

EMT 303: METHODS IN ENVIRONMENTAL ANALYSIS II

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SYNOPSIS

EMT 303: METHODS IN ENVIRONMENTAL ANALYSIS II (2 UNITS)

Ultraviolet and Visual absorption spectrophotometry: Principles of ultraviolet and visual absorption spectrophotometry. Basic principles of the instrument and techniques. Sample preparation solvents, concentration and dilutions, solid sample, infrared spectrophotometry: Theory, Basic principles of the instrument and techniques sample preparation solutions, liquids and merits, solid and gas qualitative and quantitative application. Photometric titrations: General discussion, Apparatus and techniques used. Flame photometry: principle, instrumentation, advantages of the method, limitations of the method, elimination of interference effects, elements determinable, standards and their preparation, typical determinations. Polarimetry: principle, equipment (a typical automatic recording) polarimeter (should be described), typical determinations, optical rotator dispersion.

LECTURE CONTENT

FLAME METHODS

The use of flame emission spectra or flame photometry for quantitative analysis dates back to about 1930. The first reported application of atomic absorption spectroscopy was due to Kirchoff in 1860, who deduced the presence of various elements in the solar atmosphere. Flame emission and absorption are complementary techniques in that some elements can be detected at lower concentration by emission measurement and some by absorption.

CLASSIFICATION OF FLAME METHODS

1. Flame Emission Spectrophotometry
 - (a) FAES (hot flame) flame atomic emission spectroscopy
 - (b) Flame molecular emission (cool flame)

2. Flame Absorption Spectrophotometry
 - (a) Flame atomic absorption
 - (b) Non-flame atomic absorption

WHAT IS A FLAME

A flame is the product of combustion of fuel often accompanied by emission of light and radiation of heat.

FLAME COMPOSITION

Analytically we are interested in burning of gaseous fuels for production of flame

Flame = fuel + oxidant

Fuels: - hydrocarbon fuels (C_2H_2 , C_3H_8 , C_4H_{10}) hydrogen and air.

Oxidants are oxygen, nitrous oxide

It is possible to dilute the flame i.e. reducing the temperature. Inert diluents are used so that it does not impact any interference to the flame e.g. N_2 , He and Ar.

It means that the flame can at times consist of fuel, inert diluents and oxidant.

Flames are therefore dependant on type of fuels and ratio of mixture

Flame	flame temp $^{\circ}k$	Burning velocity CmS^{-1}
Air propane	2,000	40
Air acetylene	2,600	160
Oxy acetylene	3,080	1130
Air - H_2	1,000	20
CH_4 - H_2	2,670	1,000

FLAME CELL

Gases start to burn in the region of primary reaction. There is incomplete combustion in this zone and as such radicals are formed. Flame colour is blue due to emission of radicals produced in the excited state. This emission is usually due to the C_2 band and CH (flame background)



Depending on the amount of fuel used, the flame can be fuel rich or fuel lean. This flame background is also referred to as the background noise. The radicals move up to the interconal zone, this zone is the most important analytically as a result of the thermodynamic equilibrium set up and also because of the little background emission in the interconal zone. The primary reaction zone has a lower flame temp than the interconal zone.

The secondary combustion or diffusion zone is aided by atmospheric air. The combustion of the radicals is completed in this region. Temp in this region is lower than that of other regions due to dilution from atmospheric air



FLAME EMISSION SPECTROPHOTOMETRY

In flame emission spectrometry a fine aerosol of the sample solution following nebulization is introduced into a flame where it is desolvated, vaporized and atomized. Subsequently, atoms and molecules are raised to an excited electronic state via thermal collisions with the constituents of the partially burned flame glasses. Upon their return to a lower or ground electronic state, the excited atoms and molecules emit radiations that are characteristic for each. The emitted radiation passes through a monochromatic (filter) that isolates the desired feature which is then registered by a photo detector whose output is amplified and read on a meter or recorder.

In summary flame emission spectrometry is the measurement of light emitted by excited ground state atoms. Any emission by ions and molecules are termed as interference.

The purpose of a flame is to (a) produce atoms (b) thermal energy to release atoms from chemical bonds and (c) excitation
Processes occurring when analyte solution is introduced into flame.

It is possible to have association with flame radicals and also to have interference in the form of molecular emission or emission from ionization.

