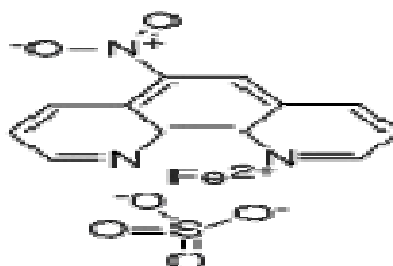**Introduction:**

The accurate determination of metal ion at trace and ultra trace levels is very important in analytical chemistry. Spectrophotometric method is essentially trace analysis technique and is one of the most powerful tools in chemical analysis. In this study use in very sensitive, highly selective spectrophotometric method for determination of trace iron. By using a derivative of 1,10- phenanthrolin reagent .The advantage of this method over existing methods with respect to sensitivity, selectivity, rang of determination, simplicity, speed, PH/acidity range, accuracy, precision, and ease of operation was studied.

1, 10-phenanthroline is a tricyclic nitrogen hetrocyclic compound that reacts with metals such as iron, nickel, ruthenium and silver to form strongly colored complexes, this property provides an excellent a sensitive method for determining this metal ion in aqueous solution.

5-nitro1, 10-phenanthroline forms an intensely red complex with iron (II) that may be exploited to determine iron concentration in the rang of part per million.

The complex formula is:

2.1 INTRODUCTION:-

Iron is a chemical element with the symbol Fe (from Latin: *ferrum*) and atomic number 26. It is a metal in the first transition series. It by mass is the most common element on Earth, forming much of Earth's outer and inner core. It is the fourth most common element in the Earth's crust. Iron's very common presence in rocky planets like Earth is due to its abundant production as a result of fusion in high-mass stars, wherein the production of nickel-56 (which decays to the most common isotope of iron) is the last nuclear fusion reaction that is exothermic. Therefore, radioactive nickel is the last element to be produced, before collapse of a supernova causes the explosion that abundantly scatters this precursor radionuclide into space.

Like other group 8 elements, iron exists in a wide range of oxidation states, −2 to +6, although +2 and +3 are the most common. Elemental iron occurs in meteoroids and other low oxygen environments, but is reactive to oxygen and water. Fresh iron surfaces appear lustrous silvery-gray, but oxidize in normal air to give hydrated iron oxides, commonly known as rust. Unlike many other metals which form passivating oxide layers, iron oxides occupy more volume than iron metal, and thus iron oxides flake off and expose fresh surfaces for corrosion.

Iron metal has been used since ancient times, though copper alloys, which have lower melting temperatures, were used first in history. Pure iron is soft (softer than aluminium), but is unobtainable by smelting. The material is significantly hardened and strengthened by impurities, such as carbon, from the smelting process. A certain proportion of carbon (between 0.002% and 2.1%) produces steel, which may be up to 1000 times harder than pure iron. Crude iron metal is produced in blast furnaces, where ore is reduced by coke to pig iron, which has a high carbon content. Further refinement with oxygen reduces the carbon content to the correct proportion to make steel. Steels and low carbon iron alloys along with other metals (alloy steels) are by far the most common metals in industrial use, due to their great range of desirable properties and the abundance of iron.

Iron chemical compounds, which include ferrous and ferric compounds, have many uses. Iron oxide mixed with aluminium powder can be ignited to create a thermite reaction, used in welding

and purifying ores. It forms binary compounds with the halogens and the chalcogens. Among its organometallic compounds is ferrocene,

Iron plays an important role in biology, forming complexes with molecular oxygen in hemoglobin and myoglobin; these two compounds are common oxygen transport proteins in vertebrates. Iron is also the metal used at the active site of many important redox enzymes dealing with cellular respiration and oxidation and reduction in plants and animals.

2.2 PHYSICAL PROPERTIES:

Atomic Number: 26

Mass Number: 55.846

Electron Configuration: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$

Crystal Structure: Body-Centered Cubic

Atomic Radius: 117 pm

Ionic Radius: 76 pm (Fe^{2+}), 64 pm (Fe^{3+})

Density: 7.87 g/cm^3

Melting Point: 1535°C

Important Oxidation States: +2 (ferrous), +3 (ferric)

