).

3.2.1.2 Fajan's method (the adsorption indicator method):

The adsorption of certain dyestuffs on freshly precipitate colloidal silver halide is strongly affected by excess of silver or halide ion. In (1932) Fajan and Hassel \(^{13}\) proved that this phenomenon could be used to indicate the end points in argentimetric titrations.

For example in the titration of chloride, the silver chloride particles will be adsorbed chloride ions before the equivalence point, where is just after equivalence point, excess of silver is adsorbed and the dyestuff anion is then adsorbed on the layer of silver ions. In this process the color of the dyestuff changes is not due to the formation of a colored silver salt, but occurs only on the surface of the precipitate.
The classical dyestuff for this purpose is flourescine, but dichloro flourescine is more satisfactory, being more sensitive and applicable over the pH range 4 – 10. Eosin can be used at even lower pH. Other frequently used adsorption indicators are di-iodo dimethyl flourescine, rhodamine G and phenosafranine.

Chloride, bromide, iodide and thiocyanate can be determined by direct titration with silver solution in the presence of a suitable adsorption indicators, the great disadvantage of these indicators is that the end-point deteriorate in the presence of moderate amounts of neutral electrolyte; with high concentrations of neutral electrolyte, no end-point may be detected because the essential feature is that some of the precipitate is in a colloidal form, is lacking\textsuperscript{[14]}.

Only a few of many adsorption indicators that have been proposed give really satisfactory end-points, and of these dichloro flourescine is probably the best. Even this is not really satisfactory for a wide range of applied analysis and the adsorption indicator method, despite its apparent ease, has not replaced the Mohr’s titration\textsuperscript{[7]}.

3.2.1.3 Volhard’s method:

In this method an excess of standard silver nitrate solution is added to the halide solution and un-reacted silver (I) is back titrated with a standard thiocynate solution; ferric aluminum is used as indicators. The latter forms the hexa thiocynateo ferric (III) complex at the end-point.

This method is not only very sensitive, but is also of a wide applicability because it can be operated in fairly strong acid solutions, although generally attributed to Volhard, it was first suggested by Charpentier\textsuperscript{[15]}. The method is also used for direct titration of silver.

Although Volhard mentioned that the back-titration could carried out in the presence of the precipitated silver chloride, Drechsel\textsuperscript{[16]} and subsequent investigators indicated that thiocynate reacted with silver chloride.

\[ \text{AgCl} + \text{SCN}^- \rightarrow \text{AgSCN} + \text{Cl}^- \]
Indeed this is to be expected from the wide difference in the solubilities of the silver salts.

\[
[\text{Cl}^-] = K_{\text{AgCl}} = 1.1 \times 10^{-10} = 157 \\
[\text{SCN}^-] K_{\text{AgSCN}} = 7 \times 10^{-13}
\]

The minute amount of thiocynate is excess, which would otherwise mark the end-point, reacts with precipitates as in the above reaction continuing with further addition of thiocynate until the concentration of chloride ions librated during the reaction is 157 times the concentration of thiocynate ions. Hence, the color fades rapidly after each addition and the end-point occurs some milliliters too late.

To overcome this effect Derchel\textsuperscript{[16]}, and later Rosanoff and Hill\textsuperscript{[17]}, who made an extensive study of the titration, recommended filtering the silver chloride before back titrating. Immediate filtration can cause errors owing to adsorption of excess of silver ions; hence it is necessary to shake the mixture for about 5 minutes before filtering, or to boil for a short time to coagulate the silver chloride.

Several workers recommended the addition of organic solvents to minimize the reaction between thiocynate and silver chloride and thus avoid filtration. The best solvent is nitrobenzene which was recommended by Caldwell and Moyer\textsuperscript{[18]}. The effect of solvent is obscure. It seems likely; however, that if forms a water proof coating around the silver chloride and thus prevents its dissolution. Adsorbing of silver ions on the precipitate is also inhibited.

This method is to be recommended although it has been claimed\textsuperscript{[19]} that the filtration is more accurate.

Schulek\textsuperscript{[20]} and his co-workers ascribed the fading end-point obtained in the presence of silver chloride to the slow reaction of adsorbed silver ions with thiocynate.

They recommended that after addition of silver nitrate, potassium nitrate also be added and the mixture boiled for few minutes, cooled and then titrated immediately. Desorption of silver ions occurs on boiling and dissolution of this aged precipitate is so slow that no fading effect can be observed.
Because silver bromide and iodide are less soluble than silver thiocyanate, no reaction can take place between the precipitate and excess of thiocyanate; hence it is unnecessary to add nitrobenzene or to filter before the back-titrating. In the case of iodide, the indicator shouldn’t be added until excess of silver is present. Otherwise oxidation of iodide occurs according to the following equation\(^7\):

\[
2\text{Fe}^{+3} + 2\text{I}^- \rightarrow 2\text{Fe}^{+2} + \text{I}_2
\]

### 3.2.1.3.1 Optimum conditions for Volhard's titration:

The indicator error with method is negligible when 0.1 M solutions are used, a pale orange color been obtained with 0.1 cm\(^3\) of 0.1M thiocyanate in a volume of 100 cm\(^3\).

This is equivalent to a thiocyanate concentration of 10\(^{-5}\) M. the end-point occurs to soon, however, owing to adsorption of silver ions by freshly precipitated silver thiocyanate.

Accordingly, when the first perceptible color is obtained, the solution should be shaken vigorously and the titration be continued until permanent color is obtained.

The titration is usually carried out at an acid concentration of about 0.5 M although the range generally specified is 0.2 – 1.6. When arsenate or phosphate is present, it is better to use a concentration of about 2M to prevent their precipitating.

Low results are obtained if the temperature is much above 25\(^\circ\)c before the titration is carried out\(^7\).

### 3.2.1.4 Other methods

Mercury (I) nitrate or perchlorate can be used for the titration of chloride and bromide, various adsorption detectors have been used to mark the end point. These methods are not widely used.

The best methods for determination fairly small amounts of bromide and iodide are known as "amplification methods". In these methods iodide is oxidized to iodate and bromide to bromate. The excess of oxidant is selectively destroyed, excess of potassium iodide is added
and the solution is acidified. Six equivalents of iodine are then liberated for each one original equivalent of bromide or iodide.

\[
\begin{align*}
\text{IO}^-_3 + 5\text{I}^- + 6\text{H}^+ & \rightarrow 3\text{I}_2 + 3\text{H}_2\text{O} \\
\text{BrO}^-_3 + 6\text{I}^- + 6\text{H}^+ & \rightarrow 3\text{I}_2 + \text{Br}^- + 3\text{H}_2\text{O}
\end{align*}
\]

Finally, the iodine is titrated with a thiosulphate.

An interesting method for the titration of iodide is based on the fact that in the absence of iodide ions, starch and iodine can not give the well known blue color. Accordingly, if an iodide solution containing starch and iodine is titrated with silver nitrate, the blue color disappears when all the iodide has been precipitated.

Chloride and bromide don't interfere. Several workers have studied the method and a number of variants have been advanced\(^7\).

4. Mohr’s method for determination of halides:

As we have mentioned before, the principle of Mohr method depends on fractional precipitation of silver chloride and silver chromate under certain conditions.

4.1 Optimum conditions for Mohr’s titration

4.2 Amount of indicator:

Silver chromate does not precipitate until its solubility product “\(K_{sp}\)” has been exceeded. Accordingly, the point at which this occurs influenced by the amount of chromate present in the solution, if insufficient indicator is present, the end-point comes too late because undue excess of silver ions is necessary to exceed the solubility product. On the other hand, an excessive amount not only tends to mask the end-point, but diminishes the solubility of silver chromate to such an extent that the end-point appears too soon. However, it can be shown by suitable calculations that for (0.1M) solution a fair amount of latitude is permissible. Thus, when (25cm\(^3\)) of (0.1M) sodium chloride are titrated with (0.1M) silver nitrate over a range of chromate concentration between 1.4x10\(^{-1}\) and 1.4x10\(^{-3}\)M. The error only varies from -0.015 to +0.015cm\(^3\).
It is necessary to add a little more silver nitrate beyond the amount required to cause precipitation of silver chromate so that the latter can be detected visually. This amount varies with different operators.