Ionization is prevented by introducing ionization suppressors e.g. when analyzing for Na⁺, K is introduced because K ionizes faster than Na. Using NaCl solution as an analyte introduced into a flame

INSTRUMENTATION

Consists of three main components

- (a) Excitation source
- (b) Spectral wave length selection device
- (c) Detector
- (d) Read out

The excitation source is the flame. The instrumentation is nearly the same as that for flame atomic absorption except for the source

ATOMIZATION, EXCITATION SOURCE

The sample solution is mixed with the oxidant to form an aerosol in which the sample is turned into droplets and the bigger droplets pass out from the drain. When a sample is introduced, emission is expected in all directions. To contain this, a concave mirror is introduced

For a simple flame photometer the instrumentation is nearly the same with FAEC. The difference lies in the oxidant which is propane. The monochromator, a light filter while the detector is a photo cell and the read out, a moving coil galvanometer

TYPES OF BURNERS

Total Consumption Burner

Sample is aspirated directly into the flame and as the name implies the entire sample supposedly is consumed by the burner. However the droplet size varies widely. The mean diameter is $20\mu\text{m}$ and some particles are in excess of $40\mu\text{m}$. The larger droplets pass completely through the flame without even being totally evaporated and as a result, the overall efficiency is poor. The incomplete vaporization of metal from the larger aerosol particles also makes this burner more prone to chemical interference effects than the pre-mix burner.

PREMIX BURNERS

The sample is mixed with the fuel and oxidant in a mixing chamber before being burnt. The larger droplets which would otherwise pass through the flame unexcited are removed and the remaining sample about 10 – 20% enters the burner. The average drop size entering the flame in a premix burner is less than $10\mu\text{m}$. This burner has an increased signal to noise ratio. Usually a long narrow burner which provides a longer path length for absorption is used and this results in it's been quiet in action. The removal of the larger droplets and the laminar flow characteristics of this type of burner make the flame more stable than the turbulent flame of the total consumption burner. A problem with the pre-mix burner is that the flame may burn back into the mixing chamber and cause an explosion. This is prevented by using narrow burner slots.

SPECTRAL SELECTION DEVICE:-

- (i) Use of optical light filters
- (ii) Monochromators – Prisms and Gratings

OPTICAL LIGHT FILTERS

Usually made of colored liquids or coloured glass (thin film of gelatin containing dyes). It absorbs all unwanted wavelength and transmits only desired wavelength. A broad spectrum is usually got because of broadness of glass and it \therefore Allows lot of light (even those not associated with emission from samples)

Prisms:- Separate the wavelength by refraction. Material of prism changes depending on the wave length e.g 400 – 1000nm glass < 400 quartz or fused silica prism

Prisms give a single order spectrum. The prism is rotated until the desired wave length passes through the slit. The incident ray is also reflected and as such the intensity of the refracted light is reduced and as such amplification is required.

Resolving power of a monochromator

$$\text{e.g } \frac{240.0\text{nm}}{244.0\text{nm}} \quad \frac{240 + 244}{2} = 242$$

$$R = \frac{242}{4} = 60.5$$

The higher the resolving power the better the monochromator

Grating:- Dependent upon the differences in path length experienced by a wave front incident at an angle to the individual surfaces of the grating

Path differences from adjacent surfaces or groves = $d \sin i - d \sin r$

i = angle of incident

r = angle of reflection

d = distance between groves

Spectra selection is by diffraction. It consist of several closed lining (consists of ruled lines on a glass or metal.) There can be about 100- 200 lines per nm. Therefore there exist many resolving surfaces for the light.

The greater the no of lines the better the grating.

Because of the path diff, wave front interferes with each other except the path difference is an integral of a wavelength $n\lambda = d (\sin i + \sin r)$ this equation is satisfied by a single wavelength at a time. A grating is more efficient than a prism. Produces second order spectra. Rotation of the grating changes the angle of incidence by bringing a diff wavelength in a position to satisfy the equation.

DETECTORS

Barrier layer Cell

The emission from the sample releases photons.

The intensity of a light is proportional to the number of photons. The energy of the photons releases electrons from the selenium layer, and these are reflected back to the Ag layer since the electrons cannot pass from the Se layer to the Fe layer as the charges are both Negative. The electrons will therefore be repelled from the cathode

surface (Fe). The number of electrons produced will be proportional to the deflection observed on the moving coil galvanometer.

Disadvantages

The detector has a low internal resistance and as such is affected by fatigue effect (sudden exposure to high intensities of incident light.) The current cannot be amplified.