2.3 OCCURRENCE :

Iron is one of the most widely used metals. It is the fourth most abundant element in the Earth's crust and appears as several different minearals. These include hematite (Fe_2O_3), magnetite (Fe_3O_4), siderite ($FeCO_3$), and iron pyrite (FeS_2). Note that hematite is a compound of Fe(III) whereas magnetite contains both Fe(III) and Fe(II) and may better be formulated as [Fe(II)(Fe(III)$_2$)]O_3. Iron pyrite is gold in color and has a distinctive lustor. For this reason it is often referred to as fool's gold. Since sulfur is in the same group as oxygen it is tempting to think of this compound as containing Fe(IV). However, this is not a stable oxidation state for iron. In pyrite, the sulfur is present as the disulfide ion (S_2^{2-}); therefore the iron is present as Fe(II). While an abundant mineral, pyrite is not used as   source of iron as the sulfur is not easily removed.

2.4 PROPERTIES AND REACTIONS :

Iron is fairly reactive and will react with acids. An exposed iron surface quickly develops a coating of rust, which is a hydrated form of iron(III) oxide. This process is acceleretd in a most environment. Finely divided iron will burst into flame when heated in an atmosphere of pure oxygen.

Iron is a ferromagnetic material. In a ferromagnetic substance, the magnetic fields of individual atoms are aligned and reinforce each other to produce a large magnetic field. The phenomenon is most pronounced for iron but also occurs in cobalt and nickel to a lesser extent. Iron and alloys of iron are used to make such things as magnets and transfomer cores.

Steel is an important alloy of iron. All steel contains 0.50 - 1.50 percent carbon. Generally, the the higher the carbon content, the harder and more brittle the steel. Other metals are sometimes added depending upon the desired properties. For example, magnets are often made of steel containing nickel and cobalt. Stainless steel contains chromium and nickel and is resistant to corrosion. The addition of manganese produces a steel which is very hard and durable.

2.5 THE +2 OXIDATION STATE :

Iron in the +2 oxidation state is known as the *ferrous* ion. This ion is pale green in color and is very easily oxidized to the ferric ion; even traces of dissolved oxygen in solution will accomplish this oxidation. For this reason, solutions of the ferrous ion are sometimes used as reducing agents.

Complexes of the ferrous ion usually have octahedral geometry; examples include $[Fe(H_2O)_6]^{2+}$ and $[Fe(CN)_6]^{4-}$. The latter is a pale yellow solid commonlu known as the *ferrocyanide* ion. Despite the toxicity of cyanide, the ferrocyanide ion is stable because the cyanide molecules are tightly bound. When added to a solution contianing the ferric ion, a precipitate known as prussian blue is formed . This compound is used in making blueprints and as a bluing agent in certain lundry detergents.

The ferrous ion has a particular affinity of amine ligands, and forms a characteristic red-orange complex ion $\{Fe(phen)_3\}^{2+}$ is formed when 1,10-phenanthroline is added . This serves as the basis of a chemical test for the ferrous ion.

2.6 THE +3 OXIDATION STATE:

Iron in the +3 oxidation state is known as the *ferric* ion. The color of the hydrated ferrous ion $[Fe(H_2O)_6]^{2+}$ is actually violet. However, most solutions contining the ferric ion are usually yellow or yellow-brown due to the formtion of $[Fe(H_2O)_5(OH)]^{2+}$. This ion is formed due to the high charge density of Fe^{3+} ion. Water molecules are coordinated so strongly that one of the O-H bonds weakens, resulting in the formation of H_3O^+. As a result solutions of ferric ion are often acidic.

$$[Fe(H_2O)_6]^{3+} + H_2O = [Fe(H_2O)_5(OH)]^{2+} + H_3O^+$$

The ferric ion forms an ion analgous to the ferrocyanide ion, known as the *ferricyanide* ion, $[Fe(CN)_6]^{3-}$. This is a red-orange solid that is considerably more toxic than the ferrocyanide ion, as the cyanide ions are not as tightly bound. Therefore, care should be taken not to confuse these two ions.

The ferric ion forms a characteristic blood-red complex ion with the thiocyanate (SCN^-) ion; this serves as the basis for a chemical test for the ferric ion.

2.7 ISOTOPES:

Naturally occurring iron consists of four stable isotopes: 5.845% of ^{54}Fe, 91.754% of ^{56}Fe, 2.119% of ^{57}Fe and 0.282% of ^{58}Fe. Of these stable isotopes, only ^{57}Fe has a nuclear spin ($-1/2$). The nuclide ^{54}Fe is predicted to undergo double beta decay, but this process had never been observed experimentally for these nuclei, and only the lower limit on the half-life was established: $t_{1/2} > 3.1 \times 10^{22}$ years.

