Analytical Chemistry

For

4th year students (Chemistry Group)

2023-2024

Instrumental analysis

Analytical chemistry is concerned with the determination of the composition of matter (the elements present or the compounds content in materials) and it involves both qualitative and quantitative analysis.

Instrumental analysis deals with the determination of chemical species in chemical systems using instruments. Each instrumental analytical method has its strength and weakness. An instrumental analytical method can be used for a certain kind of analysis but not for all or the other kinds of analysis.

Instrumental analysis plays the major role in the field of characterization of matter and generally a number of analytical methods are carried out to characterize a sample.

Instrumental methods belong to the physical analytical methods and include many branches such as spectral methods, electrical methods, separation methods and miscellaneous methods.

The spectral methods of concern include: Colorimetry, UV-Visible Spectrometry, IR and Raman Spectrometry, X-ray Analysis, Atomic Absorption, Atomic Emission, Atomic Fluorescence, Flame Photometry, Refractometry, Polarimetry, etc.

Electric methods include: Conductometry, Potentiometry, Amperometry, etc.

Separation methods include: Chromatography (gas chromatography, ion chromatography, high performance liquid chromatography, etc.)

Miscellaneous methods: like the Thermal Analysis; Thermogravimetric Analysis (TGA), Differential Thermal Analysis (DTA), Differential Scanning Calorimetry (DSC),...

Conductometry

When an electric field is applied across an electrolytic solution, ions in the electrolyte solution will move due to the force exerted upon them by the electric field. Ions will move towards the electrode of the opposite charge carrying a current with them. Ohm´s law applies for this situation and the conductance of this electrolyte solution can be measured through measuring the resistance in a conductance cell.

Conductance measurements of an electrolyte solution can be used to get some information about the electrolyte solution like its concentration.

The speed of the ions

The speed of the ions in the solution depends on the strength of the electric field, the charge of the ion and the size of the ion in that solution.

In water H^+ and OH^- move with high speed compared to the other ions through a special mechanism. As a result, the increase or the decrease of the concentration of any of these two species, in particular, is accompanied with a significant change in conductance. This is the idea of using conductance measurements for the determination of the equivalence point in neutralization reactions.

The speed of an ion in an electric field of 1 V/m, is called the mobility v ($m^2s^{-1}V^{-1}$). The ionic mobility is given at a specified temperature.Ions of smaller size move faster:

For example: in water, K^+ has smaller ionic size than Na^+ and as a result K^+ moves faster than Na^+.

Conductance

Like metallic conductors, Ohm´s law (E=IR) can be used with electrolytes, where, (E) is the applied potential, (I) is the current and (R) is the resistance of the conductor (in this case it is the resistance of the electrolytes in the conductance cell).

It is known that the conductance (G) is the reciprocal of resistance R:

$G = 1/R$.

R is measured in Ohm (Ω) so the conductance (G) is measured in Ohm^{-1} (Ω^{-1}).

The conductance cell

The electrical conductance of an electrolyte solution can be measured in a conductance cell by using the Wheatstone bridge.

The conductance cell has two electrodes separated by a suitable and fixed distance (ex. 1cm).The electrodes are made of a suitable metal like Pt (to avoid corrosion,…) coated with platinum black (of high surface area).

- An alternating voltage is used to avoid the accumulation of charges near the electrode surface and to decrease the resistance at the electrode/solution interface).

Conductance and the cell dimensions

It is known that $R = \rho (l/A)$, where, (A) is the area of the electrode and (l) is the distance (length) between the two electrodes and ρ (rho) is the specific resistance (of the conductor that present between the two electrodes like the electrolyte).

$R = \rho (l/A)$ and

$1/R = (1/\rho) (A/l)$

The reciprocal of ρ is termed the specific conductance κ. i.e. $1/\rho = \kappa$

Because G=1/R, the previous relation becomes:

$G = 1/\rho (A/l) = \kappa (A/l)$.

In practice, the conductivity cell is calibrated and the cell constant l/A can be practically determined using a suitable electrolyte (like 0.1N KCl at 25°C) and using the data in some physical chemistry textbooks for this electrolyte at the specified conditions.

To compare the conductivity of two electrolytes, it is important to usethe same number of conducting species for both of them (like the Avogadro's number). It is therefore important to use the equivalent conductance (Λ) for comparison purposes.

Equivalent conductance

Equivalent conductance $(\Lambda)(\Omega^{-1}m^2)$ is related to the conductance of an electrolyte solution containing one equivalent weight of an electrolyte. The conductance cell

required to hold the whole volume of the electrolyte containing one equivalent can be a very large one. To deal with this difficulty let us consider an imaginary conductance cell where the distance between its two electrodes is the unity (1 cm or 1 m) and the width of each electrode is also the unity, however, the length of each electrode can be increased so that the cell can hold all the volume of that electrolyte solution which contain one equivalent weight of the electrolyte.

Suppose that you filled the imaginary cell with the electrolyte solution. The imaginary cell is composed of $1000cm^3/C$ or $10^{-3}m^3/C$ of the unit cells (one upon another) each of which correspond to the specific conductance k. Then, the total conductance of all unit cells in the imaginary cell = (1000/C) X (k) or (10^{-3}/C) X (k). Because the total conductance of all unit cells = Λ, then,

$\Lambda = 1000$ k/C or

10^{-3} k/C.

It is worth mentioning that contrary to G and k, Λ increases with dilution.

The units of Λ is (Ω^{-1} cm^2) or (Ω^{-1} m^2).

Applications

Determination of the ionization constant α for CH_3COOH

$CH_3COOH = H^+ + CH_3COO^-$

$C(1-\alpha) = C\alpha + C\alpha$

Arrhenius equation

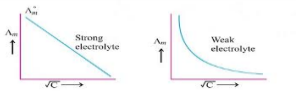
$\alpha = \Lambda/\Lambda_\infty$

- Λ is the equivalent conductance, Λ_∞ is the equivalent conductance at infinite dilution.

Λ can be determined from conductance measurements:

(Λ = 1000 k/C or 10^{-3} k/C).

Λ_∞ for weak electrolytes cannot bedetermined directly from the conductance measurements.



However, Λ_∞ can be determined experimentally for strong electrolytes because strong electrolytes give straight lines when the relation between Λ vs. $C^{1/2}$ is plotted for their solutions.

As a result, Λ_∞ for strong electrolytes can be used to calculate Λ_∞ for weak electrolytes.

Determination of Λ_∞ (or Λ_0) for strong electrolytes

Λ_∞ for a strong electrolyte can be determined practically by drawing the relation between $C^{1/2}$ and Λ. For a number of concentrations (C= 0.1N, 0.2N, 0.3N, ….) of the strong electrolyte.The conductance (G) for each concentration is measured. By using the cell constant k can be determined, where G=k(A/l). In the next step (Λ) is calculated for each concentration.

$\Lambda=10^{-3}k/C$**.**

Finally, we can draw the values of Λ vs. $C^{1/2}$. Because strong electrolytes give a straight line when Λ is

plotted vs. $C^{1/2}$, the extrapolation of the straight line to a C = zero crosses the Y axis at Λ_∞ (or Λ_0). Now we can use Λ_0 of the strong electrolytes to determine Λ

$_0$ for weak electrolytes using the Kohlrausch´s law.

Determination of Λ_∞ (or Λ_o) for strong electrolytes

Kohlrausch´s law

$\Lambda_\infty = \lambda_{\infty\,(cation)} + \lambda_{\infty\,(anion)}$

At infinite dilution, the value of Λ_∞ involves contributions from the positive and the negative ions of the electrolyte:
$\Lambda_\infty = \lambda_{\infty\,(cation)} + \lambda_{\infty\,(anion)}$

This relation can be explained as follows: at infinite dilution ions are separated by large distances so that the migration of each of ion to the oppositely charged electrode is independent of the other ions and hence maximum conductance is measured.

Determination of Λ_o for CH_3COOH

As was previously mentioned, strong electrolytes are used to determine Λ_o for weak electrolytes so, HCl, NaOH and CH_3COONa are used to calculate Λ_o of

CH_3COOH as follows:
Λ_o for $CH_3COOH = \lambda_o(H^+) + \lambda_o(CH_3COO^-)$
using the Kohlrausch´s law:
Λ_o for $\underline{CH_3COOH} = \Lambda_o(HCl) + \Lambda_o(\underline{CH_3COONa}) - \Lambda_o(NaCl)$

Λ_o for $\underline{CH_3COOH} = \underline{\lambda_o(H^+)} + \lambda_o(Cl^-) + \lambda_o(Na^+) + \underline{\lambda_o(CH_3COO^-)} - \lambda_o(Na^+) - \lambda_o(Cl^-)$

The value of Λ_o can be used to determine the degree of ionization α: $\alpha = \Lambda/\Lambda_o$

α can be used for the determination of K_a for CH_3COOH: $K_a = \alpha^2 C$

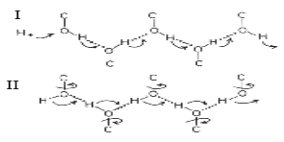
Conductometric titrations

In a conductometric titration, the conductivity of the mixture of reaction is recorded as one reactant is added to the other.

For example: the continuous determination of the conductivity of a solution of HCl as a standard solution of NaOH is added.

Using of conductance measurements in neutralization reactions

As mentioned before, H^+ or OH^- moves in water through exchanging water molecules (i.e. through the hydrogen bond network of water molecules). This mechanism (the Grotthuss mechanism) by which these ions move is different from that of other ions like Na^+, Ca^{2+}, …etc. - H^+ and OH^- have the highest mobility among other ions and this makes it easy to determine the equivalence point in neutralization reactions.

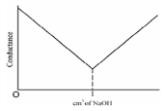


Grotthuss mechanism

$HCl + NaOH \rightarrow NaCl + H_2O$

The volume of NaOH required to react with the acid can be determined from the plot of conductance vs. volume of NaOH and then the concentration of HCl can be determined from the relation:

$N_1 V_1(HCl) = N_2 V_2(NaOH)$



Analysis of a mixture of a strong acid and a weak acid
A strong base like NaOH is used to analyze this mixture. NaOH is added to the mixture while the conductance is continuously measured.