Advantages

It is portable and rugged, it is of low cost, Operates without battery, for less sensitive analysis.

PHOTOCELL

Consist of a cathode which has an inner surface coated with a compound with relatively loosely bound electrons such as alkaline earth oxide (Ce, K_2O , Ag_2O). A central metal anode. A potential difference of approx. 90V is applied across the electrode

When the incident light is incident on the cathode., the photons are absorbed and transfer their energy to the loosely bound electrons of the surface material. The electrons escape from the surface and are collected at the anode (attracted to) causing current to flow in the circuit. If the electron collection is essentially 100% efficient, the phototube current is proportional to the radiant power of the incident light.

Phototube current are quite small ($< 10^{-11}$ ampere) and require amplification in order to operate a readout device.

PHOTOMULTIPLIER TUBE

Operates on a similar principle of the phototube. When an electron is ejected and strikes another electron active surface it may transfer some of its energy, ejecting several more electrons. These electrons are in turn accelerated to another surface and produce even more electrons. This process is repeated as a result of a system of dynodes. Each succeeding electron active plate, or dynode is at higher electrical potential and thus acts as an amplification stage for the original photon. The more the dynodes the more current produced. Photomultiplier tubes are used for low radiant power levels.

INTERFERENCES IN FLAME EMISSION SPECTROMETRY

The interferences in FES can be classified into five (5)

- (a) Spectral
- (b) Physical
- (c) Chemical
- (d) Ionization
- (e) Temperature

SPECTRAL

- (a) If two elements have their resonance lines very close and the monochromator is not good enough to separate them, then interference occurs.

For example Cu 324.754nm E μ 324.755nm

Mg 285.21nm, Na 285.28nm

It is then possible to have spectra overlap of the two elements

This is removed by using a high resolving monochromators.

- (b) Flame radicals emission close to resonance lines of some elements also cause interference. Similarly use of organic solvents also gives rise to interference though formation of radicals like C₂, CH. To eliminate this error, the solvent is aspirated alone before it is used for the sample. A correction can be effected
- (c) Self absorption or self reversal: - This occurs when the emitted light from an atom is absorbed by the unexcited ground state atoms. The distortion leads to reduced sensitivity and more pronounced curvature of the calibration plots. This effect is nullified by using a hotter flame

PHYSICAL INTERFERENCE

Is also referred to as matrix effect. These are factors that influence the amount of sample reaching the flame. These include viscosity, density, surface tension and the volatility of the solvent used to prepare the test solution. To eliminate matrix effect, standard and sample solutions must be of similar composition. Matrix effect is removed by method of standard addition or internal standard.

That an element may serve as a source of interference is eliminated by adding the element to the sample and observing if the emission intensity is affected.

Standard Addition

Take some aliquot of sample into different test tubes. Take the reading for the unknown R₀, Now add about 5ppm, 10ppm, 15ppm into same aliquot and take the reading such that any error in R₀ will also give errors in the tubes.

A plot of the intensity is plotted against conc. and the graph is then extrapolated to get the concentration of sample.

CHEMICAL INTERFERENCE

Occurs as the result of formation in the flame of compounds that are incompletely volatilized or dissociated. Most chemical interference takes place during the formation of solid particles in the flame prior to their evaporation. There are two types

(a) Cation - Anion interference

A good example is the calcium compounds of CaCl_2 , CaSO_4 and $\text{Ca}_3(\text{PO}_4)_2$. CaCl_2 gives the most intense emission because it is more volatile than the others. CaSO_4 is more refractory and as such it reduces the intensity of emission of the pure Ca^{2+} ion. It is also possible to have CaOH^+ and CaH^+ emission as Ca reacts with radicals in the flame. PO_4^{3-} has a greater effect on the Ca^{2+} ions, in that it reduces emission intensity to a greater extent than SO_4^{2-} .

The decrease in emission intensity of Ca^{2+} can be used for quantitative determination of phosphate

As PO_4^{3-} conc. is increasingly added to Ca^{2+} ions there occurs a gradual decrease in the Ca^{2+} emission intensity until at a certain stage when the increase in PO_4^{3-} no longer affect it. Plot of decrease in Ca^{2+} / PO_4^{3-} conc. gives a quantitative consideration. In general 3 methods are applied to remove chemical interference (a) Increase in flame temp (b) Use of Releasing agents (c) Extraction or concentration technique

To remove effect of PO_4^{3-} on Ca^{2+} then a hotter flame should be used. This shows that flame was not hot enough to break the $\text{Ca} - \text{PO}_4^{3-}$ bond. In case of hotter flame an ionization buffer should be added to the sample to prevent the sample from ionizing.