^{60}Fe is an extinct radionuclide of long half-life (2.6 million years).[12] It is not found on Earth, but its ultimate decay product is the stable nuclide nickel-60.

Much of the past work on measuring the isotopic composition of Fe has focused on determining [60]Fe variations due to processes accompanying nucleosynthesis (i.e., meteorite studies) and ore formation. In the last decade however, advances in mass spectrometry technology have allowed the detection and quantification of minute, naturally occurring variations in the ratios of the stable isotopes of iron. Much of this work has been driven by the Earth and planetary science communities, although applications to biological and industrial systems are beginning to emerge.

2.8 NUCLEOSYNTHESIS:

Iron is created by extremely large, extremely hot (over 2.5 billion kelvin) stars through the silicon burning process. It is the heaviest stable element to be produced in this manner. The process starts with the second largest stable nucleus created by silicon burning, which is calcium. One stable nucleus of calcium fuses with one helium nucleus, creating unstable titanium. Before the titanium decays, it can fuse with another helium nucleus, creating unstable chromium. Before the chromium decays, it can fuse with another helium nucleus, creating unstable iron. Before the iron decays, it can fuse with another helium nucleus, creating unstable nickel-56. Any further fusion of nickel-56 consumes energy instead of producing energy, so after the production of nickel-56, the star does not produce the energy necessary to keep the core from collapsing. Eventually, the nickel-56 decays to unstable cobalt-56, which in turn decays to stable iron-56. When the core of the star collapses, it creates a supernova. Supernovas also create additional forms of stable iron via the r-process.

2.9 CHEMISTRY AND COMPOUNDS:

Iron forms compounds mainly in the +2 and +3 oxidation states. Traditionally, iron(II) compounds are called ferrous, and iron(III) compounds ferric. Iron also occurs in higher oxidation states, an example being the purple potassium ferrate (K_2FeO_4) which contains iron in its +6 oxidation state. Iron(IV) is a common intermediate in many biochemical oxidation reactions. Numerous organometallic compounds contain formal oxidation states of +1, 0, −1, or even −2. The oxidation states and other bonding properties are often assessed using the technique of Mössbauer spectroscopy. There are also many mixed valence compounds that contain both iron(II) and iron(III) centers, such as magnetite and Prussian blue ($Fe_4(Fe[CN]_6)_3$). The latter is used as the traditional "blue" in blueprints.

The iron compounds produced on the largest scale in industry are iron(II) sulfate ($FeSO_4 \cdot 7H_2O$) and iron(III) chloride ($FeCl_3$). The former is one of the most readily available sources of iron(II), but is less stable to aerial oxidation than Mohr's salt (($NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$). Iron(II) compounds tend to be oxidized to iron(III) compounds in the air.

Unlike many other metals, iron does not form amalgams with mercury. As a result, mercury is traded in standardized 76 pound flasks (34 kg) made of iron

2.9.1 BINARY COMPOUNDS:

Iron reacts with oxygen in the air to form various oxide and hydroxide compounds; the most common are iron(II,III) oxide (Fe_3O_4), and iron(III) oxide (Fe_2O_3). Iron(II) oxide also exists, though it is unstable at room temperature. These oxides are the principal ores for the production of iron (see bloomery and blast furnace). They are also used in the production of ferrites, useful magnetic storage media in computers, and pigments. The best known sulfide is iron pyrite (FeS_2), also known as fool's gold owing to its golden luster.

The binary ferrous and ferric halides are well known, with the exception of ferric iodide. The ferrous halides typically arise from treating iron metal with the corresponding binary halogen acid to give the corresponding hydrated salts.

$$Fe + 2\,HX \rightarrow FeX_2 + H_2$$
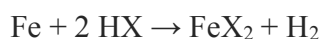
Iron reacts with fluorine, chlorine, and bromine to give the corresponding ferric halides, ferric chloride being the most common:

$$2\,Fe + 3\,X_2 \rightarrow 2\,FeX_3\ (X = F, Cl, Br)$$

2.9.2 METAL COMPLEXES:

Metal complexes, also known as coordination compounds, include all metal compounds, aside from metal vapors, plasmas, and alloys. The study of "coordination chemistry" is the study of "inorganic chemistry" of all alkali and alkaline earth metals, transition metals, lanthanides, actinides, and metalloids. Thus, coordination chemistry is the chemistry of the majority of the

periodic table. Metals and metal ions only exist, in the condensed phases at least, surrounded by ligands.