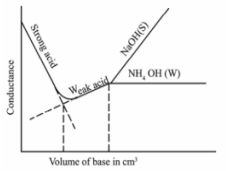
$HCl + NaOH = NaCl + H_2O$

$CH_3COOH + NaOH = CH_3COONa + H_2O$

In the presence of the strong acid, the weak acid is in the molecular form and hence the strong acid reacts with the base at first.

After the reaction of the strong acid, the weak acid starts to ionize and reacts with the base.

The volume of the base required to react with each acid can be obtained as shown below:



It is noteworthy that other types of reactions, like precipitation reactions, can be carried out byconductance measurements. Salinity and total dissolved solids (TDS) is related to conductivity and hence may be calculated from conductance measurements.

Potentiometry

Potentiometry is an electroanalyticl method in which potential of a cell is measured in the absence of appreciable current. By performing potentiometry it is required to determine the concentration of some chemical species (the analyte).

An electrochemical cell is required to measure an electrode potential, the indicator electrode, which acts as a sensor responding to the activity of the analyte.

The electrochemicalcell required for this purpose includes two electrodes: the indicator electrode and a reference electrode beside a potential measuring device.The potential of the indicator electrode should be reversible, reproducible and ideally should be related to the analyte concentration only.

The measured potential is proportional to the activity of the analyte (or to the concentration, through the activity coefficient where γ: a= γm). For dilute solutions, when the activity coefficient approaches unity, activity can be replaced by concentration. The potential measured for a cell is related to the concentration of the analyte.

Characteristics of an Ideal reference electrodes:

It should be reversible and obeys the Nernst equation, its potential should be known and constant with time, it should returns to its original potential after passing the

currents and it also should exhibit a Little hysteresis with cycling of temperature.

Examples of reference electrodes are the standard hydrogen electrode (SHE) and the calomel electrode. The saturated calomel electrode, SCE, is easy to prepare but when temperature changes it takes long time to attain equilibrium. Silver/Silver chloride electrode reference electrode can be used at temperature higher than 60°C.

Indicator electrodes

The potential of these electrodes is a function of the concentration of the analyte. Two types will be discussed: metallic indicator electrodes and ion selective indicator electrodes.

Metallic indicator electrodes

Metals like silver and copper provide a suitable surface for a reversible electrochemical reaction (electrons transfer to and from species in solution) and are used as a sensor for their ions. The potential develops on these electrodes with the tendency of the redox reaction to occur. An example of these electrodes is the silver electrode with the calomel reference electrode for the direct determination of the activity of Ag^+. This is a metallic indicator electrode of the first kind.

Metallic indicator electrode of the first kind

In the potentiometric determination using metallic indicator electrode of the first kind, a metal can be used to detect its own ions.

EX: a strip of copper in a solution containing Cu^{2+}. The copper electrode is used for the determination of the Cu^{2+} activity:

$Cu^{2+} + 2e = Cu_{(s)}$ and,

$E_{ind} = E^0_{Cu}(0.0591/2) \log 1/{}^aCu^{2+}$

$E_{ind} = E^0_{Cu} - (0.0591/2)$ pCu (the last equation says that the potential of the indicator electrode is related to pCu). Other metals that behave in a reversible manner in potentiometry include, zinc, silver, mercury, cadmium, and lead. These metals can be used to determine their ions in solutions. Metals that behave irreversibly (like Fe, Ni, Co etc) cannot be used for the determination of their ions.

Metallic indicator electrodes of the second kind

An anion can be detected and determined by a cation. The anion makes a complex or a sparingly soluble salt with this cation.

An example for this kind is Cl^-which can be determined using the silver electrode.

Because they form AgCl (sparingly soluble salt), a layer of AgCl is deposited on the surface of a silver wire acts as

the electrode when immersed in a solution containing silver ions.

The following reaction is considered: $AgCl_{(s)} + e = Ag_{(s)} + Cl^-$

$E_{ind} = 0.222 – 0.0591 \log {}^aCl^-$

$E_{ind} = 0.\ 222 + 0.0592\ pCl$

Metallic indicator electrodes of the third kind
A metal electrode responds to a different metal ion Example: Mercury can be used to detect Ca^{2+} Mercury forms a stable complex with EDTA and can be used as an electrode of the second kind for the determination of EDTA (Y^{4-}).

A small volume of HgY^{2-}, added to the analyte solution, is required.

- The indicator electrode potential is:

E_{ind}= K- (0.0591/2) $\log {}^aY^{4-}$

Ca^{2+} also can form a complex with EDTA:

$CaY^{2-} = Ca^{2+} + Y^{4-}$

The formation constant of the complex:

$K_f = a_{CaY2-} / a_{Ca2+}\ a_{Y4-}$

Substitution by the value of ${}^aY^{4-}$ f (rom the equation of K_f) into the previous expression:

E_{ind} = K- (0.0591/2) $\log {}^aY^{4-}$) gives:

$E_{ind} = K' - 0.0591/2 \ . \log 1/{}^{a}Ca^{2+}$

$E_{ind} = K' - (0.0591/2) \ pCa$

where, $K' = k - (0.0591/2)\log k_f \ . \ a_{CaY2}^{-}$

To use the electrode, a small volume of the CaY^{2-} is added to the test solution.

Metallic redox indicators

Inert metals like Pt can be used as indicator electrodes for redox reactions like Ox + ne = Red

$E_{ind} = E° - (0.0591/1) \log {}^{a}Red/{}^{a}Ox$

$E_{ind} = E° + (0.0591/1) \log {}^{a}Ox/{}^{a}Red$

Obviously, the electrode potential E_{ind} is dependent on the ratio ${}^{a}Ox/{}^{a}Red$

To use the electrode for a redox reaction, it must be reversible on the electrode surface (these electrodes cannot be used for a reaction that do not proceed reversibly on electrode surface)

Ion-Selective Membrane Electrodes

The potential is developed across a membrane that separating the investigated solution from a reference one as a kind of junction potential.

The selective binding of the analyte species with the surfaces of the membrane generates an electric potential.

- The electric potential develops across the membrane due to the difference in activity of the ion on the two sides of the membrane.

Properties of Ion-Selective Electrodes:

- The solubility of the ion-selective membrane in the analyte solution should be very small (insignificant)
- It should conduct electricity (through the movement or the migration of ions).
- The selective reactivity of the electrode with the analyte (through ion-exchange, crystallization, or complexation) is an important property.

Glass Electrodes for pH measurements

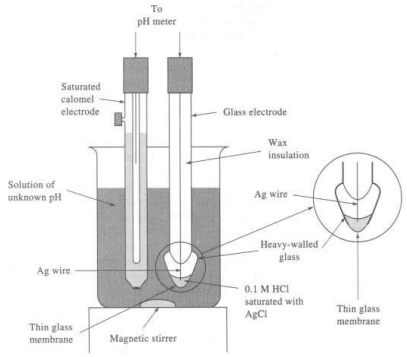
Two reference electrodes (the calomel and the Ag/AgCl) are required to measure the potential difference across the glass membrane.

- The Ag/AgCl reference electrode is slightly modified to include a thin glass membrane at the bottom which is the sensor and is selective to H^+.

The thin glass is made of silicate as the major component. Other species exists like sodium, calcium, …

Conduction within the membrane is through the movement of the singly charged cation (like sodium).

Conduction across the surface hydrated gel layer of the membrane is through H^+.



The thin glass membrane separates an inner solution of the electrode from the outer solution (the test solution). The outer surface of the membrane exchanges its cations (Na^+) with H^+ from the solution.

$H^+ + Na^+Gl^- = Na^+ + H^+Gl^-$.

The potential of the glass electrode depends on the ratio of activity of protons on the outer side and the inner side.

The of activity of protons on the outer side depends on the activity of H^+ in the tested solution while the activity of H^+ in the inner side is supposed to be fixed.

The potential across the membrane (the boundary potential, $E_b = E_1 - E_2$, E_1) is related to outer surface of the glass membrane (the activity of H^+ in the test solution (a_1)) while E_2 is related to the inner surface of the glass membrane (activity of H^+ in the inner solution (a_2)).

E_{cell} for the previous cell used for pH measurements consists of four potentials, E_{ref1}, E_j, E_b , E_{ref2}.

The potential of the glass electrode

The potential of the glass electrode is related to pH as: $E_{ind} = L - 0.0591pH$, L is a constant. However, the

electrode may respond to alkaline ions (Li^+, $Na^{+,\cdots}$). High concentrations of these species cause the pH to be lower than the true pH (yielding alkaline error). In strong acid solutions, the measured pH is always higher than the actual pH because the glass surface becomes saturated with H^+.

Calibration of the Glass Electrode:

Glass electrodes must always be calibrated before being used. Calibration is done using standard buffer solutions. Also, the electrode must be soaked in water before being used because dry glass cannot be used as a sensor for H^+. It is also important that, a pH is measured at a specific temperature and generally, calibration is required when potentiometry (pH-metry) is directly used to determine the activity of an analyte.

Determination of the equivalence point in neutralization reactions using a pH-meter:

Determination of the concentration of HCl using a standard solution of NaOH:

The pH of a known volume of HCl (V_1) is continuously determined while the standard solution of NaOH (concentration, N_2) is added. A curve is constructed of pH vs. the added volume (V) of NaOH, …

The required volume (V_2) of NaOH solution which is equivalent to HCl (at the equivalence point) can be determined from the point of inflection on the curve.

The concentration of the analyte (N_1) is determined from the following relation:

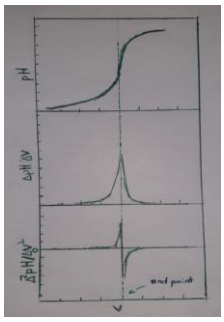
$N_1V_1(HCl)=N_2V_2(NaOH)$

Detection of the end point

1- pH vs. V (the inflection point of the curve is taken as the end point)

2- $\Delta pH/\Delta V$ (pH change perunit volume) vs. V (the equivalence point is taken at the maximum of the curve)

3- $\Delta^2pH/\Delta V^2$ against V (values change sign at the equivalence point)



Crystalline membrane electrodes are used. The LaF_3 crystal in the fluoride electrode responds selectively to fluoride. AgCl crystal respond to Cl^- and Ag_2S crystal is used for Ag^+ and S^-.