Releasing agent e.g LaCl_3 or $\text{La}(\text{NO}_3)_3$ can also be used. These act as masking agents, La has a greater affinity for PO_4^{3-} and as such when added to CaPO_4^{3-} it displays Ca^{2+} from PO_4^{3-} , $\text{La}(\text{PO}_4)_3$ has a smaller solubility than CaPO_4^{3-} and is also more stable.

Similarly complexing agents like EDTA (ethylene diamine tetra acetic acid) or oxime could be added. These also form a stable complex with Ca^{2+} and are easily broken down in the flame.

The use of solvents to extract the metal ion of interest and as such have the ion in high conc. has also been used. Solvent like MIBK (methyl Iso butyl ketone) and APPC (ammonium pyridine dithiocarbonate). The solvents extract the ions of interest leaving behind the anions that may interfere in the analysis.

(b) Cation- Cation interference

This is not very common.

Al forms a refractive compound with Ca and as such it reduces the emission intensity of Ca

$\text{Ca} + \text{Al} \rightarrow \text{Ca AlO}_2$, the interference is removed by increase in flame temp or use of releasing agents.

IONISATION INTERFERENCE

Observed mostly for alkali metals. It is possible that during atomization, ionization can also take place

To prevent this, an ionization buffer is added e.g. in the determination of Na, K is used as the ionization buffer.

Since K is easily ionized than Na it produces electrons which then forces the back reaction $\text{Na}^+ + e \rightarrow \text{Na}^0$ to take place.

TEMPERATURE INTERFERENCE

Any temp change will affect the E.I because of the change in population of the upper energy state; which simply put means that the hotter the flame, the greater the number of excited atoms. It is necessary to control the temp so as to get the same no of excited atoms for the same measurements.

Effect of temperature is better seen from the differentiation of the equation

Normally the presence of other chemical compounds in the flame affects the emission by changing the flame temperature.

\therefore A 1% change in the number of atoms in the upper state dN^* / N^* is equivalent to a temperature change ΔT given by

$$\begin{aligned} \Delta T &= 0.01 KT^2 / E \\ \Delta T &= 7.0 \times 10^{-10} \lambda m T^2 \end{aligned}$$

QUANTITATIVE ANALYSIS

Sample preparation: - This depends on the element to be determined, the substrate material and method of atomization. Using a graphite furnace, samples do not require any chemical pretreatment as the chemical matrix is removed by aching prior to atomization.

For flame atomization most liquid samples can be sprayed directly into the flame after dilution with a suitable solvent. Solid samples are generally dissolved in acid. A 3:1:1 mixture of Nitric, sulfuric and perchloric acids is used for wet oxidation of organic

matter. Also an organic solvent may be used to selectively extract metals after complexing from an aqueous solution and the solvent can then be aspirated directly into the flame.

Standards: Standards and sample solution should be as similar as possible both in chemical and physical properties

CALIBRATION GRAPH / CURVES

Flame emission is directly proportional to concentration if the conc. range of samples to be analyzed is known then a stock solution of a standard is prepared which can then be diluted to different conc. from which the calibration curve is drawn. Conc. is reported in ppm

For example preparation of 10ppm Ca^{2+} from CaCO_3
10ppm Ca^{2+} contains 25mg CaCO_3 dissolved in 1L of water. Dilutions 1, 2, 4, and 8 ppm can be prepared from the equation $M_1V_1 = M_2V_2$

The solutions are then aspirated into the flame and the intensities measured after the wavelength corresponding to the emission maximum has been picked.

The working curve must be checked from time to time since the slope of the curve may change due to minor fluctuations in the fuel and oxidant pressures or in sample flow rate.

APPLICATIONS

1. Determination of alkali and alkaline earth metals in agricultural and chemical samples (blood samples, body fluids)
2. With hot flames for determination of earth metals in petroleum, agricultural and Geochemical samples.

ATOMIC ABSORPTION SPECTROPHOTOMETRY (AAS)

There are two types

- (a) Flame AAS
- (b) Non flame or flameless AAS

PRINCIPLE

Measurement of electromagnetic radiation or light absorbed by unexcited ground state atoms.