The ions or molecules surrounding the metal are called ligands. Ligands are generally bound to a metal ion by a coordinate covalent bond (donating electrons from a lone electron pair into an empty metal orbital), and are thus said to be coordinated to the ion. The areas of coordination chemistry can be classified according to the nature of the ligands, broadly speaking:

- Classical (or "Werner Complexes"): Ligands in classical coordination chemistry bind to metals, almost exclusively, via their "lone pairs" of electrons residing on the main group atoms of the ligand. Typical ligands are H_2O, NH_3, Cl^-, CN^-, en^-

Examples: $[Co(EDTA)]^-$, $[Co(NH_3)_6]Cl_3$, $[Fe(C_2O_4)_3]K_3$

- Organometallic Chemistry: Ligands are organic (alkenes, alkynes, alkyls) as well as "organic-like" ligands such as phosphines, hydride, and CO.

Example: $(C_5H_5)Fe(CO)_2CH_3$

- Bioinorganic Chemistry: Ligands are those provided by nature, especially including the side chains of amino acids, and many cofactors such as porphyrins.

Example: hemoglobin

Many natural ligands are "classical" especially including water.

- Cluster Chemistry: Ligands are all of the above but also include other metals as ligands.

Example $Ru_3(CO)_{12}$

- In some cases there are combinations of different fields:

Example: $[Fe_4S_4(Scysteinyl)_4]^{2-}$, in which a cluster is embedded in a biologically active species.

Mineralogy, materials science, and solid state chemistry as they apply to metal ions are subsets of coordination chemistry in the sense that the metals are surrounded by ligands. In many cases these ligands are oxides or sulfides, but the metals are coordinated nonetheless, and the principles and guidelines discussed below apply. It is true that the focus of mineralogy, materials

science, and solid state chemistry differs from the usual focus of coordination or inorganic chemistry. The former are primarily concerned with polymeric structures, properties arising from a collective effects of many highly interconnected metals. In contrast, coordination chemistry focuses on reactivity and properties complexes containing individual metal atoms or small ensembles of metal atoms.

2.9.3 STRUCTURE OF COORDINATION COMPOUNDS:

2.9.3.1 GEOMETRY:

Structure in complex chemistry begins with a focus on "coordination number," the number of ligands attached to the metal (more specifically, the number of σ-type bonds between ligand(s) and the central atom). Usually one can count the ligands attached but sometimes even the counting can become ambiguous. Coordination numbers are normally between two and nine, but large numbers of ligands are not uncommon. The number of bonds depends on the size, charge, and electron configuration of the metal ion. Most metal ions may have more than one coordination number.

Typically the chemistry of complexes is dominated by interactions between s and p molecular orbitals of the ligands and the d (or f) orbitals of the metal ions. The s, p, and d orbitals of the metal give the possibility to allocate 18 electrons (see 18-Electron rule; for f-block elements this extends to 32 electrons). The maximum coordination number for a certain metal is thus related to the electronic configuration of the metal ion (more specifically, the number of empty orbitals) and to the ratio of the size of the ligands and the metal ion. Large metals and small ligands lead to high coordination numbers, e.g. $[Mo(CN)_8]^{4-}$. Small metals with large ligands lead to low coordination numbers, e.g. $Pt[P(CMe_3]_2$. Due to their large size, lanthanides, actinides, and early transition metals tend to have high coordination numbers.

Different ligand structural arrangements result from the coordination number. Most structures follow the points-on-a-sphere pattern (or, as if the central atom were in the middle of a polyhedron where the corners of that shape are the locations of the ligands), where orbital overlap (between ligand and metal orbitals) and ligand-ligand repulsions tend to lead to certain regular geometries. The most observed geometries are listed below, but there are many cases which deviate from a regular geometry, e.g. due to the use of ligands of different types (which

results in irregular bond lengths; the coordination atoms do not follow a points-on-a-sphere pattern), due to the size of ligands, or due to electronic effects (see e.g. Jahn-Teller distortion):

- Linear for two-coordination,

- Trigonal planar for three-coordination,

- Tetrahedral or square planar for four-coordination

- Trigonal bipyramidal or square pyramidal for five-coordination,

- Octahedral (orthogonal) or trigonal prismatic for six-coordination,

- Pentagonal bipyramidal for seven-coordination,

- Square antiprismatic for eight-coordination, and

- Tri-capped trigonal prismatic (Triaugmented triangular prism) for nine coordination.