T.B. Smith considers that the minimum detectable amount varies between 0.3 and 0.7 mg and, therefore should not exceed on drop “0.1M” silver nitrate when the chromate concentration lies between $1.4 \times 10^{-2}$ and $1.4 \times 10^{-3}$M. With 0.01M solution the error is considerable and a blank determination should be done under the same condition as the actual determination. On theoretical grounds, it is unsound to titrate an equal volume of distilled water containing the same quantity of indicator because the diluting effect of the silver chloride precipitate on the colored silver chromate is then not taken into account; moreover, no silver ions are present at the start of the titration, where as in the actual determination is appreciable near the end-point. It would appear better to add an amount of freshly prepared, well washed silver chloride, roughly equal in amount to that likely to be obtained in actual determination. Kolthoff\textsuperscript{[21]} however, claimed that the differences were negligible. Mohr\textsuperscript{[8]} recommended that the solution should be back-titrated with (0.1M) sodium chloride just to clear yellow color and this value be deducted from the volume of silver nitrate, although this method seems sound, it doesn’t appear to have been pursued to any extent by later workers, possibly because of the difficulties associated with the back-titration.

Sometimes a suspension of calcium carbonate is used. This method is the most recommended.

If it is considered desirable to determine this blank value for (0.1M) solutions, the titration should be done with (0.01M) silver nitrate, so that the amount required can be measured accurately. The volume of titrant used is then converted to (0.1M). This value deducted from those obtained in an actual determination. The amounts of indicator recommended in the literature vary considerably. Winkler\textsuperscript{[22]} amongst other workers recommended 1 – 2 cm$^3$ of a 5% solution for each 100cm$^3$ of solution (i.e., [CrO$_4^{2-}$] = $5 \times 10^{-3}$). This is the amount generally used by later workers and gives a concentration only slightly more than that calculated by T.B. Smith\textsuperscript{[8]} to give a positive
error of 0.015 cm$^3$ in final volume of about 50 cm$^3$. The concentrations recommended by Van Urk, 0.7x10$^{-3}$ to 1.5x10$^{-4}$ M, have too small lower units. It can be calculated that at this concentration a positive error of 0.05 cm$^3$ of 0.1M silver nitrate would result in a final volume of about 50 cm$^3$[7].

4.3 Hydrogen ion concentration:

The pH of the solution should be carefully controlled. The second dissociation constant of chromic acid is small and chromate ions react with hydrogen ions.

\[ \text{CrO}_4^{2-} + \text{H}^+ \rightleftharpoons \text{HCrO}_4^- \]

Hence, the sensitivity falls with increasing acidity, and eventually a point is reached where silver chromate does not precipitate at all.

In alkaline solutions, the hydroxyl concentration may be sufficient to cause precipitation of silver hydroxide before silver chromate.

Klothoff [21] recommends an optimum pH range is off 6.5 – 10.5, although latter workers [23] have claimed that good results are obtained at pH of 5.5.

Acid solutions may be neutralized with calcium carbonate, sodium bicarbonate, magnesium oxide or borax, alkaline solutions may be made slightly acid with acetic acid; slight excess of calcium carbonate is then added.

Berry and Driver [24] have pointed out that no previous investigators have taken into account the alkalinity of the indicator which can cause a slight in pH of from 1-2 units. The examined the accuracy of the titration at varying pH values using 2ml of 1.5% potassium chromate solution ([CrO$_4^{2-}$] = 1.5x10$^{-3}$) which had first been neutralized with nitric acid. The errors were less than 4 parts per 1000 over the pH range 5 - 5.7; below 3.8 no end-point could be obtained. This observation is important because when ammonium salts are present, the pH must not be allowed to exceed 7.2 otherwise the end-point comes too late. If the solution is first adjusted to pH 7 and then the conventional indicator is added, the pH may rise to 8 to 9 and errors will arise when ammonium salts are present.
These observations were confirmed by Belchers, Macdonald and Parry [25] who reexamined Mohr’s method. These investigators also recommended that neutralized indicators be used, but found it more convenient to prepare it by mixing appropriate amounts of potassium chromate and dichromate. This mixed indicator has a buffering effect and automatically adjusts the pH of the solutions to 7 ± 0.1 so long as the original pH was 5.5 – 10.0 [7].

4.4 Temperature

The solubility of silver chromate increases with the increase of temperature hence the sensitivity of the method decrease. According to Kohlrausch [26], the solubility of silver chromate at 14.8ºC is 22.5mg/l and at 75ºc is 84mg/l. Therefore, it is necessary to work at room temperatures [7].

5. Sources of errors in Mohr’s titration

5.1 Adsorption errors

It is surprising that there is no tendency for silver chromate to precipitate before the end-point is reached in view of the colloidal nature of silver halides (that is, a part from temporary precipitation owing to local concentrations of silver nitrate).

Nevertheless, it is an experimental fact that silver chromate precipitate independently of the silver halide.

It is probable that with (0.1M) solutions a small amounts of chloride is adsorbed by the precipitate and less titrant is used. The effect passes unnoticed, however, because it is compensated by the end-point errors.

When iodides are titrated, the precipitate formed at the end-point appears to be an adsorption complex of silver chromate. Accordingly, only approximate results can be obtained for the end-point is not sharp. Adsorption errors also occur with thiocynate. For this reason iodide and thiocynate are never determined by the Mohr’s method, which is a restricted to the determination of chlorides and bromides [7].
5.2 Interferences

Some conflicting statements have been made concerning the ions which interfere in Mohr’s method, for example, it is often stated that anions which form insoluble silver salts, e.g. arsenate or phosphate, must be absent. The work of Pellet [27] on this subject, though of long standards, appears to have escaped the attention of the later investigators. He stated that these anions don’t interfere because their silver salts precipitate later than silver chromate. Even so, an error would be expected with moderate amounts of phosphate and arsenate. It has been found, however, that moderate amounts of either anion cause only slight error which could be ignored for some purpose or allowed for by appropriate correction. Hence, the effect of these anions is less marked than has been supposed.

Oxalate interferes but its effect can be overcome by adding an excess of calcium carbonate and sufficient 2M nitric acid to furnish sufficient calcium ions to precipitate all the oxalate sulphide interferes, which can be oxidized to sulphate; carbonate and sulfide are removed by acidifying the solutions and boiling. The pH must then be adjusted before the titrations. Contrary to statements sometimes made, fluoride does not interfere.

Metals which form hydrolysable chlorides are said to interfere, because basic salts which contain chloride are precipitated when the solutions is neutralized. Aluminum, iron (III) and zinc are said to behave in this way. However, it has been shown that zinc has no effect, and small amounts of aluminum can be tolerated; even moderate amounts cause only a slight positive error. Iron interferes by masking the color of the end-point, this effect can be overcome to some extent by masking with the fluoride, but the end-points are then poor.

Chlorides of metals which yield colored ions (e.g. cobalt or nickel) can’t be titrated because the end-point is obscured.

Ammonium salts of strong acid don’t affect the determination appreciably. There is however, as light but decided effect as the molar concentration increases. Thus, at 5:1 NH\(^+\)Cl\(^-\), the consumption of silver nitrate increased by 7 ppt ammonium salts of
weak acids have a more pronounced effect at 5:1 NH$_4^+$/AC$^-$ the increase in titer reaches about 2%.

If pH is adjusted with sodium hydrogen carbonate to a value of 8, sufficient ammonia is formed to increase the solubility of silver chromate and halides, and the end-point comes too late. Hence, when ammonium salts are present, the pH must not exceed (7.20).

Alkali acetates, bicarbonates, nitrates and sulphate in moderate amounts have no effect, although with large amounts, silver chromate formed by local excess of the titrant, agglomerates and then reacts more slowly than usual with the excess of chloride remaining in solution. The end-point may then be observed too early.

This effect can be overcome by shaking vigorously when the end-point is approached and allowing the mixture to stand for a short time before proceeding with the titration$^7$.

6. Conductimetric titrations:

The conduction of an electric current through an electrolyte solution involves a migration of positive charge species toward the cathode, and negative charge ones toward the anode. All of the charged particles contribute to conduction process; the contribution of any given species, however, is governed by it is individuals.

When all other factors are held constant, variations in the concentration of a given electrolyte results in a regular change in the ease with which a solution will conduct; it is therefore possible to relate concentration to the property of conductance$^{28}$.

\[
\Lambda = 1000 \, k \, C
\]

Where:
\[ \Lambda = \text{equivalent conductance of the electrolyte.} \]

\[ K = \text{specific conductance of the electrolyte.} \]

\[ C = \text{concentration.} \]

The conductance method can be employed to follow the course of a titration, provided that there is a significant difference in specific conductance between the original solution and the reagent or the products of reaction.