The flame provides the temperature for desolvation, analyte vapour and atomization
 $M-X \rightarrow M^0 + X^0$

Most of the atoms remain in the ground state and very few are excited.

Light source from AAS is direct current and also excited atoms give D.C and as such in the simple direct current AAS one is measuring $I_0 + I_{ex}$. The instrument was latter modified such that light from the source is AC and as such I_{ex} is no longer detected.

SIMPLE SINGLE BEAM AC AAS

Due to the chopper the light becomes AC and also the detector is modulated to respond to only alternating current.

In this instrument spectra interference is not a problem as no light from the flame is seen i.e. no contribution from flame.

LIGHT SOURCE

Usually a hollow cathode lamp (HCL)

Consists of a glass envelope containing an inert gas which can be argon or neon. Contains a hollow cathode and a tungsten anode. The analyte of interest is made the cathode.

When lamp is connected to voltage source inert gases become ionized giving rise to current in the lamp – about 5 – 30mA depending on the pressure of the gas. Negative ions go to the cathode and positive ions to the anode. The collision of the ions with the cathode causes cathodic sputtering formation of atoms of analyte by collision with inert with inert gas ions

SINGLE ELEMENT LAMP

The atoms formed collide with each other and the inert gas ions, this leads to collisional excitation of sputtered atoms. The analyte under test thus absorbs light emitted from the light source produced by a substance made of the same material as the analyte, this eliminates spectra interference.

MULTI-ELEMENT LAMP

Here the cathode is an alloy of 3-4 elements e.g Mg, Zn Cu, Ag – Pb – Fe.

There is preferential sputtering (relative volatilization) There is condensation of the atom cloud of each element on the other, which reduces the emission of the cathode for the analyte under test. Multi element lamps are cheap. In double beam instrument the condensation effect (reduction in emission intensity of cathode) is eliminated. Atomic absorption obeys the beer lamberts law

$$P_{0\lambda} = P_{\lambda} e^{-kc\delta}$$

$P_{0\lambda}$ = incident light energy at wave length λ

P_{λ} = transmitted light energy

δ = optical light path C = conc.

$\text{Log } \frac{P_0}{P} = kcl = Ecl$ (molar absorbance)

$\text{Log } \frac{P_0}{P} = A$ (absorbance)

$A = Ecl$

Absorbance measured is independent of temperature whereas emission is dependent on temperature.

OTHER LIGHT SOURCES

Electrodeless discharge lamps (EDLS)

Introduced because of problems encountered in hollow cathode lamps. E.g some elements do not make suitable hollow cathodes (Se, Sb, Ge.).

A tube is evacuated of air and a volatile metal or metal halide of the substance under test is put into the tube. An inert gas is introduced into the tube and sealed.

A micro wave frequency or Radio frequency is then applied to volatilize the metal / metal halide. The atomization is achieved by the collision of the vapour of the metal with the inert gas. Problem here is that the light must be optimized in terms of pressure in tube and other parameters for each element. There is also the problem of stability over a long period of use. Tube must not be too long or else condensation of the atoms can take place and this leads to a decrease in intensity.

NON FLAME METHODS OF ATOMISATION

The flame is referred to as the atom cell because it breaks down the bond between the metal and the anion to produce atoms. it has the following advantages

- (1) It is relatively easy to obtain precise conditions in the flame (0.1 – 1%)
- (2) Automation of sample injection improves analysis time
- (3) Can be used to determine about 60 elements

Disadvantages

- (1) Because of flame temp which is limited, atomization is difficult for element that from refractive compound e.g W, V.
- (2) Only about 5 – 15% of sample nebulised reaches the flame (0.2ml – 0.6ml of sample / min gets to the flame)
 - (a) Sample loss
 - (b) Sensitivity is limited by dilution effect of the flames gases.
- (3) Non-atomic absorption, a back ground correction usually a deuterium lamp is used
- (4) Sample must be in solution
- (5) Chemical interference

NEED FOR NON-FLAME METHODS

The desire to analyze small samples containing low level low of the component has resulted in the development of a number of flame atomization devices

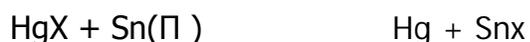
VAPOUR GENERATION TECHNIQUES

Used for volatile elements or elements that form volatile metal halides As, Se, Ge, Te Tellurian Sb, Pb, Bi

Can also be used as a separation method because non volatile elements remain unvaporised.

Hg determination

The sample Containing Mercury is reduced to the metallic Hg with Sn.