Polarography

Polarography is an interfacial, dynamic electroanalytical method. It is voltammetry when the working electrode is the dropping mercury electrode (DME). Voltammetry is the study of current as a function of the controlled voltage in a three electrode cell (the working electrode, the reference electrode and the counter electrode). The working electrode is a solid like platinum and the reference electrode can be the SCE.

The three electrode cell contains the electroactive species (species that can be reduced and oxidized (may be meals or organics) and the supporting electrolyte. Before analysis, oxygen is removed from the cell through bubbling nitrogen (the sparging process).

The purpose of polarography is to get some information about the electroactive species like their concentration.

The process is diffusion controlled and this means that other modes of electroactive species movements during analysis, convection and migration, are excluded and the only mode of electroactive species is by diffusion.

Convection current is mainly due to the movement of the electroactive species by mechanical forces like due to stirring. Convection can be excluded by keeping the solution away of any mechanical forces (no stirring).

The addition of a relatively high concentration of the supporting electrolyte eliminates migration current of ions

to the electrode. Migration current is additional current due to the movement of the electroactive species towards the electrode of the opposite charge due to the electroastatic attraction under the effect of electric field.

The potential is changed in a constant manner (like by a constant scan rate). The potential scan begins from a value where the analyte is electro inactive (less than its decomposition potential) to a value where a limiting current is observed (at the plateau). Concentration of the analyte can be determined from the Ilkovic equation or through calibration.

$E_{1/2}$ under certain conditions identifies the electroactive species) ($E_{1/2}$ can be determined from the experiment)

Advantages of the DME:

- The concentration of any pollutants on the electrode surface never large because of the frequent renewal of the mercury droplet (the working electrode) (i.e. minimum adsorptive contamination).

- Reduced metals diffuse in the droplet and form an amalgam, so, droplet surface always clean and analysis data are reproducible.

- It exhibits high overvoltage with respect to the reduction of water thus in the absence of oxygen it is possible to polarography electroactive species using more negative potential, against (SCE), (i.e. wide polarization range, more metals in water can be analyzed)

Notice that the electroactive species is determined in water and water can be reduced under the conditions of analysis.

Disadvantages

Hg is toxic, the electrode is not easy to assemble and operate and anodic analysis is not possible (because $Hg \rightarrow Hg^{+}$)

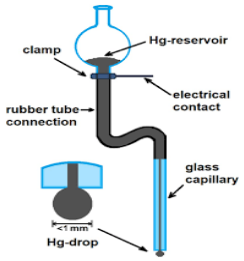
The working electrode

The working electrode in polarography is the dropping mercury electrode. A small mercury droplet emerges at the end of a fine-bore capillary at a constant adjustable rate. The diameter (and accordingly the surface area) of the drop increases with time, reaches a maximum and then separated.

Droplets are identical and has a known life time (since emerged from the end of the capillary till separated).

Each droplet is subjected to a certain potential more negative than the previous one (say by -20 mV).

The growth and fall of the droplets results in serration in the polarogram. The smooth polarogram, presented in figures, excludes serration (the current is recorded right awaybefore falling of the droplets)

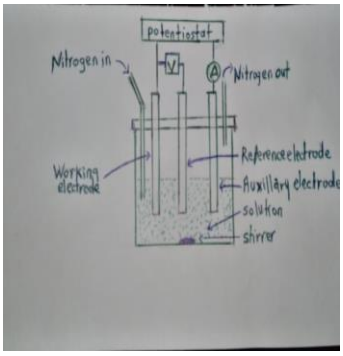


Measurements in polarography

Polarographic measurements are carried out in a three electrode cell. The working electrode (DME) where electrolysis occurs (reduction of electroactive species) is of small size and a polarizable electrode (and we are interested in events at this electrode).

The reference electrode: the potential of the working electrode is measured with respect to this electrode and the potential is measured in the absence of current in this part of the cell. The composition of the reference electrode is constant, its potential is known, stable and insensitive to the composition of the cell solution (and during analysis it remains unpolarized).

The counter electrode: the current flows between the counter electrode and the working electrode. It can be a platinum wire of suitable surface area and current flow in this part of the cell. The three electrodes are connected to an electronic device, the potentiostat.



Oxygen removal

During cathodic processes, oxygen is electro active and is reduced and as a result develops a non faradiac current. This current interferes with the diffusion current due to the reduction of the electroactive species.

The oxygen can be removed by bubbling nitrogen in the solution (the process is called sparging) for sufficient time (about 10 minutes) and some nitrogen is blown in the headspace over the solution (to prevent oxygen from diffusing back to the solution).

Before measurement, sparging process should be stopped and the cell is kept without any mechanical disturbance (no stirring) to prevent any mechanical movement of the electro active species towards the working electrode (the process should be under diffusion control where the only mode of electractive movement is by diffusion).

Supporting electrolyte

Supporting electrolytes decreases the IR drop of the cell (increases the cell conductivity). High concentration of an

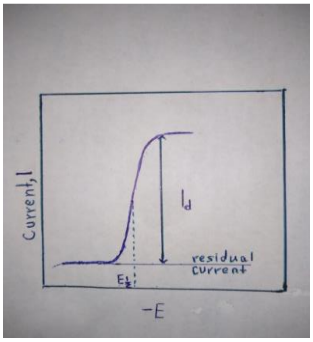
electrolyte Keeps constant ionic strength (I) during measurements ($I= 0.5 \sum C_i Z_i^2$). It makes sure that the double layer was formed in a reproducible manner and cancels the migration current (the process is required to be diffusion controlled).

Polarogram

For an electrochemical species to be reduced, the applied potential must exceeds a certain value (the decomposition potential of the electroactive species).

The decomposition potential is usually the theoretical value plus the overvoltage due different processes in the cell, beside that required due to the cell resistance, IR drop.

At the decomposition potential the variation of potential is accompanied with a high current (due to the reduction of the electroactive species)



The polarogram

The regions of the polarogram

Residual current: At lower potentials than the decomposition potential, only residual current passes and no reduction of the electroactive species occurs. Electrons contribute to charge the double layer in this part. Reduction of other species (not the analyte) like small concentration of impurities and charging current resulting from charging the double layer on front of the electrode surface may contribute to the current (activation polarization, the potential increases without a corresponding increase in current).

Current increase: At potential high enough to reduce electroactive species at the electrode surface, reduction occurs and current increases, depletion of surface electroactive species is made up by diffusion of electroactive species through a diffusion layer (from the bulk of solution towards the electrode).

At potential high enough to make surface electroactive species almost zero, diffusion brings electroactive species in a constant rate (proportional to bulk concentration (C–zero)) (i.e. the current (I_d) is proportional to the bulk concentration (C). I_d is measured with respect to the residual current

The plateau: the third region of the polarogram. When the electrode acts as an ideal polarized electrode (concentration polarization), potential increase but no corresponding current change (here the rate of diffusion is

constant and it is proportional to (C-0) and cannot be further increased due to increasing the potential.

The diffusion current I_d: I_d is measured from the residual current up to the plateau**.** I_d increases with increasing the concentration of the electroactive species

Half wave potential

The point at which the current is ½ its maximum value (I_d) is called the half wave potential $E_{1/2}$ ($E_{1/2}$ is characteristic to the electroactive species at certain conditions).

Ilcovic equation

$I_d = 706\ nD^{1/2}m^{2/3}\ \tau^{1/6}C$

It describes the diffusion current at potentials corresponding to the plateau.

I_d is the diffusion current (measured at the plateau region, independent of the potential, in Amperes);

D is the diffusion coefficient of the analyte (cm^2s^{-1});

t is the life time of the drop;

n is the number of electron involved in the redox reaction;

m is the mercury flow rate (Kgs^{-1}).

Notice: when n, D, m and τ are known exactly, the value of I_d is used to calculate C.

Heyrovsky –Ilkovic equation

The current in general can be given by the following equation

$I = 706\ nD^{1/2}m^{2/3}\tau^{1/6}C\ (1/1+\theta)$

where, $\theta = C_{ox}/C_{red}$

The potential of the working electrode:

$E = E^{\circ'} + RT/nF\ (\ln C_{ox}/C_{red})$ ……(*)

but $I_d = 706\ nD_{1/2}m^{2/3}\tau^{1/6}C$

$I = I_d\ (1/1+\theta)$

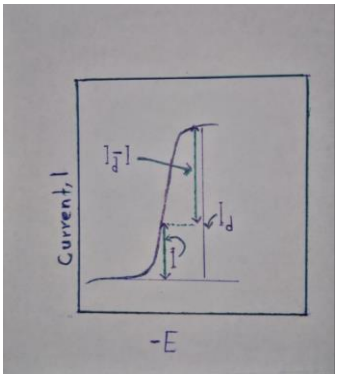
$\theta = I_d - I/I$

Substitution in ….(*)

$E = E_{1/2} + RT/nF\ (\ln I_d - I/I)$

To obtain $E_{1/2}$, plot ln $(I_d - I/I)$ (x axis) against E (Y axis), the intercept gives the value of $E_{1/2}$.

$E_{1/2}$ is characteristic of the electrode reaction at certain conditions.



Maxima

Maxima is a hump or a peak on the polarogram due to surface effects. It may encountered with concentrated solutions and can be suppressed by using some surface active agents like gelatin, Triton X-100, …….(these are called maxima suppressors)

Chromatography

Chromatography was developed by Tswett and is widely used for separation in chemistry. Different types of chromatography allow separation of complex mixtures of organic and inorganic mixtures beside their qualitative and quantitative analysis.

Principle

In chromatography, the components of a mixture are separated due to their distribution between a stationary phase and a mobile phase. This distribution depends on the rate at which each component of the mixture in the mobile phase is transported to the stationary phase (where it is retained). It is important to realize that during the process of chromatography, each component of the mixture transfers back and forth between the stationary phase and the mobile phase. This mechanism involves sorption and desorption of the solutes in each stage. Depending on the affinity of each component of the mixture for the stationary phase and the mobile phase they are separated. Different distribution ratios of mixture components between the two phases lead to different rates of migration (or elution).

Ideally, each component eluting the column develops a symmetrical signal (or a peak). The quality of separation of the mixture components is determined by the efficiency and the resolution. Chromatography therefore involves

separation beside the qualitative analysis and quantitative analysis.

