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ANALYTICAL TECHNIQUES AND APPLICATIONS

(From the Academic year 2022-23 onwards)

Introduction: Analytical chemistry is a branch of chemistry that deals with chemical analysis. Chemical analysis involves identifying and determining the percentage composition in a sample of a substance. The identification step is carried out by *Qualitative analysis*. *Quantitative analysis* gives the percentage composition of the constituents. Analytical chemistry deals with the qualitative and quantitative characterization of materials. It includes a wide variety of fields like environmental science, agricultural science, clinical chemistry, solid-state research and electronics. It is an integral part of R & D section of any industry.

The two steps of chemical analysis in the characterization of matter are identification and estimation of constituents of substance. The identification step is called the quantitative analysis, which gives information regarding the presence or absence of one or more components of the sample. The estimation step is called the quantitative analysis, which determines the exact quantity of the constituents present in a substance.

The quantitative analysis can be classified into two types, depending upon on the method of analysis.

i) Chemical methods of analysis or classical methods of analysis.
ii) Modern methods of analysis or Instrumental methods of analysis.

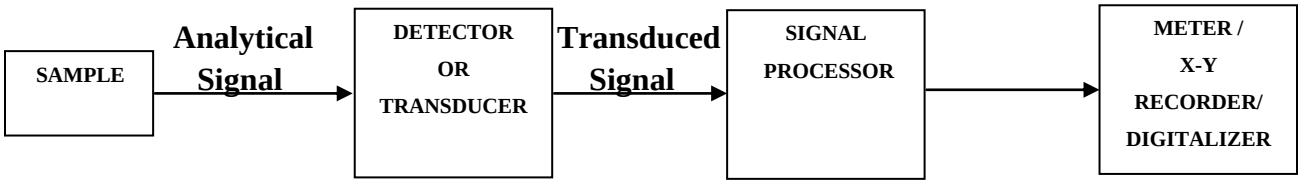
Chemical methods of analysis involve gravimetric and volumetric or titrimetric analysis. Gravimetric analysis is the quantitative estimation by weight, which involves the process of isolating and weighing of an element. In volumetric analysis, a known amount of the substance to be analyzed is allowed to react with a standard solution of an appropriate reagent. The volume of the standard reagent required to react with known amount of analyte is determined by titration. But, volumetric analysis is time consuming and has lack of versatility and lack of accuracy when the small amount of substances is involved.

In instrumental methods of analysis, a physical property of a substance is measured to determine its chemical composition. An instrument converts physical property into a form that can be readily measured and it is related quantity or quality of the sample.

For example, a photodetector measures the amount of light absorbed by a colored solution by converting the light radiation into an electrical signal. The latter is measured by a galvanometer. Similarly, a pH meter measures the electrical potential developed at an electrode interface due to hydrogen ion concentration. Thus an analytical instrument is defined as a device

that converts the analytical signal (absorption of radiation, concentration, *etc*.) into an electrical signal that can be read on a meter. The meter reading is a measure of the quantity of the sample. The schematic representation of an analytical instrument is as shown in the figure.

The Block diagram of an Analytical Instrument



Transducers used in some instruments are listed below.

Colorimeter → **Photocell** → detects the change in color.

Potentiometer → **Electrochemical cell**→ detects the change in potential

Conductmeter → **Conductivity cell**→ detects change in conductance

The detector identifies the analytical signal from the sample and converts it into an electrical signal. It is then processed by the signal processor, which transforms the signal in such a form that it can be recorded on a meter, x-ray recorder or digitalizer. The signal processor can amplify, attenuate, differentiate, integrate or compare the analytical signal.

Advantages of instrumental methods of analysis:

i) It is faster than volumetric or gravimetric methods of analysis.
ii) It requires only small quantities (less than a milligram) of the sample.
iii) Easy when a large number of samples have to be analyzed.
iv) The results are accurate.

Electro optical methods:

Colorimetry

Principle Colorimetry is an analytical technique used for the determination of concentration of the compounds in a solution. The variation of the color of a system with change in concentration of some component constitutes the basis for colorimetric analysis. It is used for the solutions, which are themselves colored or which give color when mixed with a suitable reagent. The color is generally developed by the addition of an appropriate coloring agent. The intensity of the colour depends on the concentration of the constituent present. The determination of the concentration of a substance by measuring the relative absorption of light with respect to a known concentration of the substance forms the basis of colorimetry.

In colorimetric analysis, light from a suitable source is passed through a filter to produce monochromatic light. The monochromatic light is passed through a solution to be tested when a part of light is absorbed by the solution. The extent of absorption depends on the concentration of the solution and on the path length of the light through the solution.

When a monochromatic light of intensity I is incident on a transparent medium, a portion of the radiation is absorbed I_a, a portion of the radiation is reflected Ir and the remaining part is transmitted I_t.

$$I_o = I_a + I_r + I_t$$

For a air-glass interface, I_r is negligible and hence,

$$I_o = I_a + I_t$$

Lambert studied the relation between I_o and I_t while Beer extended the experiments to solutions. Hence, colorimetry is based upon Lambert's and Beer's laws.