Air is pumped through the solution of the metallic mercury to vaporize the Hg. The vapor of the mercury is dried by passing it through a desiccation tube then passed the dried vapour to an Hg absorption cell.

Regent like Zn / HCl, Ti / HCl, sodium borohydride NaBH₂ is commonly used

N₂ or Ar is used as carrier for the hydride vapour from the hydride generating chamber to the flame. (Note atomization in flame, but not vaporization).

ELECTROTHERMAL ATOMIZATION PROCESS

Consists of a hollow graphite cylinder about 50cm in length and 9mm internal diameter and so situated that the radiation beam passes along the axis of the tube. The graphite tube is surrounded by a metal jacket through which water is circulated and which is separated from the graphite tube by a gas space. An inert gas e.g argon is used. The solution to be analyzed (100µl) is introduced by inserting the tip of a micro-pipette through a port in the outer water jacket – and into the gas inlet orifice in the centre of the graphite tube. The graphite cylinder is then heated by the passage of an electric current to a temp high enough to evaporate the solvent. Current is then increased so that the sample is ashed then vapourised so that metal atoms are produced.

Commercial flameless atomizers are based on the mass Mann furnace.

A sample a few µl of a liquid or a few mg of a solid is placed in a graphite tube or cup and is heated electrically. The heating is in 3 stages

1. Low temp to remove solvent
2. A higher temp to ash the sample (i.e. to remove the chemical matrix by volatilization and pyrolysis).
3. Heated to incandescence to atomize the sample. Oxidation of the graphite is prevented in a air of N₂ or Ar.

The Detection limit for Se, Fe, Ge, Sb and As is improved X 1000 by use of non – flame atomization instead of the normal flame method.

PRACTICAL AAS

Plot a calibration curve and from this read up the conc. of your sample.

Use flameless AAS for trace metals in water or Hg in human air (AAS is no longer use full) Methods that can be used to improve FAAS

1. Preconcentration technique
2. Solvent extraction

Most metals of interest may be extracted by 1-2% APAC at pH 2-3 into an organic solvent, Extract the element into methyl isobutyl ketone (MIBK) then aspirate directly into flame

Comparison of performance of flame and Hydrogen generation technique

	Flame AAS	Hydride generation
Sb	0.05	0.0005
As	0.5	0.008
Bi	0.1	0.0002
Pb	0.2	0.1

	Flame AAS	Electrothermal Atomizer
Al	0.09	0.002
Ba	0.05	0.0045
Cd	0.03	0.0002
Pb	0.02	0.001

DOUBLE BEAM INSTRUMENT

In a double beam instrument, the instrument electronic noise is cancelled out. The loss of intensity does not constitute a problem because the incident and emergent ray is received by the monochromatic detector directly.

INTERFERENCE IN AAS

Temp (none)

Spectral: Does not occur in theory, however practical details show non-atomic absorption interference due to molecular absorption which is greater in the UV region. Because of this a back ground corrector device is introduced

HCL measures atomic + molecular absorption. To correct aspirate the sample and put on the deuterium lamp. Any absorption observed will be due to molecular absorption.

In general FES is better for elements with wave lengths over 350.nm. White FAAS is better for element with wavelength less than 350mm

Response (Detection Limit)				
e.g	Element	λ nm	FAAS	FES
	Zn	213.9	0.009	80
	Mg	285.2	0.003	1
	Na	589.0	0.003	0.001
	Li	670.8	0.02	0.001
	Ca	422.7	0.02	0.01

Atomic absorption spectroscopy has been used for the determination of approximately 70 elements. Applications include clinical and biological samples, forensic materials,

food & beverages, water and effluent soils, plants and fertilizers, iron, steel, various other alloys, minerals, petroleum products pharmaceuticals and cosmetics.

POLARIMETRY

Is the measurement of the change of the direction of vibration of polarized light after its interaction with optically active materials.

Natural light (white) consists of electromagnetic waves vibrating in all possible orientations around the direction of propagation

If the light can be sorted out, such that we have the rays vibrating in a particular plane then we have – plane polarized light. (Note light wave consists of an electric and a magnetic component vibrating at right angles to each other.). Circularly polarized light represents a wave in which the electrical component & magnetic component spirals around the direction of propagation of the ray, either clock wise (right handed or dextrorotatory) or counter clock wise (left handed or laevorotatory.)