The only additional apparatus required is a burette. It is not necessary to know the cell constant, since relative values are sufficient to permit location the equivalence point. It is essential, however, that the spacing of electrodes doesn't vary during the titration \[^{29}\].

**6.1. Principles of Conductimetric titrations:**

Measurement of the conductance of an electrolyte solution using an alternating current source. Rate of change of conductance as a function of added titrant used to determine the equivalence point \[^{30}\].

**6.2. Instrumentation:**

Platinum electrodes, low- potential ac source, Conductance Bridge \[^{30}\].

**6.3. Conductimetric titration in precipitation reactions:**

The conductance method is well suited to the determination of equivalence points in precipitation reactions. A degree of solubility of the precipitate can be tolerated which would render it unfit for gravimetric analysis. The effect of appreciable solubility of the precipitate is to round off the intersection of the two arms of the graph. If the effect is not too great, adequate precision can still be obtained by extending the straight portions to their intersection.

Sometimes the solubility can be reduced by the addition of alcohol, and the precision of results is increased accordingly.
A particularly favorable titration is that of silver sulfate by barium chloride, where the two substances are precipitated simultaneously. The conductance drops to a very low value at the equivalence point. Magnesium and other sulfates can be similarly titrated by barium hydroxide [29].

6.4. Disadvantages of conductimetric titration:

Conductance is a non-specific property. High concentrations of other electrolytes can be troublesome.

The electrical conductance of solution is a measure of it is current carrying capacity and is therefore determined by the total ionic strength. It is a non-specific property and for this reason direct conductance measurements are of little use unless the solution contains only the electrolyte to be determined or the concentrations of other ionic species in the solution are known.

Conductimetric titrations, in which the species of interest are converted to non-ionic forms by neutralization, precipitation, etc..., are of more value. The equivalence point may be located graphically by plotting the change in conductance as a function of the volume of titrant added [30].
7. Ion-selective electrodes:

Various types of membrane electrodes have been developed in which the membrane potential is selective toward a given ion or ions, just as the potential of the glass membrane of conventional glass electrode is selective toward hydrogen ions. These electrodes are important in the measurement of ions, especially in small concentrations. Generally, they are not “poisoned” by the presence of proteins, as some other electrodes are, and so they are ideally suited to measurements in biological media. This is especially true for the glass membrane ion selective electrodes.

None of these electrodes is specific for a given ion, but each will possess certain selectivity toward a given ion or ions. So they are properly referred to as ion-selective electrodes (ISE’s), rather than ion-specific electrode [4].

7.1. Types of ion selective electrodes:

(i) Glass membrane electrodes.

(ii) Precipitate electrodes.

(iii) Solid-state electrodes.
(iv) Liquid-liquid electrodes.
(v) Coated-wire electrode \(^4\).

### 7.2 Use of Ion-Selective Electrodes:

As with pH glass electrodes, most ion selective electrodes have high resistance, and electrometer or pH-meter must be used to make measurements. An expanded-scale pH-meter is generally used. It is often necessary to pretreat ion-selective electrodes by soaking in a solution of the ion to be determined.

A calibration curve of potential versus log activity is usually prepared. If concentrations are to be measured, then the technique of maintaining a constant ionic strength is used, for example, the concentration of unbound calcium ion in serum is determined by diluting samples and standards with 0.15M NaCl. Only the unbound calcium is measured and not the fraction that is complexed.

The activity coefficient of sodium ion in normal human serum has been estimated, using ion-selective electrodes to be 0.780 ± 0.001, and in serum water to be 0.747 (serum contains about 96% water by volume). Standards solutions of sodium chloride and potassium chloride are usually used to calibrate electrodes for the determination of sodium and potassium in serum. Concentrations of 1.00, 10.00 and 100.00 ppm can be prepared with respective activities 0.965, 9.03 and 77.8 ppm for sodium ion in pure sodium chloride solution and 0.965, 9.02 and 77.0 ppm for potassium ion in pure potassium chloride solution.

The response of ion-selective electrode is frequently slow, and a considerable time must be taken to establishment an equilibrium reading. The response becomes sluggish as the concentration is decreased.

We can summarize some of the advantages and disadvantage of ion selective electrodes and some precautions and limitation in their use as follow:
1. They measure activities rather than concentration, a unique advantage but a factor that must be considered the obtaining from measurements, interference can occur from ionic effect.

2. They measure free ions (i.e., the portion that’s not associated with other species). Chemical interference can occur from complexation, protonation and the like.

3. They are not specific but merely more selective towards a particular ion. Hence, they are subject to interference from other ions. They respond to hydrogen ions and are, therefore, pH-limited.

4. They function in turbid and colored solution, where photometric methods fail.

5. Except in dilute solutions, their response is fairly rapid, often requiring less than one minute for a measurement. Electrode response is frequently rapid enough to allow process stream monitoring.

6. The response is temperature dependent.

7. The required measuring equipment can be made portable for field operations, and small samples (e.g., 1cm³) can be measured.

8. The sample is not destroyed in measurements.

9. While certain electrodes may operate down to 10⁻⁶M, many will not, and electrodes are not ultrasensitive tools as some other techniques that may approach 10⁻⁹M sensitivities or lower.

10. Frequent calibration is generally required [⁴].
7.3 Ion-Selective electrode:

Fig 1
Experimental and results:

1. Reagents preparation:

1.1 Silver nitrate (AgNO₃):

Chemical assay (on dried material) 99% (analr)

M.W. 169.87

Chloride (Cl⁻) 0.001%

Sulphate (SO₄²⁻) 0.01%

Iron (Fe) 0.001%

Lead (Pb) 0.002%

Substances not precipitated by hydrochloric acid (as sulphate) 0.01%

1.2 Preparation of 0.1M silver nitrate:

1.6997 gm silver nitrate was dissolved in 100cm³ volumetric flask.

1.3 Preparation of 0.1M sodium chloride:

1.4615 gm sodium chloride was dissolved in 100cm³ volumetric flask.

1.4 Preparation of 5% potassium chromate (indicator):

4.2004 gm potassium chromate and 0.7 gm potassium dichromate were dissolved in 100cm³ volumetric flask.

2. Method of (Mohr’s titration):
10 cm$^3$ of sodium chloride (0.1M) was transferred into a 250 cm$^3$ conical flask, 1 cm$^3$ indicator was added. The contents of the conical flask were titrated against silver nitrate (0.1M) slowly, whilst swirling the flask, till the first color change from the yellow to the brick red of the solution. Results were recorded.

3. **Standardization of sodium chloride (0.1M) vs. silver nitrate (0.1M), 5% indicator:**

3.1 Table (1) showing the vol. of silver nitrate (0.1M)

<table>
<thead>
<tr>
<th>No. of titration</th>
<th>Initial vol.</th>
<th>Final vol.</th>
<th>Vol. consumed</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.00</td>
<td>19.90</td>
<td>9.90</td>
</tr>
<tr>
<td>2</td>
<td>20.00</td>
<td>29.90</td>
<td>9.90</td>
</tr>
<tr>
<td>3</td>
<td>20.00</td>
<td>29.80</td>
<td>9.80</td>
</tr>
<tr>
<td>4</td>
<td>29.80</td>
<td>39.70</td>
<td>9.90</td>
</tr>
</tbody>
</table>

Vol. mean

|               | 9.86         |

Concentration of sodium chloride = 0.1 x 9.86 = 0.0986M
4. Concentrations of reagents:

4.1 Titration of different volumes of sodium chloride (0.1M) vs. silver nitrate (0.1M), 5% indicator:

Table 2:

<table>
<thead>
<tr>
<th>No. of tit.</th>
<th>Vol. of NaCl(cm³)</th>
<th>Vol. of AgNO₃(cm³)</th>
<th>Conc. of NaCl</th>
<th>According to ten(cm³)</th>
<th>Dev. Of ten</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.00</td>
<td>9.96</td>
<td>0.0996</td>
<td>9.96</td>
<td>0.00</td>
</tr>
<tr>
<td>2</td>
<td>9.00</td>
<td>8.99</td>
<td>0.1000</td>
<td>8.9640</td>
<td>-0.026</td>
</tr>
<tr>
<td>3</td>
<td>8.00</td>
<td>8.00</td>
<td>0.0100</td>
<td>7.960</td>
<td>-0.04</td>
</tr>
<tr>
<td>4</td>
<td>7.00</td>
<td>6.98</td>
<td>0.0997</td>
<td>6.927</td>
<td>-0.053</td>
</tr>
<tr>
<td>5</td>
<td>6.00</td>
<td>5.95</td>
<td>0.0992</td>
<td>5.976</td>
<td>0.026</td>
</tr>
<tr>
<td>6</td>
<td>5.00</td>
<td>5.00</td>
<td>0.1000</td>
<td>4.980</td>
<td>-0.02</td>
</tr>
<tr>
<td>7</td>
<td>4.00</td>
<td>4.00</td>
<td>0.1000</td>
<td>3.984</td>
<td>-0.016</td>
</tr>
<tr>
<td>8</td>
<td>3.00</td>
<td>2.95</td>
<td>0.0983</td>
<td>2.98</td>
<td>0.03</td>
</tr>
<tr>
<td>9</td>
<td>2.00</td>
<td>1.96</td>
<td>0.0980</td>
<td>1.992</td>
<td>0.032</td>
</tr>
<tr>
<td>10</td>
<td>1.00</td>
<td>1.02</td>
<td>0.1020</td>
<td>0.996</td>
<td>-0.024</td>
</tr>
</tbody>
</table>
4.2 Mohr’s titration using (0.01M) silver nitrate and (0.1M) sodium chloride, 5% indicator:

(0.01M) silver nitrate was prepared by completing 10cm\(^3\) silver nitrate (0.1M) to 100cm\(^3\) in a graduated flask.

Table 3:

<table>
<thead>
<tr>
<th>No. of tit.</th>
<th>Vol. of NaCl(_{(cm^3)})</th>
<th>Vol. of AgNO(<em>3)(</em>{(cm^3)})</th>
<th>Conc. of NaCl</th>
<th>According to four (_{(cm^3)})</th>
<th>Dev. Of four</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.00</td>
<td>40.73</td>
<td>0.1018</td>
<td>40.73</td>
<td>0.00</td>
</tr>
<tr>
<td>2</td>
<td>3.00</td>
<td>31.54</td>
<td>0.1051</td>
<td>30.549</td>
<td>-0.991</td>
</tr>
<tr>
<td>3</td>
<td>2.00</td>
<td>19.43</td>
<td>0.0972</td>
<td>20.366</td>
<td>0.936</td>
</tr>
<tr>
<td>4</td>
<td>1.00</td>
<td>10.25</td>
<td>0.1025</td>
<td>10.183</td>
<td>-0.067</td>
</tr>
</tbody>
</table>
4.3 Mohr’s titration using (0.1M) silver nitrate and (0.01M) sodium chloride, 5% indicator:

(0.01M) sodium chloride was prepared by diluting 25cm³ sodium chloride (0.1M) to 250cm³ in a graduated flask.

Table 4:

<table>
<thead>
<tr>
<th>No. of tit.</th>
<th>Vol. of NaCl(cm³)</th>
<th>Vol. of AgNO₃(cm³)</th>
<th>Conc. of NaCl</th>
<th>According to ten (cm³)</th>
<th>Dev. Of ten</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.00</td>
<td>1.03</td>
<td>0.010</td>
<td>1.03</td>
<td>0.00</td>
</tr>
<tr>
<td>2</td>
<td>9.00</td>
<td>0.91</td>
<td>0.010</td>
<td>0.927</td>
<td>0.017</td>
</tr>
<tr>
<td>3</td>
<td>8.00</td>
<td>0.84</td>
<td>0.010</td>
<td>0.824</td>
<td>-0.016</td>
</tr>
<tr>
<td>4</td>
<td>7.00</td>
<td>0.73</td>
<td>0.010</td>
<td>0.721</td>
<td>-0.009</td>
</tr>
<tr>
<td>5</td>
<td>6.00</td>
<td>0.65</td>
<td>0.010</td>
<td>0.618</td>
<td>-0.023</td>
</tr>
<tr>
<td>6</td>
<td>5.00</td>
<td>0.51</td>
<td>0.010</td>
<td>0.515</td>
<td>0.005</td>
</tr>
<tr>
<td>7</td>
<td>4.00</td>
<td>0.43</td>
<td>0.010</td>
<td>0.421</td>
<td>-0.009</td>
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<tr>
<td>8</td>
<td>3.00</td>
<td>0.32</td>
<td>0.010</td>
<td>0.309</td>
<td>-0.011</td>
</tr>
<tr>
<td>9</td>
<td>2.00</td>
<td>0.22</td>
<td>0.011</td>
<td>0.206</td>
<td>-0.014</td>
</tr>
</tbody>
</table>
4.4 **Mohr’s titration using (0.01M) silver nitrate and (0.01M) sodium chloride, 5% indicator:**

Table 5:

<table>
<thead>
<tr>
<th>No. of tit.</th>
<th>Vol. of NaCl (cm³)</th>
<th>Vol. of AgNO₃ (cm³)</th>
<th>Conc. of NaCl</th>
<th>According to ten (cm³)</th>
<th>Dev. Of ten</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.00</td>
<td>10.00</td>
<td>0.0100</td>
<td>10.00</td>
<td>0.00</td>
</tr>
<tr>
<td>2</td>
<td>9.00</td>
<td>9.03</td>
<td>0.0100</td>
<td>9.00</td>
<td>0.03</td>
</tr>
<tr>
<td>3</td>
<td>8.00</td>
<td>8.06</td>
<td>0.0100</td>
<td>8.00</td>
<td>0.06</td>
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<tr>
<td>4</td>
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<td>7.23</td>
<td>0.0103</td>
<td>7.00</td>
<td>0.23</td>
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<tr>
<td>5</td>
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<td>6.75</td>
<td>0.0112</td>
<td>6.00</td>
<td>0.75</td>
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<td>5.00</td>
<td>0.05</td>
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<td>4.19</td>
<td>0.0104</td>
<td>4.00</td>
<td>0.19</td>
</tr>
<tr>
<td>8</td>
<td>3.00</td>
<td>3.05</td>
<td>0.0100</td>
<td>3.00</td>
<td>0.05</td>
</tr>
</tbody>
</table>
4.5 Mohr’s titration using (0.1M) silver nitrate and (0.001M) sodium chloride, 5% indicator:

The dilute sodium chloride was prepared by completing 2.5cm³ sodium chloride (0.1M) to 250cm³ in a graduated flask.

Table 6:

<table>
<thead>
<tr>
<th>No. of tit.</th>
<th>Vol. of NaCl(cm³)</th>
<th>Vol. of AgNO₃(cm³)</th>
<th>Conc. of NaCl</th>
<th>According to 100 (cm³)</th>
<th>Dev. Of 100</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.00</td>
<td>0.16</td>
<td>0.0016</td>
<td>0.098</td>
<td>-0.062</td>
</tr>
<tr>
<td>2</td>
<td>20.00</td>
<td>0.28</td>
<td>0.0014</td>
<td>0.169</td>
<td>-0.111</td>
</tr>
<tr>
<td>3</td>
<td>30.00</td>
<td>0.35</td>
<td>0.0012</td>
<td>0.294</td>
<td>-0.056</td>
</tr>
<tr>
<td>4</td>
<td>40.00</td>
<td>0.46</td>
<td>0.0012</td>
<td>0.398</td>
<td>-0.062</td>
</tr>
<tr>
<td>5</td>
<td>50.00</td>
<td>0.55</td>
<td>0.0011</td>
<td>0.490</td>
<td>-0.060</td>
</tr>
<tr>
<td>6</td>
<td>60.00</td>
<td>0.68</td>
<td>0.0011</td>
<td>0.588</td>
<td>-0.092</td>
</tr>
</tbody>
</table>
5. Indicator concentrations

Mohr’s titration were carried using various concentrations of the indicator, the concentrations of the indicator used were: 2.5%, 10%, 1.25% and 20%.

The 2.5% indicator was prepared by weighing exactly 2.1005gm potassium chromate (K₂CrO₄), 0.3507gm potassium dichromate (K₂Cr₂O₇). The two salts were mixed, dissolved in 100cm³ volumetric flask.