Some exceptions and provisions should be noted:

- The idealized descriptions of 5-, 7-, 8-, and 9- coordination are often indistinct geometrically from alternative structures with slightly different L-M-L (ligand-metal-ligand) angles. The classic example of this is the difference between square pyramidal and trigonal bipyramidal structures.

- Due to special electronic effects such as (second-order) Jahn-Teller stabilization, certain geometries are stabilized relative to the other possibilities, e.g. for some compounds the trigonal prismatic geometry is stabilized relative to octahedral structures for six-coordination.

2.9.3.2 ISOMERISM:

The arrangement of the ligands is fixed for a given complex, but in some cases it is mutable by a reaction that forms another stable isomer.

There exists many kinds types of isomerism in coordination complexes, just as in many other compounds.

2.9.3.2.1 STEREOISOMERISM:

Stereoisomerism occurs with the same bonds in different orientations relative to one another.

2.9.3.2.2 GEOMETRIC ISOMERISM:

Geometric isomerism occurs in octahedral and square planar complexes (but not tetrahedral). When two ligands are opposite each other they are said to be *trans*, when mutually adjacent, *cis*. When three identical ligands occupy one face of an octahedron, the isomer is said to be facial, or *fac*. If these three ligands are coplanar, the isomer is said to be meridional, or *mer*. For example, in an octahedral compound with three of one ligand and three of another, there are two geometric isomers: the *mer* in which each set of three same ligands is in a meridian and the *fac* in which each set of three is on a face of the octahedron.
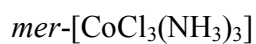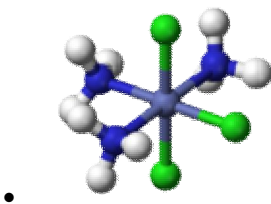
-
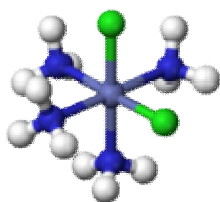
cis-[CoCl$_2$(NH$_3$)$_4$]$^+$

-
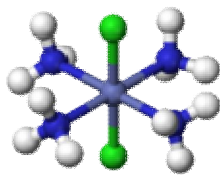
trans-[CoCl$_2$(NH$_3$)$_4$]$^+$

-
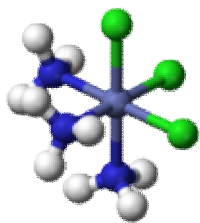
fac-[CoCl$_3$(NH$_3$)$_3$]

mer-[CoCl$_3$(NH$_3$)$_3$]

2.9.3.2.3 OPTICAL ISOMERISM:

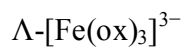Optical isomerism occurs when the mirror image of a compound is not superimposable with the original compound. It is so called because such isomers are optically active, that is, they rotate the plane of polarized light. The symbol Λ *(delta)* is used as a prefix to describe the left-handed propeller twist formed by three bidentate ligands, as shown. Similarly, the symbol Δ *(lambda)* is used as a prefix for the right-handed propeller twist.

Λ-[Fe(ox)$_3$]$^{3-}$

Δ-[Fe(ox)$_3$]$^{3-}$

Λ-*cis*-[CoCl$_2$(en)$_2$]$^+$

-

Δ-*cis*-[CoCl$_2$(en)$_2$]$^+$
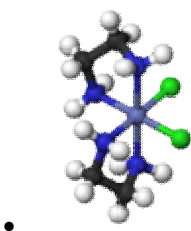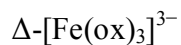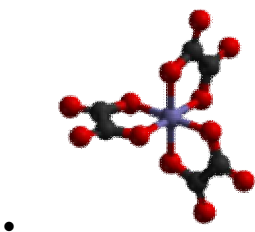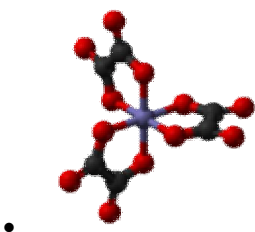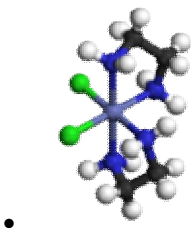
2.9.3.2.4 STRUCTURAL ISOMERISM:

Structural isomerism occurs when the bonds are themselves different. Linkage isomerism is only one of several types of structural isomerism in coordination complexes (as well as other classes of chemical compounds). Linkage isomerism occurs with ambidentate ligands which can bind in more than one place. For example, NO$_2$ is an ambidentate ligand: it can bind to a metal at either the N atom or at an O atom.