A plane polarized ray can be represented as the vector sum of two circularly polarized rays, one moving clock wise and one counter clock wise and with the same magnitude of vibration.

At zero time, sum of C_{lo} and C_{do} (right and left circularly polarized rays) equals P_o (plane – polarized ray). At the time when C_{lo} becomes C_{l_1} , and for C_{d_1} , etc. the vector sum is P_1 etc. However when the plane polarized ray passes through some material and one of the circularly polarized component e.g the laevorotatory is slowed down then the resultant would be a plane polarized ray rotated relatively to the right from its original position. E.g if the right handed ray is 90° ahead of the left handed ray. The diagram below results in which the plane polarized resultant ray is rotated 45°

The rotation α is one-half of the phase difference of the two circular components.

The index of refraction η is the ratio of the velocity of a ray of light in a vacuum C , to its velocity in a medium V

$$\eta = C/v.$$

\therefore If a substance showed different indices of refraction for the l and d component of a plane polarized ray, then one beam would be slowed down on passage through the medium and the plane of polarization of the ray would be rotated.

$$\text{Then } \eta_l = \frac{C}{v_l} \quad \alpha \quad \eta_d = \frac{C}{v_d}$$

$$u_l \quad u_d$$

$$\therefore \eta_l u_l = \eta_d u_d \text{ or } u_l/u_d = \eta_d/\eta_l$$

If b represent the length of the column of material traversed by the ray, λ_0 the wavelength of the light, γ the frequency of rotation (or vibration) of the light and C the velocity of light in a vacuum, then the difference in degrees between the two rays is given by

$$\Psi = 2\pi b/\lambda_0 (\eta_d - \eta) \quad \text{Since } \Psi/2 = \alpha$$

$$\alpha = \pi b/\lambda_0 (\eta_d - \eta)$$

$$\text{Or } \eta_d - \eta = \alpha\lambda_0/\pi b$$

OPTICAL ROTATORY DISPERSION AND CIRCULAR DICHROISM

Circular dichroism is the relationship between rotatory power and light absorption in optically active compound. A compound is optically active in solution if its structure cannot be brought to coincide with that of its mirror image that is the compound does not possess a plane or a center of symmetry. A polarimeter combined with a monochromator such that measurement of optical rotation at various wavelengths gives the optical rotatory dispersion (ORD) while if d and 1 circularly polarized light can be produced and a spectrophotometer used to measure the differing absorption by compounds at certain wavelengths then the circular dichroism (CD) can be measured. Both ORD and CD are useful in structural determination of optically active compounds

It was observed that for certain optically active absorption bands in a compound, the rotatory power first increases strongly then falls off and changes sign. This effect, is known as cotton effect, within the absorption band the molar absorptivity for R and L hand circularly polarized light is different i.e. $(E_d - E_l) \neq 0$. This effect changes linearly polarized light into elliptical polarized light known as circular dichroism.

MEASUREMENT OF OPTICAL ROTATION

Rotation is dependent on thickness of the layer traversed by the light, wavelength of the light and temperature (also dependent on Conc. if substance measured is a solution.) Some substances change their rotation with time e.g some change from one structure to another with a different rotatory power – mutarotation. Common among sugars. Some substances owing to enolization within the molecules may rotate so as to become symmetrical and thus lose their rotatory power – racemization.

Mutarotation and racemization are affected not only by time but by pH, temp, and other factors, Therefore in a polarimetric measurement all the experimental conditions must be known

- length for liquids 10cm, solids 1mm wavelength, (546. 1mm) – green mercury line or sodium doublet (589.0 / 589.6nm), Temp 20°C.

∴ If b is the thickness in decimeters, C is the conc. of solute in gm / 100ml of solution, α is the observed rotation in degrees and [α] is the specific rotation or $[\alpha] = 100a / bC$

Temp of the measurement is indicated by a superscript and the wavelength by a subscript

For pure liquids, unit density is assumed as standard

∴ $[\alpha] = a/b\rho$ where ρ is density.

Temp changes have several effects upon the rotation of a solution or liquid. An increase in temp increases the length of the tube, decrease the density ∴ Reducing the no of molecules involved. It causes changes in the rotatory power of the molecules themselves due to association or dissociation, increased mobility of the atoms.

Temp effect can be equated thus

Where z is the temp coefficient of rotation.

Interest in polarimetry is to determine the conc. of substance although there is correlation between rotation and chemical structure. Relationship between rotation and conc. is strictly not linear and as such [α] of a solution is not constant.