5.1 Mohr’s titration using (0.1M) silver nitrate and (0.1M) sodium chloride, 2.5% indicator:

Table 7:

<table>
<thead>
<tr>
<th>No. of tit.</th>
<th>Vol. of NaCl(cm³)</th>
<th>Vol. of AgNO₃(cm³)</th>
<th>Conc. of NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.00</td>
<td>10.03</td>
<td>0.1003</td>
</tr>
<tr>
<td>2</td>
<td>9.00</td>
<td>9.08</td>
<td>0.1009</td>
</tr>
<tr>
<td>3</td>
<td>8.00</td>
<td>8.06</td>
<td>0.1008</td>
</tr>
<tr>
<td>4</td>
<td>7.00</td>
<td>7.05</td>
<td>0.1007</td>
</tr>
</tbody>
</table>
5.2 Mohr’s titration using more concentrated indicator 10%, (0.1M) silver nitrate and (0.1M) sodium chloride:

The 10% indicator was prepared by weighing exactly 8.40gm potassium chromate ($K_2CrO_4$) and 1.40gm potassium dichromate ($K_2Cr_2O_7$). The two salts were mixed, dissolved in 100cm³ volumetric flask.

Table 8:

<table>
<thead>
<tr>
<th>No. of tit.</th>
<th>Vol. of NaCl(cm³)</th>
<th>Vol. of AgNO₃(cm³)</th>
<th>Conc. of NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.00</td>
<td>9.96</td>
<td>0.0996</td>
</tr>
<tr>
<td>2</td>
<td>9.00</td>
<td>9.06</td>
<td>0.1007</td>
</tr>
<tr>
<td>3</td>
<td>8.00</td>
<td>7.93</td>
<td>0.0991</td>
</tr>
<tr>
<td>4</td>
<td>7.00</td>
<td>7.15</td>
<td>0.1021</td>
</tr>
<tr>
<td>5</td>
<td>6.00</td>
<td>6.01</td>
<td>0.1002</td>
</tr>
<tr>
<td>6</td>
<td>5.00</td>
<td>5.04</td>
<td>0.1008</td>
</tr>
<tr>
<td>7</td>
<td>4.00</td>
<td>4.03</td>
<td>0.1008</td>
</tr>
</tbody>
</table>
5.3 Mohr’s titration using more diluted indicator 1.25%, (0.1M) silver nitrate and (0.1M) sodium chloride:

The 1.25% indicator was prepared by weighing exactly 1.0503gm potassium chromate (K₂CrO₄) and 0.1755gm potassium dichromate (K₂Cr₂O₇). The two salts were mixed, dissolved in 100cm³ volumetric flask.

Table 9:

<table>
<thead>
<tr>
<th>No. of tit.</th>
<th>Vol. of NaCl(cm³)</th>
<th>Vol. of AgNO₃(cm³)</th>
<th>Conc. of NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.00</td>
<td>10.16</td>
<td>0.1016</td>
</tr>
<tr>
<td>2</td>
<td>9.00</td>
<td>9.23</td>
<td>0.1026</td>
</tr>
<tr>
<td>3</td>
<td>8.00</td>
<td>8.25</td>
<td>0.1031</td>
</tr>
<tr>
<td>4</td>
<td>7.00</td>
<td>7.03</td>
<td>0.1004</td>
</tr>
<tr>
<td>5</td>
<td>6.00</td>
<td>6.04</td>
<td>0.1067</td>
</tr>
<tr>
<td>6</td>
<td>5.00</td>
<td>5.04</td>
<td>0.1008</td>
</tr>
<tr>
<td>7</td>
<td>4.00</td>
<td>4.01</td>
<td>0.1003</td>
</tr>
<tr>
<td>8</td>
<td>3.00</td>
<td>3.01</td>
<td>0.1003</td>
</tr>
<tr>
<td>9</td>
<td>2.00</td>
<td>1.98</td>
<td>0.0990</td>
</tr>
</tbody>
</table>
5.4 Mohr’s titration using more diluted indicator 20%, (0.1M) silver nitrate and (0.1M) sodium chloride:

The 20% indicator was prepared by weighing exactly 16.80gm potassium chromate (K₂CrO₄) and 2.80gm potassium dichromate (K₂Cr₂O₇). The two salts were mixed, dissolved in 100cm³ volumetric flask.

Table 10:

<table>
<thead>
<tr>
<th>No. of tit.</th>
<th>Vol. of NaCl(cm³)</th>
<th>Vol. of AgNO₃(cm³)</th>
<th>Conc. of NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.00</td>
<td>9.98</td>
<td>0.0998</td>
</tr>
<tr>
<td>2</td>
<td>9.00</td>
<td>9.03</td>
<td>0.1003</td>
</tr>
<tr>
<td>3</td>
<td>8.00</td>
<td>8.06</td>
<td>0.1008</td>
</tr>
<tr>
<td>4</td>
<td>7.00</td>
<td>7.11</td>
<td>0.1016</td>
</tr>
<tr>
<td>5</td>
<td>6.00</td>
<td>6.25</td>
<td>0.1042</td>
</tr>
<tr>
<td>6</td>
<td>5.00</td>
<td>5.04</td>
<td>0.1008</td>
</tr>
<tr>
<td>7</td>
<td>4.00</td>
<td>4.03</td>
<td>0.1008</td>
</tr>
<tr>
<td>8</td>
<td>3.00</td>
<td>3.08</td>
<td>0.1027</td>
</tr>
<tr>
<td>9</td>
<td>2.00</td>
<td>2.05</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>1.00</td>
<td>1.03</td>
<td>-</td>
</tr>
</tbody>
</table>
Note:

All the concentrations calculated in the above tables were given by the formula:

\[ M_a \cdot V_a = M_b \cdot V_b \]

Where

- \( M_a \) = molarity of silver nitrate (mol/dm³).
- \( V_a \) = volume of silver nitrate (cm³).
- \( X \) = molar ratio of silver nitrate (1).
- \( M_b \) = molarity of sodium chloride (mol/dm³).
- \( V_b \) = volume of sodium chloride (cm³).
- \( Y \) = molar ratio of sodium chloride (1).

\[ \text{AgNO}_3 + \text{NaCl} \rightarrow \text{AgCl} + \text{NaNO}_3 \]

5.5 different indicator concentrations table:

Table 11:

<table>
<thead>
<tr>
<th>No.</th>
<th>Vol. of NaCl(cm³) (0.1M)</th>
<th>Vol. of AgNO₃(cm³) (0.1M)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1.25 %</td>
</tr>
<tr>
<td>1</td>
<td>10.00</td>
<td>10.16</td>
</tr>
<tr>
<td>2</td>
<td>9.00</td>
<td>9.23</td>
</tr>
<tr>
<td>3</td>
<td>8.00</td>
<td>8.25</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>---</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td></td>
<td>7.00</td>
<td>6.00</td>
</tr>
<tr>
<td></td>
<td>7.03</td>
<td>6.04</td>
</tr>
<tr>
<td></td>
<td>7.05</td>
<td>6.13</td>
</tr>
<tr>
<td></td>
<td>6.98</td>
<td>5.95</td>
</tr>
<tr>
<td></td>
<td>7.15</td>
<td>6.01</td>
</tr>
<tr>
<td></td>
<td>7.11</td>
<td>6.25</td>
</tr>
</tbody>
</table>

5.6 indicators graphs:

![Graph showing 1.25% indicator](image)

**Fig 2**

4 points are out of the trend line, in upper limits.
Fig 3
3 points are out of the trend line, in lower limits.
Fig 4

No points are out of the trend line.

Fig 5

4 points are out of the trend line, in upper limits.
3 points are out of the trend line, in upper limits. Deviation

Fig 7: indicator deviation points histogram.
6. Hydrogen ion concentration effect (pH):

We use model M555 pH meter.

6.1. pH meter specifications:

Operating ranges

- pH: -1.999 to 19.999
- mV: ±1999.9
- rel_mV: ±1999.9 (-offset)
- Temp.: -30 to 130°C
- Conc.: 1.00E-9 to 1.00E+9

Resolutions

- pH: 0.001
- mV: 0.1
- rel_mV: 0.1
- Temp.: 0.1

Relative accuracy

- pH: ± 0.001
- mV: ± 0.1
- rel_mV: ± 0.1
- Temp.: ±0.5

ATC
- -30.0 to 0.0°C: ±0.4°C
- -0.0 to 100.0: ±0.2°C
- 100.0 to 130.0°C: ±0.4°C
Timer
User selectable

Memory
100 memories
10 calibration memories

Isopotential point
7.000 pH, user adjustable

pH calibration
5 points

Temperature compensation
-5 to 105°C, automatic and manual

Display
Dot matrix LCD display

Outputs
RS232
Recorder (channel A only)

Input conditions
Impedance greater than $10^{12}$ ohms

Operating conditions
Operating temperature: 5 to 40°C
Operating humidity: max 85% at 35°C

Installation category 2
Pollution category degree 2
Size/ weight

10\(1/2\)×8×2\(1/2\) inches

(270×200×60 mm)

2\(1/4\) lbs (1.1Kg)

Power requirements

The M555 is supplied with an

Appropriate power supply unit, e.g.