Definitions

Transmittance (T): Transmittance is the ratio of intensity of transmitted light by the sample (It) to intensity of incident light on the sample (I_o), both being measured at the same spectral position and with the same slit width.

$$T = \frac{I_t}{I_o}$$

Absorbance (A) or Optical density: Absorbance is the logarithm to the base 10 of the reciprocal of the transmittance.

$$A = \log_{10} \frac{1}{T}$$

Or $A = \log_{10} (I_o/I_t)$

Statement of Lambert's law and Beer's law

Lambert's law

The relation between the incident, absorbed, transmitted light with thickness of the cell is expressed in the form of Lambert's law. The law states that when a beam of monochromatic radiation passes through a homogeneous absorbing medium, the rate of decrease in the intensity of radiation with the *thickness* of absorbing medium is proportional to the intensity of the incident radiation.

i.e. $-\frac{dI}{dx} \alpha I$

$-\frac{dI}{dx} = k_1 I$

k_1 -- Proportionality constant

(In Lambert's law concentration remains constant but path length varies.)

Integrating this between I_o and I_t and x = 0 and x = t

$$\int_{I_o}^{I_t} \frac{dI}{I} = -k_1 \int_{x=0}^{x=t} dx$$

$$\ln \frac{I_t}{I_o} = -k_1 t$$

$$I_t = I_o e^{-k_1 t} \quad \text{_____(1)}$$

The intensity of a beam of monochromatic light (intensity of transmitted light) decreases exponentially with increase in the thickness of the absorbing substance arithmetically.

Beer's law

It states that when a beam of monochromatic radiation is passed through a solution of an absorbing medium, the rate of decrease in the intensity of radiation with the *concentration* of absorbing medium is proportional to the intensity of the incident radiation.

i.e. $-\frac{dI}{dx} = k_2 I$

k_2 -- Proportionality constant

(In Lambert's law concentration varies but path length remains constant .)

Integrating this between I_o and I_t and x = 0 and x = c

$$\int_{I_o}^{I_t} \frac{dI}{I} = -k_2 \int_{x=0}^{x=c} dx$$

$$\ln \frac{I_t}{I_o} = -k_2 c$$

$$I_t = I_o e^{-k_2 c} \quad \text{_____(2)}$$

It means the intensity of a beam of monochromatic light (intensity of transmitted light) decreases exponentially with increase in the concentration of the absorbing substance arithmetically.

Beer-Lambert's law

When a beam of monochromatic radiation passes through a homogeneous absorbing medium, the rate of decrease in the intensity of radiation with the *thickness* and *concentration* of absorbing medium is proportional to the intensity of the incident radiation.

Combining equations for Beer's law and Lambert's law, equation for Beer-Lambert's law can be written as

$$I_t = I_o e^{-k_1 k_2 c t}$$

$$\text{lan } \frac{I_t}{I_o} = - k_1 k_2 c t$$

$$2.303 \log_{10} \frac{I_t}{I_o} = - k_1 k_2 c t$$

$$\log_{10} \frac{I_t}{I_o} = - \frac{k_1 k_2}{2.303} c t$$

$$\log_{10} \frac{I_t}{I_o} = - \varepsilon c t \qquad [\text{where } \varepsilon = k_1 k_2 / 2.303]$$

ε- Molar absorptivity and is a constant for a given substance at a given wavelength.
It is also called molar extinction co-efficient.

The above equation can be written as

$$\log_{10} \frac{I_o}{I_t} = \varepsilon c t$$

This equation is referred as Beer-Lambert's law and this is the basis for optical methods of analysis.

The term $\frac{I_t}{I_o} = T$ and $A = \log_{10} \frac{1}{T} = \log_{10} \frac{I_o}{I_t}$

Hence, $\underline{A = \varepsilon c t}$

ε is molar extinction co-efficient; t is the path length and is constant for a given substance at a given wavelength. If t, the path length or thickness is kept constant,

Then, $\underline{A \alpha C}$

Hence a plot of absorbance against concentration gives a straight line.

NOTE: $A = \varepsilon ct \Rightarrow \varepsilon = \frac{A}{ct} = \frac{1}{\text{mole/litre x cm}}$ = litre/mole/cm (or L mol^{-1} cm^{-1})

	Absorbance	Transmittance	Concentration	Path length	Molar absoptivity
Unit	No unit	No unit	mole/litre	centimeter (cm)	L mol^{-1} cm^{-1}

Instrumentation

The essential components of photoelectric colorimeter consist of a:

i) **Light source** – It gives the radiation to colorimeter. Source of visible radiation is incandescent tungsten filament, whereas the source of UV radiation is hydrogen discharge lamp.