Qualitative analysis

Generally, chromatographic data is presented as a graph of detector response (y-axis) against retention time (x-axis), which is called a chromatogram. This chromatogram provides a number of peaks for a sample which representing the analytes present in a sample eluting from the column at different retention times. Retention time can be used to identify analytes if the analysis conditions are constant.

Quantitative analysis

The area under a peak is proportional to the amount of analyte present in the chromatogram. By calculating the area of the peak, the concentration of an analyte in the original sample can be determined. Concentrations can be calculated using a calibration curve created by calculating the response (peak areas) for a series of known concentrations of the analyte,

Types of chromatographic techniques

- Paper chromatography (PC)
- Thin-Layer chromatography (TLC)
- Gas-Liquid chromatography (GLC)
- Gas-solid chromatography (GSC)

Liquid chromatography (LC)

- High performance liquid chromatography (HPLC)
- Size-exclusion chromatography (SEC
- Ion-exchange chromatography (IEC)
- Ion chromatograph (IC)
- Chiral chromatography (CC)

Distribution ratio

The rate of migration of a component through the stationary phase is governed by the distribution ratio (D) = C_S/C_M.

Large D values indicate slow solute migration in the stationary phase (notice that solutes are retained in the stationary phase). The larger the difference between the distribution ratios of the solutes, the more easily they are separated.

Retention time

The time a solute takes to pass through the column is called the retention time (t_R). It is related to the separation factor (k) as follows:

$t_R=t_M(1+k)$

t_M is known as the dead time, which is the time taken by a component which is not retained by the stationary phase to pass through the column (therefore it moves with the same velocity as the mobile phase). A component which is not retained by the stationary phase has a separation factor of zero (and a D of zero) so, $t_R = t_M$. It should be noticed that k values should not be too large. If it is larger

than about 20 the separation or retention time will be so long.

The basic mechanisms of separation in chromatography

- **Adsorption**: adsorbents like silica gel are used. Silica gel contains Si-O-Si and Si-OH structures. In this case, Adsorption involves electrostatic interactions between species to be separated and the polar sites on the adsorbent surface. This interaction may be dipole-dipole interaction, hydrogen bonding and dipole-induced dipole interaction. The more the polarity difference of the species being separated is the more efficiently they are separated.

- **Partition**: A liquid may be bonded to the surface of the stationary phase. For example, the liquid may be chemically bonded to the surface of the walls of the stationary phase.

Separation including this bonded phase is affected by partition.

- **Ion –exchange**

- **Exclusion:** in this case there is no clear or specific interaction between the stationary phase and the component molecules. The stationary phase is silica of controlled porosity or polymer with a range of pore sizes.

As species being separated, they ideally develop a Gaussian concentration bands. These become broad as the species move in the stationary phase.

For some reasons, like changes in the distribution ratio of species at high concentration, the peaks are distorted leading to peak tailing and peak fronting. These are undesirable phenomena because some peaks will be not well separated.

Efficiency and resolution

For column chromatography a plate number, N, is used as a measure of efficiency:

$N= 16(t_R/W_b)^2$

$N= 5.54(t_R/W_{h/2})^2$

W_b is the peak base width and $W_{h/2}$ is its width at half maximum.

Another measure of the efficiency is the plate height, H (or the height equivalent to a theoretical plat HETP). According to this theory, H= L/N, L is the column length and N is a dimensionless number.

Resolution

$R_S = 2\Delta t_R/(W_1+W_2)$

Δt_R is the difference of the retention times, W_1 and W_2 are the base widths of two adjacent peaks.

Gas Chromatography (GC)

Gas chromatography includes the separation of mixture gas components in a column to allow their qualitative and quantitative analysis.

The components of the mixture should be volatilized by heating without being decomposed (thermally stable).

The sample is introduced to the injector (for example by injection through a septum using a syringe), vaporized and mixed with a mobile phase (carrier gas) and then passed to the column which contains a stationary phase, where separation takes place.

The carrier gas is inert, like helium or nitrogen. It carries the mixture components through the column for separation. A mixture components eluting from the column are detected by a suitable detector (FID, TCD, ECD, NPD,..). The detector response is presented in the form of a chromatogram. The chromatogram is used for the qualitative and quantitative analysis of the mixture components.

Separation in GC

Separation in GC is achieved in a column due to the different affinities of the components of the mixture in the mobile phase to the stationary phase. The separation mechanism is related to known phenomena like adsorption and partition.

The sample components (solutes) should show different affinities towards the stationary phase in the column for efficient separation.

Detection

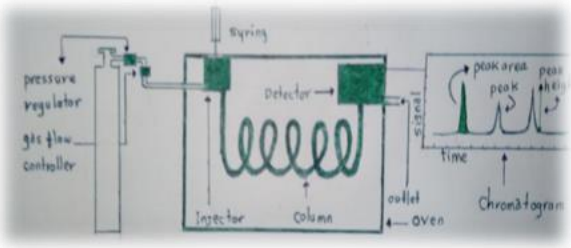
A detector is used to detect each component of the mixture eluted from the column. A number of detectors are used with GC. The choice is based on the nature and properties of substance being analyzed.

The detector response (amplified signal) vs. time is presented in the form of the chromatogram.

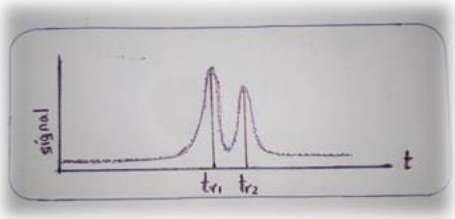
Qualitative and quantitative analyses can be performed using the data of the chromatogram (the retention time (t_r) peak height and peak area).

The retention time

The retention time is that time a certain component takes to pass through the column (the time is measured from injection till detection).



Instrument



The chromatogram

Carrier gases

Carrier gas should be:

- Inert: like nitrogen or helium

- Pure: the gas is passed through suitable adsorbents (like silica gel and activated carbon) to avoid possible adverse effects of, water, oxygen, HCs….) on the performance and instrument components)

- A carrier gas (in a cylinder) flows (at a suitable rate) and the flow rate is regulated using a gas flow regulator.

Injectors

Liquid samples are introduced to the injector using a micro syringe through a septum.

Gas samples are introduced through gas syringes or gas sampling valves.

Columns

The column contains the stationary phase which is responsible for sample components separation.

Capillary columns

Capillary columns are made of pure SiO_2, coated with a protective layer**. The column** length: up to 100 m **and the** diameter: 0.1 - 0.7 mm.

Stationary phase: a liquid layer may be deposited or chemically bonded to the internal walls.

Packed column:

These are made of stainless steel or glass. Their length: 1-2 m and the diameter: (2-3 mm). The stationary phase (packing) is a porous solid adsorbent or an inert, granular siliceous solid (diatomaceous earth) support for a liquid (of a high boiling point) stationary phase.The column is located in the oven and its temperature can be adjusted easily.

Column type determines the mode of injection

With capillary columns, split, splitless and on-column modes are used. The split mode is usually used with samples of normal concentration to prevent overloading of the stationary phase. Only a portion of the sample is passed to the column while most of the sample exits through the split outlet.

The splitless mode is used with samples of very low concentrations. While the on-column mode is of high sensitivity and is used for very dilute solutions. It is used with packed columns.

The flash-vaporization is sued with packed column.

Detectors

The detectors (universal or selective) respond to changes in some property of the eluted compounds. The high sensitivity, the rapid and stable response and the reproducibility are important features of a detector.

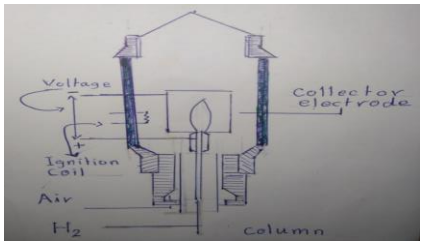
The intensity of the detector signal is proportional to the component concentration (over a certain range, linear dynamic range)

Flame ionization detector (FID)

FID is a universal detector for organics. When a carbon containing solute elutes from the column and introduced to a flame (a stream of hydrogen/air with proper ratio burnt at a small metal jet (positive) is used), cations will be produced due to the ionization of the compounds molecules. This process increases the electrical conductivity of the flame and the cations are collected by the collector electrode (negative). A DC potential difference between the positive jet and the negative collector electrode results in the passage of a current signal which can be recorded.

The current increases with increasing concentration of the ions generated in a large linear range.

FID has high efficiency, measures concentrations at very low level and the sample is combusted (i.e. destroyed)



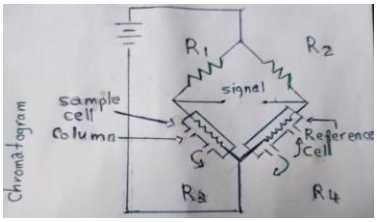
FID

Thermal conductivity detectors (TCD)

TCD is a universal detector. It has lower efficiency than the FID and the sample is not destroyed. The detection is based on the comparison of the thermal conductivity of the carrier gas in the presence of the solute (in the sample cell) and in the absence of the solute (in the reference cell).

The cells contain identical filaments whose resistance is dependent on their temperatures, which in turn depends on the heat loss due to the surrounding gas. When there is no solute coming out from the column with the carrier gas, the temperature of the two filaments is the same and a base line is recorded. When a compound elutes from the column with the carrier gas, the temperature of the two filaments becomes different and a signal is recorded. The intensity of the signal is proportional to the concentration of the analyte.

The resistance of the two filaments (which is related to their temperatures) is compared by the Wheatstone bridge like circuit.



TCD

Electron capture detector (ECD)

It is a specific detector that shows selective response for those compounds which show high electron affinity like halogens. ECD has the highest sensitivity among other GC detectors. It consists of a cavity that contains two electrodes and a radiation source like ^{63}Ni. The collision between electrons from the radiation source and the carrier gas (usually nitrogen) produces more electrons. When a compound containing electronegative atoms present (eluted from the column) those electrons will be captured to form negative ions and the rate of electron collection will decrease.

Nitrogen phosphorous detector (NPD)

It is a modified FID that is selective for nitrogen and phosphorous. It contains an electrically heated rubidium containing ceramic bed that is placed between the burner jet and the collector electrode.

In GC it is important to have a chromatogram in which the peaks are well separated and the number of peaks equals the number of components in the mixture.