USA/ Japan

100-120V, 50/60Hz, 0.85VA

6.2. Mohr’s titration using (0.1M) silver nitrate and (0.1M) sodium chloride, different pH:

5cm\(^3\) sodium chloride (0.1M) is titrated against silver nitrate (0.1M). The pH is controlled by adding sodium hydroxide (1M) for base media, hydrochloric acid (1M) acidic media, then the titration is carried out and results have been recorded as follow:

Table 12:

<table>
<thead>
<tr>
<th>No.</th>
<th>Vol. of NaCl(_{(cm^3)}) (0.1M)</th>
<th>Vol. mean of AgNO(<em>3)(</em>{(cm^3)}) (0.1M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.00</td>
<td>No end point</td>
</tr>
</tbody>
</table>

7. Effect of temperature in Mohr’s titration:
Effect of temperature has been studied by heating the sodium chloride solution in a conical flask using controlled temperature hot plate. The heat applied to the solutions were (50, 60, 70, 80, and 90°C).

5cm³ sodium chloride (0.1M) has been titrated against silver nitrate (0.1M) in various temperatures; the results were recorded as below:

Table 13:

<table>
<thead>
<tr>
<th>No.</th>
<th>Vol. of NaCl(cm)³ (0.1M)</th>
<th>Vol. mean of AgNO₃(cm)³ (0.1M)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>50</td>
</tr>
<tr>
<td>1</td>
<td>10.00</td>
<td>9.9</td>
</tr>
</tbody>
</table>

8. Conductimetric titrations:
Conductimetric titration between silver nitrate and sodium chloride was carried out using model 4320 conductivity-meter.

8.1. Instrument description:

The model 4320 is laboratory equipment which incorporates many sophisticated features but also offers simplicity of operation.

The graphics mode liquid crystal display incorporated into this meter enables a menu based approach to each analysis and allows the user to select easily the relevant operating mode.

The meter incorporates both analogue and digital interfacing capability along with high and low alarm set points.

An internal data logging facility enables 100 results to be stored in non-volatile memory for either recall into instrument display or down loading via RS232 port.

8.2 Specification:

Conductivity

Ranges 0 to 19.99S (using X10 cell)
0 to 1.999 S
0 to 199.9 mS
0 to 19.99 mS
0 to 1.999 mS
0 to 199.9 μS
0 to 19.99 μS
0 to 1.999 μS

Resolution 0.01S/0.001S/0.1mS/0.01mS/0.001mS/0.1μS/0.01μS

Accuracy ± 0.5% ± 2 digits

TDS

Ranges 0 to 2000 g/dm³
0 to 200 g/dm³
0 to 20 g/dm³
0 to 2000 mg/dm³
0 to 200 mg/dm³
0 to 20 mg/dm³

Resolution  1g/1/0.1g/1/0.01g/1/1mg/1/0.1mg/1/0.01mg/1
Accuracy  ± 0.5% ± 2 digits

Resistivity

Range  0 to 20Mohms
Resolution  0.01 Mohms

Temperature

Range  -10 to +105°C
        14 to 220°F
Resolution  0.1°C / 1°F
Accuracy  ± 0.5°C / ± 1°F

Salinity

Range  0 to 99.9
Resolution  0.1
Accuracy  0 to 35±1/35 to 99.9 ± 3 of reading
ATC range: 0 to +100°C
Cell constant: digitally settable 0.015 to 19.99

Reference temperature: 18, 20, 25°C

Temperature:  0.00 to 4.00% °C linear and nonlinear temperature coefficient characteristics
Coefficient:  Associated with low conductivity water
8.3. Conductimetric titration method:

The silver nitrate was added to 30 cm$^3$ sodium chloride in 3cm$^3$ portions under magnetic stirring, and then with the stirrer off. The equilibrium reading of the bridge was taken after each addition; equilibrium was reached within a minute and the conductance readings were stable with time.

8.3.1 Conductimetric titration between NaCl (0.1M) Vs. AgNO$_3$ (0.1M):

30cm$^3$ NaCl has been titrated.

Conductivity of water (correction) = 0.00408mS.

Table 14:
<table>
<thead>
<tr>
<th>Volume of AgNO₃ (cm³)</th>
<th>Conductivity of NaCl + H₂O (mS)</th>
<th>Conductivity of NaCl (mS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>10.640</td>
<td>10.639</td>
</tr>
<tr>
<td>3.00</td>
<td>9.730</td>
<td>9.726</td>
</tr>
<tr>
<td>6.00</td>
<td>8.820</td>
<td>8.815</td>
</tr>
<tr>
<td>9.00</td>
<td>7.930</td>
<td>7.929</td>
</tr>
<tr>
<td>12.00</td>
<td>7.550</td>
<td>7.550</td>
</tr>
<tr>
<td>15.00</td>
<td>7.040</td>
<td>7.039</td>
</tr>
<tr>
<td>18.00</td>
<td>6.520</td>
<td>6.519</td>
</tr>
<tr>
<td>21.00</td>
<td>6.170</td>
<td>6.169</td>
</tr>
<tr>
<td>24.00</td>
<td>5.760</td>
<td>5.759</td>
</tr>
<tr>
<td>27.00</td>
<td>5.460</td>
<td>5.459</td>
</tr>
<tr>
<td>30.00</td>
<td>5.100</td>
<td>5.099</td>
</tr>
<tr>
<td>33.00</td>
<td>5.310</td>
<td>5.039</td>
</tr>
<tr>
<td>36.00</td>
<td>5.540</td>
<td>5.539</td>
</tr>
<tr>
<td>39.00</td>
<td>5.790</td>
<td>5.789</td>
</tr>
<tr>
<td>42.00</td>
<td>6.000</td>
<td>5.999</td>
</tr>
</tbody>
</table>
Fig 8: Conductimetric curve 0.1M NaCl, 0.1M AgNO₃.

\[ M_a \times V_a = M_b \times V_b \]

<table>
<thead>
<tr>
<th>X</th>
<th>Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>e.v AgNO₃ (Vₐ) = 29cm³</td>
<td></td>
</tr>
</tbody>
</table>

From the graph the equivalent volume=29.00cm³

\[ 0.1 \times 29 = M_b \times 30 \]

\[ M_b = 0.0967 \text{M}. \]
8.3.2 Conductimetric titration between NaCl (0.01M) Vs. AgNO₃ (0.1M):

90cm³ NaCl has been titrated.

Conductivity of water (correction) = 0.00408 mS.

Table 15:

<table>
<thead>
<tr>
<th>Volume of AgNO₃(cm³)</th>
<th>Conductivity of NaCl + H₂O (mS)</th>
<th>Conductivity of NaCl (mS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>1.187</td>
<td>1.1866</td>
</tr>
<tr>
<td>1.00</td>
<td>1.172</td>
<td>1.1716</td>
</tr>
<tr>
<td>2.00</td>
<td>1.135</td>
<td>1.1346</td>
</tr>
<tr>
<td>3.00</td>
<td>1.129</td>
<td>1.1286</td>
</tr>
<tr>
<td>4.00</td>
<td>1.119</td>
<td>1.1186</td>
</tr>
<tr>
<td>5.00</td>
<td>1.101</td>
<td>1.1006</td>
</tr>
<tr>
<td>6.00</td>
<td>1.088</td>
<td>1.0876</td>
</tr>
<tr>
<td>7.00</td>
<td>1.077</td>
<td>1.0766</td>
</tr>
<tr>
<td>8.00</td>
<td>1.061</td>
<td>1.0606</td>
</tr>
<tr>
<td>9.00</td>
<td>1.043</td>
<td>1.0426</td>
</tr>
<tr>
<td>10.00</td>
<td>1.061</td>
<td>1.0605</td>
</tr>
<tr>
<td>11.00</td>
<td>1.151</td>
<td>1.1056</td>
</tr>
<tr>
<td>12.00</td>
<td>1.245</td>
<td>1.2536</td>
</tr>
<tr>
<td>13.00</td>
<td>1.350</td>
<td>1.3499</td>
</tr>
</tbody>
</table>
Fig 9: Conductimetric curve 0.01M NaCl, 0.1M AgNO₃.

\[ M_a \cdot V_a = M_b \cdot V_b \]

X \hspace{1cm} Y

e.v AgNO₃ (Vₐ) = 9.60cm³

From the graph the equivalent volume = 29.00cm³

0.1 \times 9.6 = M_b \times 90

M_b = 0.0107M.