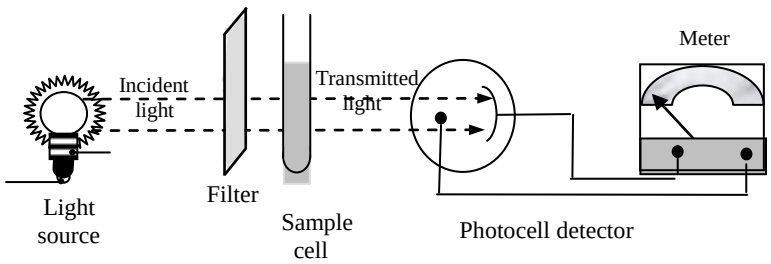
ii) **Suitable optical filter** – Filter is used for isolating any desired spectral region. It allows the radiation having a wavelength, which is a characteristic for a particular color by filtering all other wavelengths. Or filter is used to obtain the monochromatic beam of radiation. The filter selection depends on the λ_{max}. Colored glass or colored gelatin coated on glass is used as filters. The filter should give the maximum absorption or minimum transmission for a given concentration of the absorbing substance.

iii) **Sample holder** (Glass cell): This is a special glass tube (Cuvette or Nessler's tube), used to fill the sample under analysis.

iv) **Photoelectric cell** (photo detector) to receive the radiation transmitted by the solution. Its main function is to absorb the energy of photons and convert it into measurable quantity such as electric current.

v) **Measuring device** to determine the response of the photoelectric cell – It takes an input signal from circuit through electronic operations and produce an output signal.

Block diagram of photoelectric colorimeter



Procedure

The measurement in colorimetry at a particular wavelength involves the following sequence operations.

1. A series of *standard solutions* are prepared using stock solution. Using a suitable coloring reagent, the color is produced and is diluted to a known volume using distilled water. A *blank solution* is prepared without the sample or analyte and the test solution (unknown concentrated solution) is also prepared by taking given volume of sample, coloring agent and diluted with water.
2. Calibration of the instrument: Keep the filter of required wavelength and select % T mode.
   Set the % transmission to zero by placing a black tube in the sample holder.
   Set the % transmission to 100 by placing the blank solution in the sample holder.
3. Change the switch to optical density (OD) mode and record the OD for a series of standard solutions prepared and for the test solution.
4. Draw a calibration curve by plotting optical density (Y-axis) against volumes or concentrations of standard solutions (X-axis). From the calibration curve, calculate the volume of test solution or the amount of analyte present in test solution.

Advantages

i) Colorimetry gives more accurate results at low concentrations than the corresponding titrimetric or gravimetric procedure.
ii) A colorimetric method may frequently be applied where no satisfactory gravimetric or tritrimetric procedure exists i.e. for certain biological substances.
iii) This method is simple and rapid.

Applications

i) In quantitative analysis

A large number of metal ions, anions and organic compounds can be determined by colorimetry. It is based on the application of Beer's law. For example, copper content in a solution can be determined using aqueous ammonia as the color-developing reagent. Cu^{++} ions react with NH_3 to forms a deep blue colored cuprammonium complex ion.

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

cuprammonium complex ion

Or

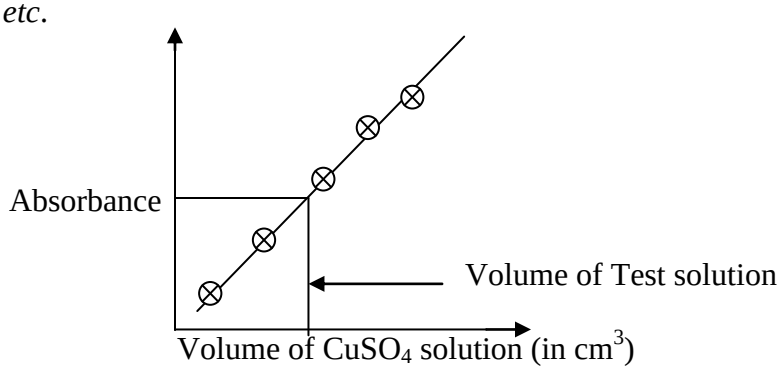
$$CuSO_4 + 4\,NH_3 \longrightarrow Cu(NH_3)_4SO_4$$

cuprammonium sulfate

Take known volumes of standard copper sulfate solutions (2, 4, 6, 8, 10 ml) in separate volumetric flasks. Add 5 ml of ammonia into each flask and make up to the mark with ion exchange water. Stopper the flasks and mix the solutions well. Blank solution is prepared for the

calibration. Select the filter number 7; because for the cupammonium sulfate complex λ_{max} (wavelength at which maximum absorbance takes place) is 620 nm. Then measure the absorbance values of the standard solutions using colorimeter. Then the calibration is obtained by plotting absorbance against volume or concentration. The test solution in which the concentration of Cu^{+2} is to be determined is also treated with ammonia to develop color and its absorbance is measured. From the calibration curve, the concentration Cu^{+2} in the solution or the given volume of $CuSO_4$ can be determined.

Colorimetric estimation can be applied to estimate copper in brass, manganese in steel, glucose in fluids, *etc*.



Problems

1) 7.25×10^{-5} M solution of potassium permanganate has a transmittance of 44.1% when measured in a 2.10 cm cell at wavelength of 525nm. Calculate (a) the absorbance of the solution (b) the molar absorptivity of $KMnO_4$.

Solution: $A = \log \frac{1}{T}$

$A = \log \frac{1}{0.441}$

$A = 0.355$

$A = \varepsilon c l$

$\varepsilon = \frac{A}{cl}$

$\varepsilon = \frac{0.355}{7.25\times10^{-5} \times 2.10}$

$\varepsilon = 2.33 \times 10^{3}\ L\ mol^{-1}\ cm^{-1}$

2) A solution of 8.75 M $KMnO_4$ has a transmittance of 0.743 in a 1.00 cm cell at 520 nm. Calculate the molar absorptivity of $KMnO_4$.