Peaks separation depends on:

- Column temperature: the quality of separation of component (A) from solute (B) in a mixture (A+B) is poor when the difference in their retention times is not large enough. The efficient separation requires that the components A and B interact with the stationary phase. It is important to control the column temperature for efficient separation (not too high and not too low).

- The flow rate of the mobile phase. A high flow rate decreases retention time and a poor separation would be observed. The analytes needs time to interact with the stationary phase. With a high flow rate little time is available for the analytes to interact with the stationary phase.

- The length of the column.

Separation is better with longer columns. Increasing the length of the column increases retention time but results in broader peaks.

- The amount of sample.

Injection of a large amount of the sample leads to a significant tailing to the peaks (and this causes a poorer separation). Detectors of GC are relatively sensitive and there is no need for a large amount of sample to give a detectable signal and most gas chromatographs operate in the split-mode.

- The vapor pressure and the polarity of the components.

If the component A in a mixture (A+B) has higher vapor pressure than component B, it spends longer time in the mobile phase and as a consequence elutes first.

- In normal-phase chromatography the stationary phase is polar and the mobile phase is non-polar. When the polarity of the stationary phase and that of the solute are similar the retention time increases (similar polarity leads to higher affinity). The large difference of polarity between A and B in the mixture allows their efficient separation.

Applications

GC can be used as a means of qualitative analysis through comparison of the retention time of the compound with that of known molecules at the same conditions.

The peak area is used as a means of quantitative analysis. A calibration curve, established at the same conditions, is used for quantification.

It is noteworthy that mass spectrometry can be used with gas chromatograph (GC-mass) to combine the features of both of them for identification of substances in a sample.

It is also noteworthy that samples, in generally, must be in a suitable form for the analysis and this means that the sample pre-treatment procedures is an essential part of the analysis. This includes a number of extraction methods like solid phase extraction/micro extraction, liquid phase extraction/micro extraction, headspace extraction, …etc.

Atomic absorption spectrometry (AAS)

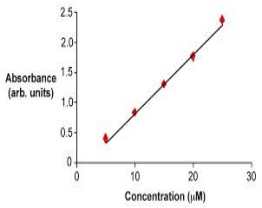
The main principle

Because the energy levels of atoms are specific, they absorb and emit radiation of specific energies. In atomic absorption spectrometry, the sample containing the analyte is transformed to a form suitable for measurement by the spectrometer. For example, in the flame atomic absorption spectrometry the sample should be in the form of solution. The sample then is converted to fine droplets and introduced in this form to the flame where the free atoms are formed. The absorption of radiation of a suitable energy by these atoms is determined. The intensity of absorption is related to the amount of the analyte in the sample (its concentration). Determination of the intensity of absorption using a specific wavelength is the basis of the quantitative analysis in AAS.

In the flame, the solvent is evaporated and the de-solvated analyte particles formed are vaporized to form gaseous molecules. The gaseous molecules are dissociated to the free atoms of the analyte.

Ionization may occur (leading to a kind of interference) if the energy is high enough to ionize the formed atoms and this depends on the flame temperature and also on the ionization energy of the atoms.

The atoms of the analyte absorb specific radiation energy from a suitable source (the hollow cathode lamp (HCL)). The specific energy (wavelength) is selected using a monochromator and a photomultiplier tube is used as the detector. The analyte concentration can be determined for example using a calibration curve established using known concentrations of the analyte at the same experimental conditions.



Example

To determine copper in a sample, the hollow cathode lamp in which the cathode is made of copper is used. By absorption of the characteristic wavelengths, copper atoms only are excited in the sample. Other elements in the sample require different characteristic radiation to be excited.

It is noteworthy that atomization also can be performed by other methods like by using a graphite furnace in the graphite furnace atomic absorption spectrometry (GFAAS).

In atomic absorption spectroscopy atomic absorbance only is recorded, so, it is important to suppress ionization. Also, qualitative and quantitative analysis of the analytes (elements) at trace levels (ppm and ppb) is possible.

Atomic fluorescence spectrometry

As it was mentioned before, the absorbance depends on the analyte concentration which can be measured using a calibration curve. Ground state atoms absorb a specific radiation of certain wavelength (characteristic to the element) and get excited. These excited atoms when return to the ground state in a short time re-emit radiation of characteristic energy (wavelengths) which can be used for analysis. This is the principle of atomic fluorescence spectrometry. To distinguish excitation and fluorescence energies, the radiation source is positioned at a right angle with respect to the fluorescence radiation used for measurement. In atomic fluorescence spectroscopy therefore the radiation source

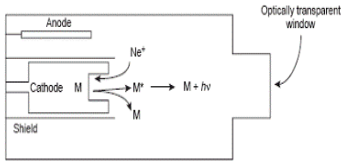
is placed at right angle with respect to the other components of the spectrometer.

It is noteworthy that in atomic fluorescence spectrometry (and atomic emission spectrometry where atoms are excited by the thermal energy of the flame), the instrument response is proportional to the intensity of emission while in atomic absorption spectrometry; absorption is related to Beer′s law..

Components of AAS

The hollow cathode lamp:

The radiation source in atomic absorption spectrometers is the hollow cathode lamp (HCL). It comprises a glass envelop having a quartz window and contains a gas such as argon at certain pressure. The argon gas is ionized by an electric field. The ionized argon atoms (having sufficient kinetic energy in the electric field) strike the cathode and hence strip atoms away from the cathode element. Metal atoms get excited in the field. When these excited atoms relax to the ground state, radiation is emitted from them. These radiations are specific for the element of the cathode. Therefore, the HCL in which the cathode is made of a certain metal like Cu is used for the determination of the same element. Another source of radiation is the electrodless discharge lamps. These can be used to excite the elements atoms and obtain their spectrum.



The source of radiation in FAAS (HCL)

The burner system:

In the case of flame atomic absorption spectroscopy, the sample is prepared in the form of solution. Samples are transformed to small droplets of suitable size. In the flame these droplets undergo a series of steps to form the atoms required for analysis. In the premix burner system, the sample is mixed with the fuel and oxidant in the spray chamber by using baffles and then the mixture is sprayed in the burner. An advantage of this type is that the larger droplets are removed and the other part of the sample enters the burner as homogeneous size droplets. Also, the premix burner system allows using of a long narrow burner. This provides a long path length for absorption. The high signal-to-noise ratio, the stability of the flame, compared to the total consumption burner, the removal of larger droplets and the laminar flow characteristics are important advantages. The fuel (acetylene, propane, hydrogen…etc.) and the oxidant (oxygen, air,….etc) are chosen depending on the required flame temperature. The flame temperature, the position of the optical pass (to meet the region of the flame where atoms are formed in high concentration) and the possibility of variation of flame temperature due to sample effects are important factors in atomic absorption spectrometry.

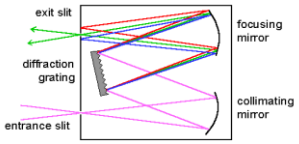
Graphite furnaces

The graphite furnace is an open-ended tube of graphite. It is heated electrically in an atmosphere of argon to prevent oxidation. The furnace has a small hole to introduce the sample. In this case a thermal program is used where heating up to about 100°C evaporates the solvent, heating to about 800°C ashes the sample then heating between 2500 and 3000°C atomizes the sample. Measurement occurs at this last stage where the sample atoms are in the gaseous phase. The graphite furnace requires

much less sample, uses a larger fraction of the sample, and keeps the atomic vapor in the light beam for a longer time than does a flame.

The monochromator

The monochromator is used to separate wave lengths though a group of mirrors and a prism or a grating. In atomic absorption, the radiation from the hollow cathode lamp is mechanically chopped. The chopped radiations pass through the burner where the sample is sprayed and burned. The atoms in the pass of the radiation absorb a fraction of these radiations. The radiation then passes through the monochromator for separation and selection of the wavelength used for measurement.



Monochromator

Background correction

If a portion of the radiation from the HCL is scattered or absorbed by species which are not the analyte atoms, then the absorbance (gross absorbance) is higher than that of the analyte atoms (the required net absorbance).

The difference between the gross and net absorbance is the background absorbance. The net analyte absorbance is measured by subtracting the ground absorbance from gross absorbance.

Background correction can be carried out using many approaches like deuterium lamps and Zeeman Effect.

Detector:

The detector in atomic absorption spectroscopy is a photomultiplier tube. It converts the radiation energy to a measurable electrical signal.

Data acquisition system: Can be a computer screen to present and manipulate the data.

Interferences

Matrix interference:

Matrix interference is encountered when the physical properties of the sample (like viscosity) is different from that of the solution used for calibration. To explain the effect of viscosity on the results of analysis of a certain analyte, the concentration of a analyte is measured at different viscosities. The viscosity of the analyte sample can be changed by the addition of some reagents like phosphoric acid. It is observed that the determined analyte n centration tends to decrease with increasing sample viscosity. This is because of that the change of viscosity affects the size of the analyte droplets and therefore a change of the rate of de-solvation, vaporization and atomization.

To avoid such effect of viscosity, the physical properties of the sample and the solution used for calibration should be the same. When the physical properties of the analyte sample and that of solution used for calibration are different the standard addition method of measurement is used. In the standard addition method, the sample to be analyzed is mixed with the standard solution used for calibration. As a result, the mixture has the same physical properties. The absorbance is measured for a number of mixtures (formed by mixing a definite volume of the sample (ex. 9 ml) with a certain volume of the standard analyte solution (ex. 1 ml) of

varying concentration (ex. 1-6 ppm)). The concentration of the analyte can be determined from the graph of absorbance vs. concentration (of the standard solution used to make each mixture).

Ionic interference:

Ionic interference is encountered when the conditions (like the temperature) of the flame leads to the formation of the corresponding ion. In this case the radiation from the HCL will not be recognized by the ion. Addition of a suitable amount of an element of low ionization potential (ion suppressor) is required to reduce the analyte ions according to the Le Chatilier principle:

$M^{n+} + ne = M$

Chemical interference

Chemical interference is encountered when a thermally stable compound is formed. Atomization therefore is not complete and the sample absorbance is reduced significantly. Changing the burner temperature (through changing the oxidant, fuel or both) or the addition of a releasing agent is performed to overcome this kind of interference.

Applications of AAS

It is used for the qualitative and quantitative analysis of about 70 elements ex, Co, Ni, Fe, Ti, Zn, Pb.. etc. in the ppm and ppb range. Agricultural, water, soil, clinical, biochemical, metallurgical, petrochemical samples, … etc can be analyzed. A calibration curve usingknown concentrations of the analyte is used for the quantitative analysis.