8.3.3 Conductimetric titration between NaCl (0.01M) Vs. AgNO₃ (0.01M):
25cm³ NaCl has been titrated.

Conductivity of water (correction) = 0.00021mS

Table 16:

<table>
<thead>
<tr>
<th>Volume of AgNO₃(cm³)</th>
<th>Conductivity of NaCl + H₂O (mS)</th>
<th>Conductivity of NaCl (mS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>1.0930</td>
<td>1.0928</td>
</tr>
<tr>
<td>3.00</td>
<td>0.9860</td>
<td>0.9858</td>
</tr>
<tr>
<td>6.00</td>
<td>0.8940</td>
<td>0.8938</td>
</tr>
<tr>
<td>9.20</td>
<td>0.8650</td>
<td>0.8648</td>
</tr>
<tr>
<td>12.00</td>
<td>0.7940</td>
<td>0.7938</td>
</tr>
<tr>
<td>15.00</td>
<td>0.7410</td>
<td>0.7408</td>
</tr>
<tr>
<td>18.00</td>
<td>0.6890</td>
<td>0.6888</td>
</tr>
<tr>
<td>21.00</td>
<td>0.6350</td>
<td>0.6348</td>
</tr>
<tr>
<td>24.00</td>
<td>0.5990</td>
<td>0.5988</td>
</tr>
<tr>
<td>27.20</td>
<td>0.5880</td>
<td>0.5878</td>
</tr>
<tr>
<td>30.00</td>
<td>0.6200</td>
<td>0.6198</td>
</tr>
<tr>
<td>33.00</td>
<td>0.6410</td>
<td>0.6408</td>
</tr>
<tr>
<td>36.00</td>
<td>0.6920</td>
<td>0.6918</td>
</tr>
</tbody>
</table>
Fig 10: Conductimetric curve 0.01M NaCl, 0.01M AgNO₃.

\[ M_a \cdot V_a = M_b \cdot V_b \]

\[ x \quad y \]

\[ e.v \ AgNO₃ (V_a) = 26.50 \text{cm}^3 \]

From the graph the equivelant volume=29.00cm³

\[ 0.01 \times 26.5 = M_b \times 25 \]

\[ M_b = 0.0106 \text{M}. \]

8.3.4 Conductimetric titration between NaCl (0.1M) Vs. AgNO₃ (0.01M):
60cm³ AgNO₃ has been titrated Vs NaCl (0.1M).

Conductivity of water (correction) = 0.00021mS.

Table 17:

<table>
<thead>
<tr>
<th>Volume of NaCl (cm³)</th>
<th>Conductivity of AgNO₃ + H₂O (mS)</th>
<th>Conductivity of AgNO₃ (mS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>1.1990</td>
<td>1.1988</td>
</tr>
<tr>
<td>1.00</td>
<td>1.1540</td>
<td>1.1538</td>
</tr>
<tr>
<td>2.00</td>
<td>1.1140</td>
<td>1.1138</td>
</tr>
<tr>
<td>3.00</td>
<td>1.0810</td>
<td>1.0808</td>
</tr>
<tr>
<td>4.00</td>
<td>1.0510</td>
<td>1.0508</td>
</tr>
<tr>
<td>5.00</td>
<td>1.0190</td>
<td>1.0188</td>
</tr>
<tr>
<td>6.00</td>
<td>1.0640</td>
<td>1.0638</td>
</tr>
<tr>
<td>7.00</td>
<td>1.950</td>
<td>1.1948</td>
</tr>
<tr>
<td>8.00</td>
<td>1.3670</td>
<td>1.3668</td>
</tr>
<tr>
<td>9.00</td>
<td>1.4540</td>
<td>1.4538</td>
</tr>
<tr>
<td>10.00</td>
<td>1.5060</td>
<td>1.5058</td>
</tr>
</tbody>
</table>
Fig 11: Conductimetric curve 0.1M NaCl, 0.01M AgNO₃.

\[ M_a \cdot V_a = M_b \cdot V_b \]

\[ X \quad Y \]

\[ e.v \text{ NaCl} (V_b) = 5.90 \text{cm}^3 \]

From the graph the equivalent volume = 29.00 cm³

\[ 0.01 \times 60 = M_b \times 5.90 \]

\[ M_b = 0.1017 \text{M}. \]

9. Ion selective electrode operations (I.S.Es):
9.1. Chloride Ion Selective Electrode specification:

**pH**
- **Ranges**: -2 to 19.999 pH
- **Resolution**: 0.1/0.01/0.001 pH
- **Accuracy**: ± 0.003 pH

**mV**
- **Ranges**: -1999.90 to 1999.90 mV
- **Resolution**: 0.1 mV
- **Accuracy**: ± 0.2 mV

**Concentration**
- **Ranges**: $1 \times 10^{-9}$ to $9.99 \times 10^9$ units
- **Resolution**: 3 significant digits
- **Accuracy**: ± 0.003
- **Input impedance**: $>10^{13}$ ohms
- **No. of electrode inputs**: 2

**Temperature**
- **Ranges**: -10 to 105°C/14 to 221°F
- **Resolution**: 0.1 °C /1°F
Accuracy \( \pm 0.5 \, ^\circ C / \pm 1 \, ^\circ \) 

ATC range \( 0 \) to \( 100 \, ^\circ C / 32 \) to \( 212 \, ^\circ F \) 

Manual temp. comp. range \( 0 \) to \( 100 \, ^\circ C / 32 \) to \( 212 \, ^\circ F \) 

No. of temperature inputs 2 

Auto buffer recognition 2, 4, 7, 9 and 10 pH 

Buffers with manual over-ride 

Pre-programmed ion \( \text{NO}_3^-, \text{ion}^+, \text{ion}^{2+}, \text{ion}^-, \text{ion}^{-2}, \text{H}^+, \text{SCN}^-, \text{Cu}^{2+}, \text{S}^{2-}, \text{CN}^-, \text{I}^-, \text{Br}^-, \text{Cl}^-, \text{Hg}^{2+}, \text{Cd}^{2+}, \text{F}^-, \text{Ag}^+, \text{CO}_3^{2-}, \text{Ba}^{2+}, \text{NO}_2, \text{ClO}^-, \text{ClO}_4^-, \text{NH}_4^+, \text{Ca}^{2+}, \text{K}^+. \) 

calibration 1,2 or 3 point pH/1,2,3, 4 or point concentration 

outputs analogue 1mV per digit 

Bi-directional RS232 

Hi/low alarm max outputs open 

Collector 0.5A  50Vmax 

data logger 100 results 

clock 24 hours, hrs/min/sec 

or day of month, month & year 


9.2 I.S.E. calibration:

The device of ion selective electrode has been calibrated using standard solutions of sodium chloride (5, 50, 100, 250, 496, and 1000ppm) by immersing the electrode (Cl⁻ electrode) in these solutions, then readings in mV has been taken and the curve is drawn.
9.3 Methodology of ion selective electrode (I.S.E.):

9.3.1. Standard sodium chloride readings:

25cm$^3$ of each standard solution(NaCl) were taken using a pipette, 0.5cm$^3$ of the buffer solution (TISAB) were added, the reading of the standard solutions are carried out. All the readings below were obtained at pH = 8.20, temperature 26.60$^\circ$C. The following table shown the readings of the chloride ion selective electrode when we use standard solutions of sodium chloride:

Table 18:

<table>
<thead>
<tr>
<th>Conc. Of standard soln. NaCl</th>
<th>Readings in mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.00</td>
<td>128.10</td>
</tr>
<tr>
<td>50.00</td>
<td>83.10</td>
</tr>
<tr>
<td>100.00</td>
<td>67.60</td>
</tr>
<tr>
<td>250.00</td>
<td>47.50</td>
</tr>
<tr>
<td>496.00</td>
<td>23.40</td>
</tr>
<tr>
<td>1000.00</td>
<td>14.80</td>
</tr>
</tbody>
</table>

9.3.2. Samples sodium chloride readings:

(0.0001M, 0.001M, 0.01M and 0.1M) solutions sodium chloride were prepared, 25cm$^3$ of each solution has been pipetted into 100cm$^3$flask, 0.5cm$^3$ of the buffer solution (TISAB) were added, the reading of the samples are then carried out and recorded below:

Table 19:

<table>
<thead>
<tr>
<th>Symbol of the sample</th>
<th>Readings of sample in mV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>
9.3.3. The curve of standard solutions sodium chloride:

To draw this curve we must to calculate the log of standard solutions concentration "logC". Then plot values of "logC" in X-axis versus readings (mV) in Y-axis.