Solution: $A = \log \frac{1}{T}$

$A = \log \frac{1}{0.743}$

$\underline{A = 0.127}$

$A = \varepsilon c l$

$\varepsilon = \frac{A}{cl}$

$\varepsilon = \frac{0.127}{1.00 \times 8.75}$

$\underline{\varepsilon = 0.0145 \text{ L mol}^{-1} \text{ cm}^{-1}}$

3) The molar absorptivity of a particular solute is 2.1×10^4. Calculate the transmittance through a cuvette with a 5.00 cm light path for 2.00×10^{-6} M solution.

Solution: $A = \varepsilon c l$

$A = 2.1 \times 10^4 \times 2.00 \times 10^{-6} \times 5$

$\underline{A = 0.21}$

But $A = \log \frac{1}{T}$

$\log \frac{1}{T} = A$

$\log_{10} T = -A$

$T = 10^{-A}$

$T = 10^{-0.21}$

$\underline{T = 0.616}$

4) An α-β unsaturated ketone of relative molecular mass 110 has an absorption band with λ_{max} at 215nm and ϵ = 10,000. A solution of this ketone showed absorbance A= 2.0 with a 1cm cell. Calculate the concentration of the ketone in this solution, expressed in grams per litre.

Solution: $A = \varepsilon c l$

$c = \frac{A}{\varepsilon l}$

$c = \frac{2.0}{10000 \times 1}$

$\underline{c = 2 \times 10^4 \text{ mol litre}^{-1}}$

Concentration in grams per litre is

c = conc. in mol litre^{-1}× relative molecular mass
c = $2 \times 10^4 \times 110$
$\underline{c = 2.2 \times 10^{-2} \text{ g } l^{-1}}$

5) A compound has a molar absorptivity of 6.74×10^3 Lmol^{-1}cm^{-1}. What concentration of the compound would be required to produce a solution having a transmittance of 7.77% in a 2.5 cm cell?

Solution: $A = \varepsilon c l$

$$A = \log \frac{1}{T} = \varepsilon c l$$

$$A = -\log T = \varepsilon c l$$

$$\log T = - \varepsilon c l$$

$$c = - \frac{\log T}{\varepsilon l}$$

$$c = \frac{-\log (0.0777)}{6.74 \times 10^3 \times 2.5}$$

$$c = \frac{1.1095}{16850}$$

$$\underline{c = 6.5 \times 10^{-3} \text{ mol litre}^{-1}}$$

6) If the molar absorptivity for iron(II)-1,10-phenanthroline complex is 12,000 litre mol^{-1}cm^{-1} and the minimum detectable absorbance is 0.001, then for a 1.00cm path length, Calculate the molar concentration.

Solution: $A = \varepsilon c l$

$$c = \frac{A}{\varepsilon l}$$

$$c = \frac{0.001}{12000 \times 1}$$

$$\underline{c = 8.30 \times 10^{-8} \text{ mol litre}^{-1}}$$

Potentiometry

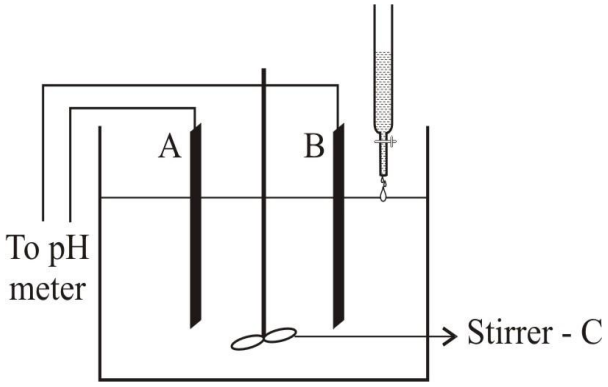
Principle We know that Expression for Nernst equation is given by

$$E = E^0 + \frac{0.0591}{n} \log [M^{n+}]$$

The potential of an electrode depends upon the concentration of the ion to which it is reversible. In a potentiometric titration, there is a change in ionic concentration, which can be followed by measuring the potential of a suitable electrode. Thus, the potentiometric titrations involve the measurement of electrode potentials with the addition of the titrant (i.e., while the

titration is in progress). The equivalence point of the reaction can be detected by a sudden change in potential plot of emf reading (y-axis) and volume of the titrant (on x-axis). The procedure of using the measurement of emf to determine the concentration of ionic solution is referred to as potentiometry.

Instrumentation The potentiometer includes a reference electrode, an indicator electrode and a potential measuring device. The electrode that maintains a constant potential is called a reference electrode while the other electrode, which serves as an indicator of the changes in ion concentration of the analyte is referred to as an indicator electrode. The indicator electrode responds rapidly to the changes in the concentration of the analyte. A simple arrangement of potentiometric titration is depicted in figure. ***A*** is a reference electrode (say SCE), ***B*** is the indicator electrode and *C* is mechanical stirrer (can be replaced by a magnetic stirrer) and the solution to be titrated (to be estimated) is taken in the beaker.