2.9.3.3 OLDER CLASSIFICATIONS OF ISOMERISM:

Traditional classifications of the kinds of isomer have become archaic with the advent of modern structural chemistry. In the older literature, one encounters:

- Ionisation isomerism describes the possible isomers arising from the exchange between the outer sphere and inner sphere. This classification relies on an archaic classification of the inner and outer sphere. In this classification, the "outer sphere ligands," when ions in solution, may be switched with "inner sphere ligands" to produce an isomer.

- Solvate isomerism occurs when an inner sphere ligand is replaced by a solvent molecule. This classification is obsolete because it considers solvents as being distinct from other ligands. Some of the problems are discussed under water of crystallization.

2.10 ELECTRONIC STRUCTURE OF COORDINATION COMPOUNDS:

Many of the properties of metal complexes are dictated by their electronic structures. The electronic structure can be described by a relatively ionic model that ascribes formal charges to the metals and ligands and does not focus on covalency. This approach is the essence of Crystal field theory (CFT). Crystal field theory, introduced by Hans Bethe in 1929, gives a quantum mechanically based attempt at understanding complexes. But crystal field theory treats all interactions in a complex as ionic and assumes that the ligands can be approximated by negative point charges.

More sophisticated models embrace covalency, and this approach is described by Ligand field theory (LFT) and Molecular orbital theory (MO). Ligand field theory, introduced in 1935 and built from molecular orbital theory, can handle a broader range of complexes and can explain complexes in which the interactions are covalent. The chemical applications of group theory can aid in the understanding of crystal or ligand field theory, by allowing simple, symmetry based solutions to the formal equations.

Chemists tend to employ the simplest model required to predict the properties of interest; for this reason, CFT has been a favorite for the discussions when possible. MO and LF theories are more complicated, but provide a more realistic perspective.

The electronic configuration of the complexes gives them some important properties:

2.10.1 COLOR:

Metal complexes often have spectacular colors. These colors arise from the absorption of light which excites electrons within the metal's orbitals or, in the case of charge-transfer, excites electrons from metal-based orbitals to ligand-based orbitals (or the reverse). An aid to explain and interpret electronic excitations within the collection of metal-based orbitals are the Tanabe-Sugano diagrams (for simple compounds with a good defined geometry) or the use of computational chemistry.

2.10.2 MAGNETISM:

Metal complexes that have unpaired electrons are magnetic. Considering only monometallic complexes, unpaired electrons arise because the complex has an odd number of electrons or because electron pairing is destabilized. Thus, monomeric Ti(III) species have one "d-electron" and must be (para)magnetic, regardless of the geometry or the nature of the ligands. Ti(II), with two d-electrons, forms some complexes that have two unpaired electrons and others with none. This effect is illustrated by the compounds $TiX_2[(CH_3)_2PCH_2CH_2P(CH_3)_2]_2$: when X = Cl, the complex is paramagnetic (high spin configuration) whereas when $X=CH_3$, it is diamagnetic (low spin configuration). It is important to realize that ligands provide an important means of adjusting the ground state properties.

In bi- and polymetallic complexes, in which the individual centers have an odd number of electrons or which are high spin, the situation is more complicated. If there is interaction (either direct or through ligand) between the two (or more) metal centers, the electrons may couple (antiferromagnetic coupling, resulting in a diamagnetic compound), or they may enhance each other (ferromagnetic coupling). When there is no interaction, the two (or more) individual metal centers behave as if in two separate molecules.

2.10.3 REACTIVITY:

Complexes show a variety of possible reactivities:

- Electron transfers

A common reaction between coordination complexes involving ligands are inner and outer sphere electron transfers. They are two different mechanisms of electron transfer <u>redox</u> reactions, largely defined by the late Henry Taube. In an inner sphere reaction, a ligand with two lone electron pairs acts as a *bridging ligand*, a ligand to which both coordination centres can bond. Through this, electrons are transferred from one centre to another.