Atomic emission spectrometry

In atomic emission spectrometry there is no need for a radiation source and it is based on using of other sources of excitation like a flame or plasma. Flames are used for atomization and excitation in flame atomic emission spectrometry (FAES). The temperature of the flame is relatively low and therefore the flame is not an ideal source of excitation for atomic emission so this technique is used for the determination of a small number of elements. In ICP (inductively coupled plasma) AES, plasma is used for atomization and excitation. The temperature of plasma is higher than in a flame (FAES) and a larger number of elements can be determined by ICP-AES.

Flame atomic emission spectrometry

In flame atomic emission spectroscopy, a monochromator is used for the selection of the wavelength used for analysis while in flame photometry filters are used for this purpose. Atoms of different elements have different electronic configuration and as a result when these atoms are excited with a suitable energy source they emit radiation of specific energies when returns to the ground state. In flame atomic emission spectroscopy, samples containing the analytes are introduced to the flame in the form of fine droplets. In the flame, the solvent is evaporated and the analyte particles formed are vaporized to gaseous molecules. The gaseous molecules of the analyte are dissociated to the free atoms in the next step

and excitation of the free atoms is accomplished by the thermal energy of the flame. When these excited atoms return back to the ground state, they emit characteristic radiation (emission spectrum). These characteristic radiations allow for the qualitative determination of the analyte and the intensity of emission allows for the quantitative estimation of the analyte.

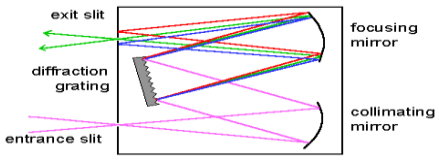
Components of the flame atomic emission spectrometer

A burner system

The burner incorporates a nebulizer. The sample is nebulized in the flame as fine droplets. The nebulization process transfers the sample solution to an aerosol. In the flame, solvents are removed and the sample is vaporized and atomized. This is followed by excitations of the electrons to higher electronic energy states and the subsequent emission of the characteristic radiation of the atoms. Different species as hydroxyl radicals and carbon monoxide, water and other combustion products are produced in the flame which may give a background emission. Flame temperatures depend on the oxidant (air, oxygen, nitrous oxide,…etc) and fuel (acetylene, hydrogen,…etc)used. The optimum burning velocity in the flame is reached by adjusting the supply of oxidant and fuel.

Monochromator

A monochromator is used to select the wavelength used in analysis. It separates the wavelengths after passing through the flame using a group of mirrors and a prism or a grating. Radiation from the entrance slit is reflected through a mirror to a diffraction grating. Another mirror is used to focus the discriminated radiation on the exit slit.



Monochromator

Filters can be used (in flame photometers) where each element to be determinedrequiresa specific filter.

The detector:

The detector used in atomic emission measurements is a photomultiplier tube (PMT). A photomultiplier tube converts radiation energy to a measurable electrical signal. A PMT usually has a wide wavelength range, a large dynamic range, a high amplification gain and low noise.

Interferences

- When other species in the sample emit the same or a very close emission line, another line can be used for analysis.

- When the analyte concentration in the flame region is high, atoms in the ground state may absorb the emitted radiation energy. This tends to the decrease the emission intensity of the sample (self absorption).

- Thermally stable compound of the metal ions also reduces the intensity of emission.

Advantages

Important advantages of FAES are the simple instrumentation and the fast determination. However, the intensity of emission is sensitive to changes in flame temperature and changes in the flow rate of gas flow.

Application

The determination of alkali and alkaline earth metals (Na, K , Rb, Ca, Sr, Ba,...) in soil samples, biological samples, environmental samples. ….etc.

Inductively coupled plasma atomic emission spectrometry (ICP-AES)

In this case an ICP torch is used instead the low temperature flame.

Formation of argon plasma

The ICP torch comprises three concentric quartzes tubes having the same axis. The larger one confines and insulates the plasma. On the top, there is an induction coil. The aerosol of the sample in a stream of argon is delivered in the central tube. When current flows in the coil, it creates a magnetic field perpendicular. If there is a spark, argon ionizes. Ions and electrons orbit in the magnetic field and the resistance makes it to glow. Tangential argon is used to cool the surface of quartz tube. At such high temperature the plasma (a homogeneous mixture of atoms, electrons and ions) is held by the magnetic field as a fireball. The sample enters the plasma as an aerosol from the inner tube. The temperature is high enough to make atomization and ionization (a state which is completely free from any molecular association). When these excited atoms and ions relax to the ground state they emit characteristic radiation. These radiations are separated using a monochromator and detection is carried out using a photomultiplier tube.

This technique is able to measure more elements of lower concentrations compared to the flame atomic emission or atomic absorption spectrometry.

It is noteworthy that:

- In the analysis region, the temperature is higher than in flame atomic absorption spectrometry. As the temperature is higher, more spectral lines are emitted. Therefore, there is a high possibility for spectral interference. However, it is possible to measure at another resonance line for the element.

- It is possible that a fraction of the plume containing the analyte species is driven to a mass spectrometer for an isotopic analysis. This is the basis of (ICP-MS).

- This kind of analysis uses very high temperature for atomization and excitation so, there is no thermal interference and oxides are not likely to be formed because of the presence of an atmosphere of argon.

- There is no molecular absorption (no molecules are present at such high temperature) so there is no need for the corresponding background correction.

- Because ionization of argon leads to the formation of large amount of electrons (Le Chatilier principle) and it is possible to add KCl as an ionization suppressor, it is easy to overcome ionic interference.

Advantages:

- No interferences compared to AAS

- Fast sample throughput

- Simultaneous multi-element analysis.

- Wide dynamic range.

- Tolerates of complex matrices.

- Safe (no flammable gas).

Disadvantage:

- Consumption of high amount of argon

- Energy required is relatively high.

- Expensive

Sample introduction methods:

- Generally, an ICP requires that the samples for analysis are in solution and are delivered to the nebulizer by a pump. The nebulizer transforms the aqueous solution into an aerosol (with the aid of Ar gas) in the spray step. Pneomatic nebulization is used and ultrasonic nebulization is also possible.

- It is possible to use the graphite furnace, then argon carries the products to the ICP plasma.

- The hydride generation technique can also be used. (for elements which forms volatile hydrides like Se, As, …..etc. an acidic medium with sodium borohydride is used to generate the hydride). Then argon carries the volatile hydrides to the plasma.

Spectral methods

Electromagnetic radiation

It is known that photons travel, in a given non-absorbing medium, with the same velocity (v): $v = \upsilon.\lambda$ (υ is the frequency and λ is the wavelength).

The energy (E) of a photon depends on its frequency:

$E= h.\upsilon= hc/\lambda$,

where h is the Plank constant and c is the speed of light (in vacuum) = 2.99792×10^{8} ms^{-1}.

In chemistry it is sometimes more convenient to consider the wave number $\bar{\upsilon} = 1/\lambda$.

Regions of the electromagnetic spectrum and interaction of photons with matter:

Because photons of different energies interact with matter in different manners, it is convenient that photons of different energies are classified into different electromagnetic regions.

Radio frequency: changes in rotational energy are involved.

Microwave: involves change of orientation

Infrared: vibrational spectra is involved

Visible: involves molecular electron excitations.

Ultraviolet: excitation of molecular and atomic valance electrons is concerned in this process.

X-rays: excitation and ejection of core atomic electrons (change in electron distribution) in inner shell electrons.

Gamma rays: involves excitation of atomic nuclei and includes dissociation of nuclei of and ejection of energetic core electrons in heavy elements.

Absorption of electromagnetic radiation

When light of intensity $I_o$passing through a cell (having a pass length = (b) and containing a solution of concentration= (c)), the intensity of the light is reduced because a fraction of the light is absorbed and hence the transmitted fraction is (I_t).

The transmittance T = I_t/I_o, and the percentage transmittance = 100T while the absorbance A= log I_o/I_t

Beer- Lamberts Law

A = εbc, ε is the molar absorptivity (L. $mol^{-1}.cm^{-1}$), b is the cell width, c is the concentration (mol L^{-1}).

As the radiation passes through the sample, the intensity decreases exponentially.

Lambert showed that this depends on the path length, l, and Beer showed thatit depends on the concentration, c.

$I_t= I_o exp^{(-\varepsilon cb)}$

Where, I_t and I_o are the intensities of the incident and transmitted lights, respectively.

Converting to the base 10log eqn.,

Log $I_o/I_t = \varepsilon cb$

ε is usually quoted for a concentration of 1 M and a path length of 1 cm.

If more than one species absorbs at the same wavelength and that they not interact with one another, then $\varepsilon_{total} = \varepsilon_1 c_1 b + \varepsilon_2 c_2 b + \varepsilon_3 c_3 b + \ldots\ldots$

As mentioned before, Transmittance (T) = I_t/I_o and %transmittance = 100T

$A = \log(1/T)$

$A = \log(100/\%T)$

$A = 2 - (\log\%T)$

It is noteworthy that when the same cell is used b is constant and therefore, Beer law suggests a linear relation between absorbance A and concentration. A calibration curve is established and used to determine the concentration of an unknown.

Ultraviolet and visible molecular spectrometry

Principle

Absorption in this region of the spectrum corresponds to transition between electronic energy levels. The energy involved covers the range100-800 nm. However, in practice, UV-Vis spectrometers operate between 200-800 nm.

Transition metals have partially occupied d orbitals and they often show absorption bands at the visible region. Organic molecules, on the other hand, contain c-c bonds and c-other atoms and also, they may contain multiple bonds (double and triple bonds). In this case, different transitions ($\rho \rightarrow \rho^*$, $\pi \rightarrow \pi^*$, n→ higher energy levels) are possible. $\pi \rightarrow \pi^*$ occurs in molecules containing multiple bonds. The greater the extent of conjugation in the molecule, the closer the energy levels are and the higher the wavelength.

UV and visible spectra of solutions, due to solvents effects on vibrational and rotational levels of molecules, give broad bands. The peak wavelength λ_{max} is determined for analytical purposes and the absorption obeys Beer law.