The emf of the cell containing the initial solution is determined and increments of 0.5 ml of the titrant solution are added until the equivalence point is approached and each time the emf is measured. The approach of equivalence point is indicated by a somewhat more rapid change of the emf. Near the equivalence point, equal increments, say, 0.1 ml of titrant should be added. Several points should be taken well beyond the end point.

Advantages

The following are the advantages of potentiometric titrations over the regular titrations involving the use of indicators.

i) Results are accurate.
ii) Potentiometric titrations can be carried out in colored solutions where indicators cannot be used.
iii) The prior knowledge of relative strengths of acids and bases to select a proper indicator is necessary in ordinary titrations, while no such knowledge is required in the case of potentiometric titrations.
iv) It is possible to determine an approximate end point in the titration of very weak acids or very weak bases when the indicator methods are quite undesirable.

Applications of potentiometry for Redox Titrations

Redox titrations are also carried out potentiometrically. The determining factor is the ratio of the concentrations of the oxidized and reduced forms of certain ion species. For a redox reaction: Oxidized form + n electrons $\Leftrightarrows$ Reduced form

The potential E acquired by the indicator electrode at 25 ^{o}C is given by

$$E = E^{0} + \frac{0.0591}{n} \log_{10} \frac{[\text{oxidized}]}{[\text{Reduced}]}$$

Determining factor for a redox reaction is the ratio of the concentrations of the oxidized and reduced forms of ionic species present in the solution. Therefore, the potential of indicator electrode is controlled by the ratio of concentrations. In redox titrations, platinum electrode is used as an indicator electrode and calomel electrode is used as a reference electrode.

Eg: Redox titration of FAS v/s $K_2Cr_2O_7$
In this both oxidation and reduction takes place. In presence of acidic medium, Ferrous sulfate in FAS is oxidized to Ferric sulfate (Fe^{2+} to Fe^{3+}) and potassium dichromate is reduced to Chromic sulfate (Cr^{6+} to Cr^{3+}).

$$6\ FeSO_4 + 7\ H_2SO_4 + K_2Cr_2O_7 \text{ ----------> } 3\ Fe_2(SO_4)_3 + K_2SO_4 + Cr_2SO_4 + 7H_2O$$

Potassium dichromate is an oxidizing agent which is taken in a burette and ferrous ammonium sulphate is a reducing agent and is taken in a beaker. Platinum indicator electrodes is dipped into a beaker containing acidified FAS and connect it to a reference calomel electrode to form a complete cell setup.

Before the addition of Potassium dichromate, FAS solution contains only ferrous ions (Fe^{2+}). When titration proceeds i.e. small amount of dichromate is added, redox reaction takes place and an equivalent amount of ferrous ions are oxidized to ferric ions (Fe^{3+}). At the same time, the chromium (Cr^{6+}) ions are reduced to chromium (Cr^{3+}). Therefore the overall redox reaction is given as

$$3\ Fe^{2+} + Cr^{+6} \rightarrow 3\ Fe^{3+} + Cr^{3+}$$

In the beginning of the titration, before the complete conversion of Fe^{2+} to Fe^{3+}, the solution in beaker contains both Fe^{2+} and Fe^{3+} ions. This will form a redox couple ($Pt/Fe^{3+}/Fe^{2+}$) and the potential developed at this couple is due to these ions and is given by,

$$E = E^{o} + \frac{0.0591}{n} \log 10 \frac{[Fe^{3+}]}{[Fe^{2+}]}$$

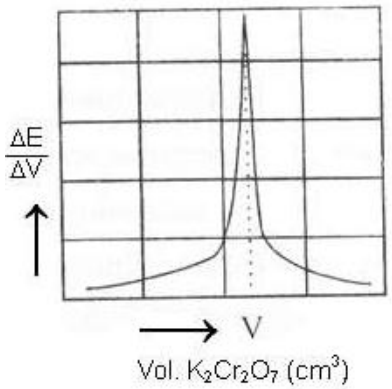
As the titration begins, the ferrous ions are oxidizing into ferric ions in the presence of $K_2Cr_2O_7$. During the titration concentration of Fe^{2+} ions is decreasing and the concentration of Fe^{3+} ions is increasing, so the ratio in the Nerst equation increases and E value also increases.
Once all the Fe^{2+} ions are converted into Fe^{3+} ions, there is sudden rise the potential which indicates equivalence point for the reaction.

But beyond equivalence point, the potential of the solution is determined by $Cr_2O_7^{2-}/Cr^{3+}$.
Based on the on the Nerst equation for the reaction Cr^{6+} ---->Cr^{3+}

$$E = E^0 + \frac{0.0591}{n} \log_{10} \frac{[Cr^{6+}]}{[Cr^{3+}]}$$

After the equivalence point the excess of Cr^{6+} ions are added from the burette, so Cr^{6+} ions concentration increases with respect to Cr^{3+} ions (which are already formed in the reaction). Since, the ratio in the above Nenrst's equation increases, hence E value increases slowly.

The graph is obtained by plotting by ploting change in e.m.f. (ordinate) versus volume of $K_2Cr_2O_7$ added.