Table 20:

<table>
<thead>
<tr>
<th>Conc. Of standard soln. NaCl</th>
<th>Readings in mV</th>
<th>logC</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.00</td>
<td>128.10</td>
<td>0.699</td>
</tr>
<tr>
<td>50.00</td>
<td>83.10</td>
<td>1.699</td>
</tr>
<tr>
<td>100.00</td>
<td>67.60</td>
<td>2.00</td>
</tr>
<tr>
<td>250.00</td>
<td>47.50</td>
<td>2.398</td>
</tr>
<tr>
<td>496.00</td>
<td>23.40</td>
<td>2.695</td>
</tr>
<tr>
<td>1000.00</td>
<td>14.80</td>
<td>3.00</td>
</tr>
</tbody>
</table>
Fig 12: ion-selective electrode calibration curve.

9.3.4. Calculations of sodium chloride samples solution:

From the curve in Fig 13 above the concentrations of different sample sodium chloride has been calculated as follows:

Sample (A):

This sample gives reading 137.50mV.

The corresponding \( \log C \) to this reading from the curve is equal to 0.75.

\[ \text{Antilog } 0.75 = 6.026. \]

So concentration of sample (A) = 6.026ppm. (0.000103M)

Sample (B):

This sample gives reading 94.90mV.

The corresponding \( \log C \) to this reading from the curve is equal to 1.45.

\[ \text{Antilog } 1.45 = 28.183. \]
So concentration of sample (B) = 28.183ppm. (0.000482M)

Sample (C):

This sample gives reading 41.60mV.

The corresponding "logC" to this reading from the curve is equal to 2.50.

Antilog 2.50 =316.228.

So concentration of sample (C) = 316.288ppm. (0.00541M)

Discussion and conclusion:
Mohr's titration was carried at different volumes of test solution versus different silver nitrate concentrations.

With respect to 0.1M for both, the results are of high reproducibility.

For (0.1M) sodium chloride against Silver nitrate (0.01M). the results are of no reproducibility. This is due to fact that it is not practical to titrate dilute silver nitrate with concentrated sodium chloride solutions as end-point detection is rather difficult ($k_{sp}$ reason).

For (0.001M) sodium chloride versus Silver nitrate (0.1M), the results are of high reproducibility.

For the very dilute solution, the reproducibility is very low. That is due to error multiplication.

5% indicator is the most suitable concentration can be used in Mohr’s titration.

As 5% indicator is the recommended value in literature all the titrations for the evaluation of concentration were carried out according to this value.

Silver chromate does not precipitate until it is solubility product $K_{sp}$ has been exceeded. If insufficient indicator is present, the end point comes too late; an excessive amount of indicator not only tends to mask the end point, but diminishes the solubility of silver chromate to such an extent that the end point appears too soon.

Other amounts (1.25%, 2.50%, 5%, 10% and 20%) were used. Showing (4, 3, 0, 4, 3) deviation respectively as shown in figures (2, 3, 4, 5, 6).

The above fact is further represented in the histogram in fig 7.

5% indicator concentration is the amount that adjusts the concentration of the precipitates; neither in short amounts nor excessive amount, so the $K_{sp}$ is satisfied.

Good results were obtained when we do Mohr's titration in slightly acidic medium (pH= 6.807).
The sensitivity of Mohr’s titration falls with increasing of acidity, the second dissociation constant of chromic acid is small and chromate ions react with hydrogen ions.

\[
\text{CrO}_4^{2-} + \text{H}^+ \rightleftharpoons \text{HCrO}_4^-
\]

In alkaline solutions, the hydroxide ions concentration may be sufficient to cause precipitation of silver hydroxide before silver chromate.

So the pH of the solution should be carefully controlled.

When Mohr’s titration is carried out in high acidic medium (pH=1.098), No end point detected because the indicator dissociated by the acidity meter.

The end point start to appear when we reach pH= 2.072, although it is not well defined.

When we use alkaline medium (pH = 9.380), the end point comes late.

When we do Mohr's titration in a very–high alkaline medium, (pH= 12.178), the detection of end-point is not clear. That is due to multiple precipitations of silver hydroxides.

Work under different temperatures pass through difficulties in temperature control. But the results show that at high temperatures, the end-point comes late. This may be due to dissolution of the precipitates silver chloride and silver chromate according to $K_{sp}$ values.

A comparative study of the three methods (titrimetry, conductimetry and ion-selective electrode) was carried out and results were recorded in the following table:

Table 21:
<table>
<thead>
<tr>
<th>NaCl , AgNO₃ conc</th>
<th>Volumetric method</th>
<th>Conductimetric titration</th>
<th>I.S.E. operations</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1M Vs 0.1M</td>
<td>0.0996</td>
<td>0.0967</td>
<td>-</td>
</tr>
<tr>
<td>0.1M Vs 0.01M</td>
<td>0.1018</td>
<td>0.1017</td>
<td>-</td>
</tr>
<tr>
<td>0.01M Vs 0.1M</td>
<td>0.0103</td>
<td>0.0107</td>
<td>0.00541</td>
</tr>
<tr>
<td>0.01M Vs 0.01M</td>
<td>0.0100</td>
<td>0.0106</td>
<td>0.00541</td>
</tr>
<tr>
<td>0.001M Vs 0.1M</td>
<td>0.0016</td>
<td>-</td>
<td>0.000482</td>
</tr>
</tbody>
</table>

0.0001M NaCl solutions give reading in ion selective electrode 0.000103M.

With “0.1M” NaCl, “0.1M” AgNO₃, the concentration calculated according to volumetric and conductimetric methods show similar results, as illustrated in table 21. At this high concentration, the ion-selective electrode gives no response.

With “0.1M” NaCl, “0.01M” AgNO₃, give the same note as in above one.

With “0.1M” NaCl, “0.01M” AgNO₃, show the same as in above note.

With “0.01M” NaCl, “0.1M” AgNO₃, the results of titrimetry and conductimetry are also close to each others, but the ion – selective electrode readings are not parallel with conductimetry and titrimetry, this will illustrated below:

As ion-selective electrode technique is of high sensitivity, it is rather unable to detect high concentrations; it is only started from the concentration (0.01M) sodium chloride. But all readings of ion-selective electrode in table (21) are coinciding with the two other techniques (titrimetry and conductimetry), that is due to human, preparation of solutions, solvents, reagent purities and glassware errors.
Appendices

Appendix (A)
Show values of solubility product of some silver precipitate.

<table>
<thead>
<tr>
<th>substance</th>
<th>solubility product</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgBr</td>
<td>7.7X10^{-13}</td>
</tr>
<tr>
<td>AgBrO₃</td>
<td>5X10^{-5}</td>
</tr>
<tr>
<td>AgCNS</td>
<td>1.2X10^{-12}</td>
</tr>
<tr>
<td>AgCl</td>
<td>1.5X10^{-10}</td>
</tr>
<tr>
<td>Ag₂C₂O₄</td>
<td>5X10^{-12}</td>
</tr>
<tr>
<td>Ag₂CrO₄</td>
<td>2.4X10^{-12}</td>
</tr>
<tr>
<td>AgI</td>
<td>0.9X10^{-16}</td>
</tr>
<tr>
<td>AgIO₃</td>
<td>2.0X10^{-8}</td>
</tr>
<tr>
<td>Ag₃PO₄</td>
<td>1.8X10^{-18}</td>
</tr>
<tr>
<td>Ag₃S</td>
<td>1.6X10^{-49}</td>
</tr>
</tbody>
</table>

References:


8. Mohr, Liebig's Ann. 97 (1856) 335.


13. Fajans and Hassel, J. Elektrochem. 29 (1923) 495.


24. Berry and Driver, Analyst 64 (1939) 730.