After excitations by a photon of sufficient energy, faster transitions to lower excited states (involving vibrational levels of the excited state) takes shorter times and hence they are favorable. Further transition to the ground state results in the emission of lower energy (fluorescence

(involves a singlet state) and phosphorescence (involves triplet states)).

Fluorescence and phosphorescence

Fluorescence which involves a singlet state is a short-lived phenomenon and the luminescence ends immediately. Phosphorescence, on the other hand, involves change in electron spin (triplet state) and therefore lasts for longer time (several seconds). In most cases, photoluminescence tends to be at longer wavelengths than excitation energy.

Molecular Multiplicity, M

$M = 2S + 1$

S = spin quantum number of the molecule = summation of the net spin of the electrons in the molecule. Most organic molecules have S = 0 because molecules have even number of electrons. As a result, the ground state must have all electrons paired so, M = 2 X (0) + 1 = 1. Molecules in the ground state have a singlet state.

While the molecules are in the excited state, one electron may reverse its spin. Therefore, S = (+1/2) + (+1/2) = 1 and M = 2(1) + 1 = 3 (Triplet State).

Notice that a molecule with an even number of electron cannot have a ground triplet state because all electrons are paired. While molecules with one unpaired electron are in the doublet state (For example, organic free radicals)

It is worse mentioning that the allowed absorption process will result in a singlet state. A change in electron spin is a forbidden process. The forbidden process means unlikely to happen.

Instrumentation

The main components are light source, optical parts (like, cuvettes, monochromators or wavelength selector (mirrors and a grating) and detector.

The source of radiation is the deuterium lamp: the electrical excitation of deuterium at low pressure produces a UV spectrum.

Deuterium and hydrogen gives radiation in the UVrange. Quarts windows and cuvettes must be used in this range. For visible radiation the tungsten halogen lamp is used. Silicate glass can be used for these longer wave lengths.

Detectors

A photomultiplier tube or a photodiode array is used. A photomultiplier tube; multiply the current produced by the incident radiation in the order of about 10^8 times. A photdiode is a semiconductor device that converts light into electric energy.

Applications

The structure of organic molecules can be classified based on the functional groups they have. As was mentioned before, most work is carried out in the range 200-800 nm. Hexane contains only sigma bonds and ethanol contains a lone pair of electrons. They absorb below 200 nm, therefore they can be used as solvents.

- The transitions which are responsible for visible and UV absorption by complexes is related to d-d transitions due

to the transition metal ion. These give rise to the color of many compounds of transition metals and are modified by changing the ligand that are bound to the central atom. These transitions have low absorptivity constants and therefore are suitable only for determination of the concentration of metals.

- The absorption band of a ligand may be modified when complexed with a metal. Charge transfer bands result due to transition between the levels of an electron donor (sigma or pi bond) of the ligand and an electron acceptor level such as an empty orbital of the transition metal.

- The absorption of photons in this range causes electron transition from the valance band to the conduction band in semiconductors. The band gap energy of a semiconductor can be estimated from their absorption spectra.

Infra Red Spectroscopy

Infrared spectra are observed due to the vibrational transitions in molecules and it involves a change in the dipole moment of the molecule due the interaction of the field with the dipole moment of the molecule. Molecules having permanent dipole moments like CO are IR active where the absorption of IR photons results in a change of the dipole moment of the molecule.

Generally, IR spectra are obtained in the wavenumber range 13000 – 10 cm^{-1} and it is usually used to get information about the functional groups in molecules. This region of the spectrum is conveniently divided to:

- Near IR (13000-4000 cm^{-1}), mid IR (4000-400 cm^{-1}) and far IR (400-10 cm^{-1}).

The basic principles:

Bonds in molecules are not rigid. As a result, they undergo bending, distortion and stretching. This phenomenon is best described by a model that relates the system to a simple harmonic oscillator (e.g. a spring having two masses (m_1 and m_2) at its two ends. The frequency (v) of such a system is given as follows:

$$v = (1/2\pi)(k/\mu)^{1/2}$$

In the previous relation μ is the reduced mass of the system ($\mu = m_1 . m_2/m_1+m_2$) and K is the force constant of the spring.

On the other hand, molecular vibrations are characterized by vibrational quantum number *v*. The stretching vibrational energy involved:

$E = h\nu_o(v+1/2)$.

It is clear from the previous relation that there is a set of levels spaced in energy by $h\nu_o$.

The allowed transitions, which give fundamental vibrational absorption peak, are observed when $\Delta v = \pm 1$. Larger energy transitions can occur where ($\Delta v = \pm 2$) or more, leading to overtones. Overtones and combinations are frequently encountered in IR spectra.

As was mentioned before, for a molecule to be IR active there must be a change in the dipole moment due to the absorption of IR photons.

Carbon dioxide

- CO_2 does not have a dipole but it has three modes of vibration:

- Symmetric stretching (ν_1): here the oxygen atoms are the same distance from the central atom, but the two CO bonds lengthen and contract together, the dipole does not change and therefore it is IR inactive.

- Antisymmetric stretching, (ν_3): here one CO stretches while the other contracts while the centre of mass of the molecule remains unchanged and thus the dipole changes and hence it is IR active

- Bending vibration (v_2): this mode is degenerate. It includes in plane bending and out -of -plane bending. This vibration is IR active.

Water molecule

Water molecule has three vibrations. All involve a change in the dipole moment and as a result they are IR active. Water cannot be used as solvent in IR because it has strong absorption peaks in IR.

Generally, there are (3N-6) fundamental vibrations for a general molecule with N atoms. For a linear molecule however, there is 3N-5 of such vibrations.

The region between 4000 cm^{-1} and 1500 cm^{-1} in the IR spectrum is known as the fingerprint region. It contains a large number of peaks so it is difficult to identify a single peak but this region for a given compound is unique and can be used for identification and distinguishes between compounds.

Important group frequencies includes the stretching mode involving hydrogen and a heavier atom, double and triple bonds and aromatic systems, the bending vibrations of organic molecules.

Instrumentation

In the mid-IR, the source of radiation isa heated rod of silicon carbide. Some sources use rhodium heater in alumina tube packed with alumina and zirconium silicate. For the NIR, tungsten or tungsten halogen lamp is used.

Sampling

For gases, a long tube of glass having NaCl window is used. For liquids, a thin film between NaCl plates is used. In solids organic powder, the samples are powdered and mixed with paraffin oil (Nujol) to form a paste or with KBr to form a disk.

Dispersion

Dispersion is performed using IR diffraction gratin or by Fourier transformation.

Detectors

Heat sensors are suitable detectors (thermocouples).

X-rays

Principles

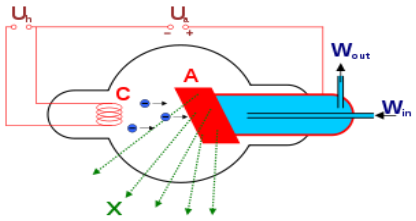
When the inner electrons of atoms (those of K or L shells) are excited, electrons from higher levels fell down to fill the vacancy created in these shells. This process of electron transition which follow the inner electron excitation is accompanied with the emission of characteristic x-ray lines (K_α, K_β, L_α, ….etc). The energies of these characteristic x-ray lines equal the difference in the binding energy of the electron in the inner and outer shells involved in this transition. For example, k and L shells are involved in the emission of K_α, while for K_β, K and M shells are the two shells taking part in the process. As result of this fact and because an atom of an element has its distinct electronic configuration these characteristic x-ray emissions (lines) are used for the identification of the elements (Moseley law is a relative subject and it describes the relation between the energy of a characteristic x-ray line and the atomic number Z of elements).

Production of x-rays

The energy required for the inner electron excitations can be obtained from highly energetic (accelerated) electrons, radioactive radiation or x-rays of suitable energy.

Production of x-rays by the Coolidge tube

The Coolidge tube is used for the production of x-rays. It comprises an evacuated glass envelop (about 10^{-3}Torr). The tube contains a tungsten filament cathode which can be heated using an electric current. The heated cathode generates electrons. These electrons are accelerated to high velocities in the electric field. The accelerated electrons strike the target anode and lose their energies (kinetic energies = $1/2mv^2$). About 1- 2% of the electrons kinetic energy is converted to x-rays as a result of the rapid deceleration. The remaining (about 98%) energy is transformed into heat and as a consequence the target requires special cooling (by water).



X-Ray spectra

X-ray spectra generated using the Coolidge tube are continuous and are similar. These continuous spectra therefore cannot be used as a means for element identification. However, when the accelerating voltage of the electrons is increased above a certain value (characteristic for the anode element) intense emission lines appear as spikes superimposed on the continuous spectrum. These intense emissions lines appear when the bombarding electrons have the sufficient kineticenergies

to knock out an electron from the K or L shells of the target atoms.

Characteristic X-ray lines

As mentioned previously, the sharp emissions in the x-ray spectrum appear when the bombarding electrons have the sufficient kinetic energies to knock out an electron from the K or L shells of the target atoms. This phenomenon leads to the creation of a vacancy in the inner shell. The characteristic lines appear when electrons from the outer shells fall to fill theses vacancies of the inner shells. The characteristic K_α line for example appears when an L electron falls to fill the vacancy in the K shell while $K_\beta$appears when an electron from the M shell falls into the vacancy of the K shell.

It is noteworthy that the sharp cut off (at the short wavelength limit of the spectrum)corresponds to λ_{min}.It is independent on the nature of the target but it depends on the accelerating voltage of the tube.At this limit, all the energy of acceleration (eV) is supposed to be converted to an x-ray photon.

According to the previous discussion, at λ_{min} it is supposed that $eV= 1/2mv^2 = hc/\lambda_{min}$, where, e is the charge of the electron, V is the applied voltage, m is the mass of the electron, v is the electron velocity, h is the Plank´s constant and c is the speed of light.

Therefore, λ_{min} can be obtained as follows:

$eV = hc/\lambda_{min}$

$\lambda_{min} = hc/eV$

λ_{min} (Å) = 12396/V

Moseley equation

Moseley found that the energy of a given K or L line increases in a regular manner with atomic number, Z: $1/\lambda = a(Z-b)^2$ where a and b are constants, Z is the element atomic number.