Thus titrations involving redox reactions (e.g., iron (II) with $KMnO_4$ or $K_2Cr_2O_7$ or Cerium (IV) sulfate) may be followed potentiometrically and afford the titration curves characterized by a sudden change of potential at the equivalence point.

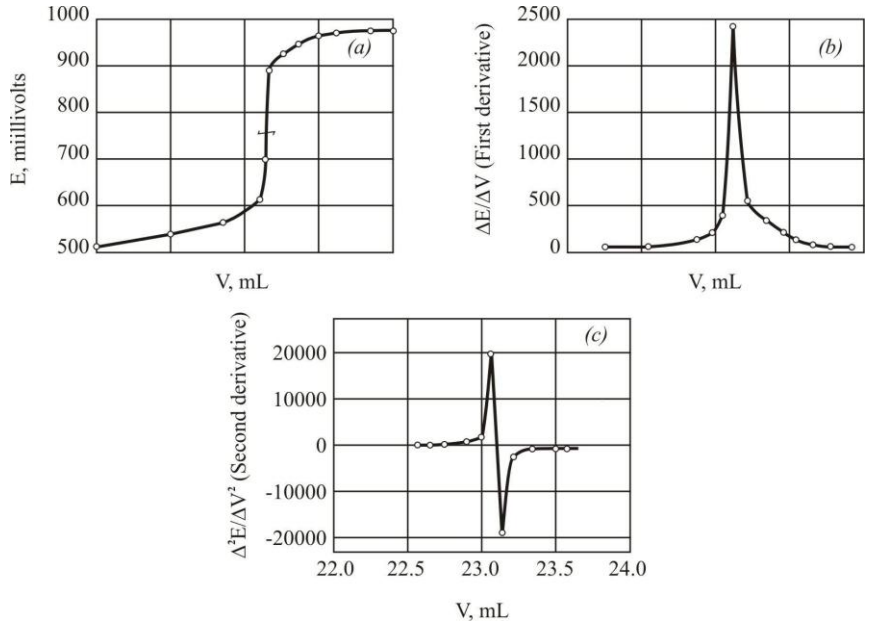


Fig. a, b and c

Conductometry

Conductometric analysis is based on the measurement of the electrical conductivity of the solution. The electrical conductivity is entirely due to the number of ions present in a system and mobility of ions.

Introduction Based on electrical conducting capacity, the substances are divided into two types, i) Insulators; which does not conduct electricity ii) Conductors; which allows electric current to pass through them. A conductor is again classified into two types based on the nature of the charge carriers.

Electronic conductors	**Electrolytic conductors**
The charge carriers are electrons	The charge carriers are ions
There is no transfer of matter	There is a transfer of matter
There is no change in the chemical property of a conductor	There is a change in the chemical property of a conductor and the chemical changes occurs on the surface of the electrode
With increase in temperature, the conductivity decreases due to increase in resistance.	With increase in temperature, the conductivity increases due to decrease in resistance.

Strong electrolyte	Weak electrolyte
An electrolyte, which undergoes complete dissociation, is called strong electrolyte. Eg: All strong acids, strong bases and almost all salts.	An electrolyte, which undergoes partial dissociation, is called weak electrolyte. . Eg: All weak acids, weak bases.

Some important Laws, Definitions and Relations

Ohm's law It states that the current i (amperes) flowing in a conductor is directly proportional to the applied electromotive force, E (volts) and inversely proportional to the resistance R (unit –ohms) of the conductor.

$$i = \frac{E}{R}$$

Conductance In the case of electrolytes, the term conductance is generally used. It implies the ease with which the current flows through a conductor. Thus the reciprocal of the resistance is called the conductance.

$$C = \frac{1}{R}$$

Unit for conductance is mhos or ohm^{-1}.

Specific resistance The resistance R of the conductor is directly proportional to length (l cm) and inversely proportional to its area of cross section (a sq. cm.) and is given by

$$R \alpha \frac{l}{a}$$

$$R = \rho \frac{l}{a}$$

Where ρ is the constant, called as specific resistance or resistivity. If l = 1 cm and a = 1 sq.cm then ρ = R ohms.

Thus specific resistance is defined as the resistance of a uniform column of the material of the conductor having a length of 1 cm and area of cross section of 1 sq.cm.

W.K.T. $\rho = R \frac{a}{l} =$ ohm. $\frac{(cm)^2}{cm}$ = ohm.cm _____unit for specific resistance

Specific conductance Specific conductance of a solution is defined as the conductance of a solution present between two parallel electrodes which have $1cm^2$ area of cross section and which have kept 1 cm apart.
The specific conductance of the solution is the reciprocal of specific resistance and is given by

$$R = \rho \frac{l}{a}$$

$$R = \frac{1}{\kappa}\left(\frac{l}{a}\right)$$

$$\kappa = \frac{1}{R} \times \frac{l}{a}$$

l/a is known as the cell constant.

Specific conductance = $\frac{\text{cell constant}}{\text{Resistance}}$

The specific conductance of an electrolytic solution at any temperature depends only on the ions present and therefore varies with their concentration. On dilution of an electrolyte solution, its specific conductance decreases as the number of ions per ml decreases.