Relationship between [α] and conc. is given by

$$[\alpha] = A + Bq \dots \dots \dots (1)$$

$$[\alpha] = A + Bq + Cq^2 \dots \dots \dots (2)$$

$$[\alpha] = A + Bq/C + q \dots \dots \dots (3)$$

Equation 1 gives straight line, (2) a parabola and (3) a hyperbola. The const. A, B, C are determined from several measurement at diff. Conc. The values of [α] extrapolated to infinite dilution may be used

Molecular rotation $[\Phi] = [\alpha] \times \text{mol wt} / 100$

SACCHARIMETRY

Polarimetry has been used in the analysis of sugar based on the fact that upon hydrolysis of sucrose when heated with acid or enzyme invertase sucrose is inverted to form one molecule of fructose and one of glucose all having different specific rotation, sucrose 66.5, fructose – 93, glucose 52.5 thus the specific rotation changes from +66.5 to $(-93+52.5) / 2 = -20.25^\circ$ ∴ By measuring the changed rotation upon inversion sucrose can be determined even in the presence of other optically active substances.

The Clerget formula is used for determination of sucrose

$$\% \text{ sucrose} = 100 (a - h) \times W / 144 - t/2 w$$

Where a = rotation of sucrose solution before inversion, h = rotation after hydrolysis.
 T = temp, W weight for saccharimeter used, w = wt of sample taken per 100ml of solution.

POLARIMETER.

Consists of (i) light source (ii) polarizer (iii) analyzer (iv) A graduated circle to measure the amount of rotation (v) sample tubes.

Most polarimeters are designed for visual observation though it is possible to be equipped with photocells or other devices for measuring the intensity of light emerging from the instrument.

LIGHT SOURCE

Sodium vapour lamps and mercury vapour lamps. The Na lamp emit light of λ 589 and 589.6 and a continuous back ground eliminated with a filter of 7% $K_2Cr_2O_7$. Hg lamp has several wavelengths prominent are 435.8, 491.6, 546.1, 577.0 and 579.1nm. Proper choice of filters permits isolation of each line.

Polarizer analyzer consists of several different types. One type consists of a crystal usually calcite or quartz, cut diagonally at such an angle that one component of the light is totally reflected. The second component passes through the second half of the crystal and thus emerges in the same direction as the original beam.

Another type of polarimeter depends on the differences in the prisms in terms of the angles of the prism and of the cut diagonally through the prism. The glan Thompson and the Nicol prism are the most common.

The nicol prism requires smaller pieces of calcite and is cheaper, but is not as good as the glan Thompson prism.

Light can also be polarized by reflection from a mirror at the proper angle – Brewsters angle. Such that if light strikes a mirror at an angle i when $\tan i = \eta$ (refractive index of mirror material)., then only the component vibrating perpendicular to the plane of incidence (parallel to the mirror surface) will be reflected. A third method is using Polaroid filters. These are made of strongly dichroitic crystals oriented in a plastic material. The crystals strongly absorb light, vibrating in one direction and only weakly absorb light, vibrating in the perpendicular direction, Polaroid's never give 100% polarization and also the light must be in the region from about 500- 680nm \therefore Polaroid are used on less expensive instrument

The graduated circle is fitted with a veirnier for more precise measurement of the angle through which the analyzing prism has been rotated. Special reading devices employing a pair of parallel index lines are used on the most precise instruments in

which a tangent screw with graduated drum allows the borders of an etched line on the main scale to be made to coincide with the two hair lines. (reading are made 0.002°).

The polarimeter tubes must have plane and parallel glass disks at the ends. The glass must be free from stain, otherwise the disks will produce a partial circular polarization of the light and complete extinction of light will not be possible. Length of polarimeter tubes is determined by measuring the rotation of a known strongly rotating solution at a definite temp (e.g nicotine in ethyl alcohol).

A: Collimating lens. B:- Lippich half shade prism

C:- Polarizing prism.

D:- Tube E:- Analyzing prism. F: Eye piece G:- Scale

H:- Level to adjust half shade angle

In cheaper instruments one measures the position of the analyzer required to give minimum intensity without the sample in the tubes, followed by with samples. The difference in the two readings is the rotation caused by the introduction of the sample. However more precise polarimeters make use of half-shade devices which results in matching two half-fields for a balance point.

The common ones are the Jellet-Cornu prism and the Lippich prism.