It is noteworthy that as the characteristic spectral lines (K_α, K_β, ….etc) are related to the energy levels of the innermost atomic orbitals, they are independent of the physical or chemical combination in which the element is. The following relation is used to calculate the emitted characteristic radiation of elements:

$1/\lambda = R(Z-b)^2 (1/n_1^2 - 1/n_2^2)$

The term $(1/n_1^2 - 1/n_2^2)$ is constant for a specific characteristic x-ray line: For K_α, it = 1- ¼ = 3/4, for K_β=1-1/9 = 8/9

Comparison with the Bohr equation: $1/\lambda = R (1/n_1^2 - 1/n_2^2)$, the term $(Z-b)^2$ accounts for the shielding effect of the electrons on the nuclear charge.

b, in the term (Z-b) is the number of electrons existing between the electron falling to fill the vacancy in the inner shell and the nucleolus.

Examples, for K_α,(b = 1) one electron in the 1s contributes to the shielding effect and for K_β , (b = 9) one electron in the 1s + 8 electrons in the L shell (2s and 2P) contribute to the shielding effect.

Examples

1- Calculate the wave length of K_α of an element (Z = Z) ($R= 1.097\times10^7$)

Answer: $1/\lambda= R(Z-b)^2 (1/n_1^2 – 1/n_2^2)$

$1/\lambda= 1.097\times10^7 (Z-1)^2 (3/4)$ = …….nm

2- Calculate the potential required for the production of K_α ($\lambda = \lambda$ nm)

$eV=hc/\lambda$

$V= hc/e\lambda= 6.63\times10^{-34}$ (J.s) × 3×10^8 (ms^{-1})/1.6×10^{-19} (C) $\times\lambda\times10^{-9}$ (m)= …….. Volts

Instrumentation

In dispersive instruments the sample is used as the target for bombardment with x-rays of suitable energy from the x-ray source like the Coolidge tube. These x-rays excite the sample and as a result x-rays characteristics to the elements of the sample are produced. The produced characteristic lines are diffracted by arotating analyzer which separates them according to the Bragg law.The separated x-rays then are directed separately to the detector (Geiger Muller tube, a scintillation counter or a proportional counter). The intensities of the characteristic

x-ray line of the elements constitutes the sample are plotted against the 2 theta.

In the other approach of electron probe microanalysis, the sample itself is used as the target for the electrons (in the SEM imaging). A solid state detector is used as the detector (it detects all the emitted radiation simultaneously) and a multichannel analyzer produces a mixture of voltage pulses forming the spectrum (the energy dispersive analysis of x-rays (EDAX).

Absorption of x-rays

Absorption of the x-rays is similar to the absorption of the other types of electromagnetic energies however in case of x-rays the energy involved is higher.

The absorption spectrum of an element consists of few broad peaks with sharp discontinuities. These are called absorption edges. Each absorption edge corresponds to the energy required to eject the K or L electron.

Because absorption of radiation strongly depends on the material density, dividing the linear absorption coefficient μ by the material density ρ gives what is called the mass absorption coefficient μ_M. In the spectra, the absorption μ_M is shown vs. energy or wavelength.

For a solid sample, the intensity of radiation after travelling a distance dx in a material will decrease.

The relation used to describe this phenomenon is:

$I=I_o\, e^{(-\mu x)}$ or

(2.303 log (I_o/I)= μx) where I_o is the initial intensity of radiation, I is the intensity of radiation after absorption.

It is important to realize that both linear and mass absorption coefficients decrease exponentially when the wavelength decreases.

It is possible to calculate %absorbed of a characteristic x-ray line when passes through a sheet of an element of known thickness, density and μ_m.

Because the broad absorption bands lead to interferences between neighboring heavy elements, X-ray absorption is limited to samples containing a single heavy element in organic matrix (such as lead in petrol).

Absorption edge analysis

The discontinuity observed in absorption edge provides a selective means of identification of an element. In this case only two measurements are required for the determination (one measurement on either side of the edge). The difference in the absorption coefficient of the sample between the two wavelengths is a measure of the amount of element the sample contains.

Filters

Generally, it is not easy to resolve K_α and K_β because they are so close together. A beta filter is a thin foil of an element with atomic number of one or two less than the target element generating the x-rays. The filter is chosen

that its absorption edge falls between the wavelengths of the characteristic lines K_α and K_β.

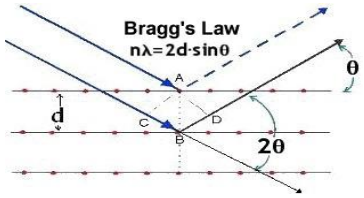
Diffraction of x-rays

An important fact is that the x-ray wavelengths are of the same order as the distance between planes of atoms in crystalline materials and as a result, crystals act as natural diffraction gratings for x-rays.

A portion of a beam of x-rays striking a crystal surface is scattered by the first layer of atoms. Another fraction of is scattered by the second layer and so on. The requirement for constructive interference is given by Bragg's equation ($n\lambda = 2d \sin\theta$).

X-ray diffraction (XRD) is used for the identification **of** crystalline materials and therefore, different phases of crystalline compounds can be identified and also useful information can be obtained from the diffraction pattern (like the crystallite size, d spacing, miller indices, micro strain etc.)

Bragg's equation



$CB+BD = n\lambda$

$CB=DB= d\sin\theta$

$CB+DB=2\ d\sin\theta$

$n\lambda = 2\ d\sin\theta$

The first order interference reflection was formed when an incident beam of x-ray interacted with a crystal at an angel of x. If d spacing in the crystal is y $\times 10^{-10}$ m, calculate the wave length of x-rays.

Answer: $\lambda = 2 \times y \times 10^{-10} \sin x =$ ……Å

X- ray diffraction

It is a rapid analytical technique that is used for phase identification of crystalline materials and it provides information about unit cell dimensions. The materials being analyzed are in the form of homogenous powder.XRD is based on the constructive interference of monochromatic X-rays with crystalline samples.

The filtered X-ray (monochromatic radiation, CuK_α = 1.5418Å) are directed toward the powdered sample. Constructive interference is observed when conditions satisfy Bragg's equation: ($n\lambda = 2d \sin \theta$).

λ is the wavelength of the radiation, θ is the diffraction angle and d isthe lattice spacing in a crystallinesample**.** The diffracted X-rays are then detected and counted.

The random orientation of the crystals of the powdered material allows that scanning the sample through a range of 2θ angles (eg. 10-90°) to attain all possible diffraction directions of the lattice.The XRD pattern (diffractogram) illustrates the relation between 2θ and the intensity (counts per second) of the diffracted beam.The d-spacingcan be determined foreach peak in the pattern.Peak position and

the corresponding d-spacing formsa fingerprint for a substance.It therefore allows identification of the substance because each has a unique d-spacing set.

This process of identification is achieved by comparing the set of d-spacing in the chromatogram with a standard reference pattern (ASTM cards, …….).

X-ray diffractometers

It consists of three basic parts:

An X-ray tube

A sample holder

An X-ray detector

The intensity of the diffracted X-rays is recorded as the sample and detector are rotated. When the position of the incident X-rays satisfies the Bragg equation, constructive interference occursleading to a signal. The detector records this X-ray signal and converts the signal to a count rate which is then recorded.

XRD is widely used for the identification of unknown crystalline materials like inorganic compounds and minerals. For determination of phase composition of samples (ex. TiO_2: rutile, anatase, brokite can be identified beside other properties of the sample)

Advantages:

Rapid technique for identification of an unknown mineral, easy sample preparation, interpretation of data is easy.

Howevera standard reference file of inorganic compounds is required for identification, relatively large amount of a sample is needed and the sample must be in the form of a powder.

The applications of XRD

XRD is used for the identification of phase composition of crystalline compounds where useful information can be obtained like the crystallite size, d spacing and miller indices microstrain etc. from the XRD results.

Example 1

The first order interference reflection was formed when an incident beam of x-ray interacted with a crystal at an angel of x. If d spacing in the crystal is y $\times 10^{-10}$ m, calculate the wave length of x-rays.

Answer

$\lambda = 2 \times y \times 10^{-10} \sin x =$ ……Å

The applications of x- rays

XRF is usually used as a powerful means of elemental analysis: Elements above calcium can easily be detected. The determination of heavy metals (like Pb) in organic samples can easily be performed by absorption edge analysis and XRD is used for the identification of phase composition of many crystalline compounds where useful information can be obtained like the crystallite size, d spacing and miller indices microstrainetc from the XRD

results.Soft x-ray is used in medicine to view images of bones.

Scherrer equation

$d = 0.9\,\lambda/\beta\cos\theta$

d is the size of the crystal, β is the full width at half maximum (FWHM) in rad., λ is the wavelength of x-rays (Cu K_α = 0.154 nm).

Type of crystal lattice

$(d^2_{hkl}) = 1/(h/a)^2 + (k/b)^2 + (l/c)^2$

For the cube system:

$(d^2_{hkl}) = 1/(h/a)^2 + (k/a)^2 + (l/a)^2$

$d_{hkl} = a/(h^2+k^2+l^2)^{1/2}$

$a = d_{hkl}\,(h^2+k^2+l^2)^{1/2}$

Example: The first two reflection lines in the XRD pattern of NaCl (fcc) is at $2\theta = 20^o\ 36'$, $\sin\theta = 0.3518$, d= 3.256 and $2\theta = 23^o\ 58'$, $\sin\theta = 0.4062$, d= 2.820.

Does the first reflection belong to (100), (110) or (111) plane?

$a = d_{hkl}\,(h^2+k^2+l^2)^{1/2}$

For (100) plane:

a= 3.256 (1+0+0) = 3.256

Now we use this value for a for the second reflection

$3.256/2.820 = (h^2+k^2+l^2)^{1/2}$

$1.156= (h^2+k^2+l^2)^{1/2}$

$(h^2+k^2+l^2)= 1.336$

No group of integer numbers for Miller indices can fulfill this requirement and as a result, the assumption that the first reflection line is (100) is not correct.

For the (111) plane:

$a= 3.256 (1+1+1) = 5.64$

When we use this value for the second line

$(h^2+k^2+l^2)^{1/2} = 5.64/2.820 = 2$

(002) , (020) and (200) planes fulfill this requirement

The assumption that the first line is the (111) is correct.

The value of a = 5.64 can be used to determine miller indices for the rest of reflections in the pattern

So, for the face centered (and for the body centered cube) systems not all crystal planes give reflections in their XRD pattern

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