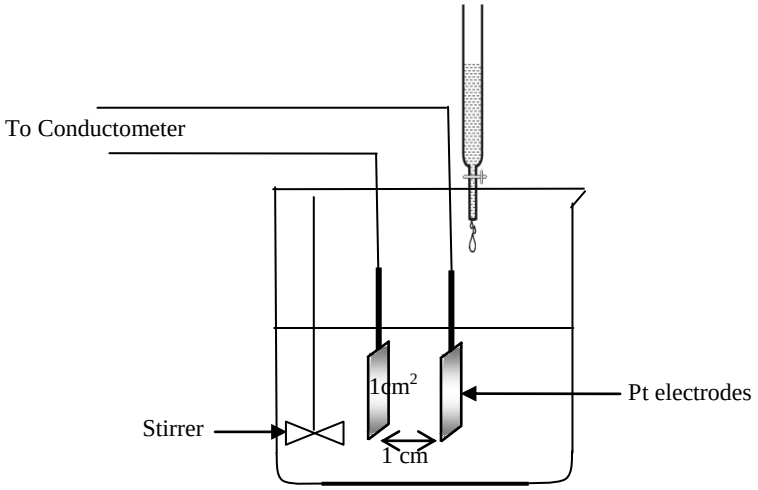
Equivalence conductance The conductance of a solution containing 1 g equivalent of an electrolyte when placed between two sufficiently large electrodes which are 1 cm apart. It is denoted by λ_V and it is measured in mhos.

Molar conductance The conductance of a solution containing 1g mole of an electrolyte between two electrodes which are placed 1cm apart. It is denoted by μ_V and it is measured in mhos.

NOTE: Conductance, molar conductance, equivalent conductance increases on dilution.
Specific conductance decreases on dilution.

Principle Measurement of conductance can be employed to determine the equivalence point in titrations. In conductometric titrations, there is a sudden change in conductance of the solution after the equivalence point. The conductance of an aqueous solution of electrolyte depends on number of total number of ions and mobility of the ions. When a solution of one electrolyte is added to another, a change in conductance is observed due to the change (decrease or increase) in the number of free ions or substitution of ions of one particular mobility by the ions of another mobility. The equivalence point is determined graphically by plotting conductance (ordinate) against titre values (abscissa).

Instrumentation Conductivity meter consists of a cell carrying a pair of platinum electrodes, which are firmly fixed in position. The cells are usually made of Pyrex glass or quartz. And the electrodes are made of two parallel sheets of platinum foil. Two electrodes have unit area of cross section and are placed unit distance apart. The assembly responds rapidly to the changes in the concentration of the analyte (the solution under the study). A simple arrangement of conductometric titration is as shown in figure. The solution to be estimated is taken in the beaker.



Procedure: Pipette out a known volume of acid solution into a beaker. Clean the conductivity cell with distilled water, dry it with filter paper strips and dip in the acid solution. Connect the conductivity cell to the conductometer and select a suitable range for conductance. So that, maximum number of digits is displayed on the display of the conductometer. Titrate the acid with a base. After each addition, mix the solution well and the conductance of the solution is measured. The titration is continued till the decreasing trend of conductance changes to increasing trend. The plot of conductance values along Y-axis and volume of base added along the X-axis gives two straight lines. The point of intersection between the two lines corresponds to the equivalence point of the reaction.

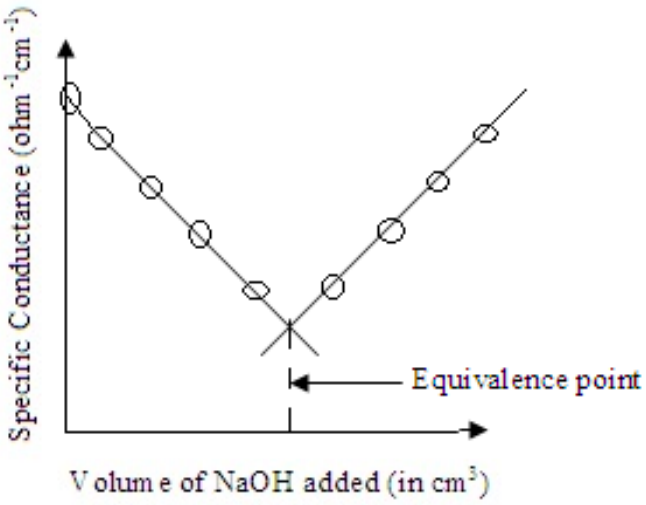
Advantages

i) Mixture of acids can be titrated more accurately by conductometric titration.
ii) Conductometric titrations may be applied where visual or potentiometric methods fail to give results owing to considerable solubility or hydrolysis at the equivalent point.
iii) Accurate in dilute solution as well as in more concentrated solution.
iv) It can be employed with colored solutions.
v) Very weak acids, which cannot be titrated potentiometrically in aqueous solutions, can be titrated conductometrically with relative ease.

Applications

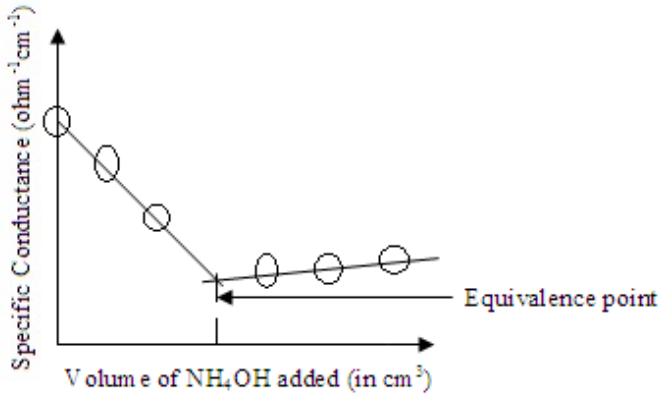
i) Strong acid against a strong base
Eg: Titration of HCl with NaOH solution

In a case of strong acid and strong base, initially the conductance value is high due to more number and mobility of H^+ ions present in HCl solution.
As the titration begins, the conductance decreases, due to the replacement of highly mobile H^+ ions by the less mobile Na^+ ions. And this decrease in conductance values continues until the complete neutralization of strong acid or until all the H^+ ions are completely replaced by Na^+ ions.
After the equivalence point, the conductance rapidly rises with further additions of strong alkali and is due to increase in the concentration of the OH^- ions.
The plot of conductance (ohm^{-1} cm^{-1}) versus volume of alkali added (cm^3) gives a graph as depicted in figure. The point of intersection of the curves gives the equivalence point.



ii) Strong acid against a weak base
Eg: Titration of dilute H_2SO_4 with dilute NH_4OH solution.

Initially the conductance value is high due to more number and mobility of H^+ ions present in HCl solution.
As the titration proceeds, conductance first falls, due to the replacement of highly mobile H^+ ions by the cations of weak base.
And this decrease in conductance values continues until the complete neutralization of strong acid.
After the equivalence point, the curve becomes almost horizontal, since the excess of weak base is not ionized appreciably.



iii) Mixture of a strong acid and a weak acid against a strong base

Eg: Titration of mixture of HCl and CH_3COOH with NaOH

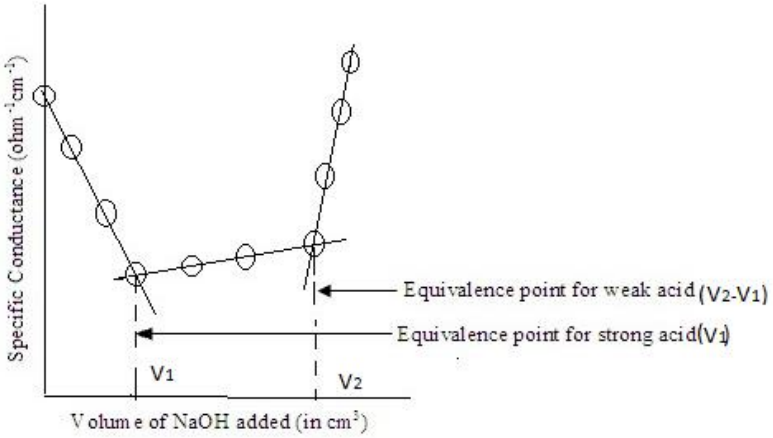
Initially the conductance value is high due to more number and mobility of H^+ ions present in HCl solution.

On adding a strong base (NaOH) to a mixture of strong acid and a weak acid (Eg: HCl + CH_3COOH), the conductance falls until the strong acid is neutralized completely, due to the substitution of highly mobile H^+ ions by less mobile Na^+ ions. The weak acid remains undissociated in the presence of a strong acid.

Once the strong acid is completely neutralized, the weak acid begins to dissociate and the added NaOH forms highly ionized sodium acetate salt thereby slowly increasing the conductance.

When the neutralization of the weak acid is complete, there is increase in conductance due to OH^- ions present in the strong base.

V_1= Equivalence point for strong acid; $V_2 - V_1$= Equivalence point for weak acid



NOTE:

Ions	Mobility (in $ohm^{-1}cm^{-1}$)	Ions	Mobility (in $ohm^{-1}cm^{-1}$)
H^+	350	Na^+	50
OH^-	198	Cl^-	77
CH_3COO^-	41	NH_4^+	74

Questions

1. What is the principle of instrumental methods of chemical analysis? Describe working of an analytical device.
2. What are the advantages of instrumental methods of analysis over conventional methods of chemical analysis?
3. State and derive Beer-Lambert's law of Colorimetry.
4. Explain the instrumentation of Colorimetry.
5. With a neat sketch label the principle components of a potentiometer and explain.
6. Explain the Potentiometric titration for a redox reaction.
7. With a graph, explain the following conductometric titrations
   (i) strong acid against a strong base (ii) strong acid against a weak base (iii) mixture strong acid and weak acid against a strong base.
8. An α-β unsaturated ketone of relative molecular mass 100 has an absorption band with λ_{max} at 215nm and ϵ = 10,000. A solution of this ketone showed absorbance A= 2.0 with a 1.5 cm cell. Calculate the concentration of the ketone in this solution, expressed in grams per litre.
9. A compound has a molar absorptivity of 8.90×10^3 $Lmol^{-1}cm^{-1}$. What concentration of the compound would be required to produce a solution having a transmittance of 8 % in a 2.5 cm cell?