- (Degenerate) ligand exchange

One important indicator of reactivity is the rate of degenerate exchange of ligands. For example, the rate of interchange of coordinate water in $[M(H_2O)_6]^{n+}$ complexes varies over 20 orders of

magnitude. Complexes where the ligands are released and rebound rapidly are classified as labile. Such labile complexes can be quite stable thermodyanically. Typical labile metal complexes have either low charge (Na^+), electrons in d-orbitals that are antibonding with respect to the ligands (Zn^{2+}), or lack covalency (Ln^{3+}, where Ln is any lanthanide). The lability of a metal complex also depends on the high vs. low spin configurations when such is possible. Thus high spin Fe(II) and Co(III) form labile complexes whereas low spin analogues are inert. Cr(III) can only exist in the low-spin state (quartet), which is inert because of its high formal oxidation state, absence of electrons in orbitals that are M-L antibonding, plus some "ligand field stabilization" associated with the d3 configuration.

- Associative processes

Complexes that have unfilled or half-filled orbitals often show the capability to react with substrates. Most substrates have a singlet ground-state , that is, they have lone electron pairs (e.g. water, amines, ethers), so these substrates need an empty orbital to be able to react with a metal centre. Some substrates (e.g. molecular oxygen!) have a triplet ground state, which results that metals with half-filled orbitals have a tendency to react with such substrates (it must be said that the dioxygen-molecule also has lone pairs, so it is also capable to react as a 'normal' Lewis base).

If the ligands around the metal are carefully chosen, the metal can aid in (stoichiometric or catalytic) transformations of molecules or be used as a sensor

2.11 IRON COMPLEXES IN ORGANIC CHEMISTRY:

Catalysis is an important field in both academic and industrial research because it leads to more efficient reactions in terms of energy consumption and waste production. The common feature of these processes is a catalytically active species which forms reactive intermediates by coordination of an organic ligand and thus decreases the activation energy. Formation of the product should occur with regeneration of the catalyticallyactive species. The efficiency of the catalyst can bedescribed by its turnover number, providing a measure of how many catalytic cyclesare passed by one molecule of catalyst. For efficient regeneration, the catalyst should form only labile intermediates with the substrate. This concept can be realized using transition metal complexes because metalligand bonds are generally weaker than covalent bonds. The transition metals often exist in different oxidation states with only moderate differences in their oxidation

potentials, thus offering the possibility of switching reversibly between the different oxidation states by redox reactions.Many transition metals have been applied as catalysts for organic reactions .

So far, iron has not played a dominant role in catalytic processes. Organoiron chemistry was started by the discovery of pentacarbonyliron in 1891, indepen- dently by Mond and Berthelot .A further milestone was the report of ferrocene in 1951 .Iron catalysis came into focus by the Reppe synthesis . Kochi and coworkers published in 1971 their results on the iron-catalyzed cross-coupling of Grignard reagents with organic halides .However, cross-coupling reactions became popular by using the late transition metals nickel and palladium.

More recently, the increasing number of reactions using catalytic amounts of iron complexes indicates a renaissance of this metal in catalysis. This chapter describes applications of iron complexes in organic chemistry and thus paves the way for an understanding of iron catalysis.

2.12 ROLE OF IRON IN THE BODY:

Iron is an essential element for most life on Earth, including human beings. Iron is needed for a number of highly complex processes that continuously take place on a molecular level and that are indispensable to human life, e.g. the transportation of oxygen around your body. Iron is required for the production of red blood cells (a process known as haematopoiesis), but it's also part of haemoglobin (that is the pigment of the red blood cells) binding to the oxygen and thus facilitating its transport from the lungs via the arteries to all cells throughout the body. Once the oxygen is delivered the iron (as part of haemoglobin) binds the carbon dioxide which is then transported back to the lung from where it gets exhaled. Iron is also involved in the conversion of blood sugar to energy. Metabolic energy is crucial for athletes since it allows muscles to work at their optimum during exercise or when competing. The production of enzymes (which play a vital role in the production of new cells, amino acids, hormones and neurotransmitters) also depends on iron, this aspect becomes crucial during the recovery process from illnesses or following strenuous exercise or competing. The immune system is dependent on iron for its efficient functioning and physical and mental growth require sufficient iron levels, particularly important in childhood and pregnancy, where the developing baby solely depends on its mother's iron supplies. Iron is lost by the body through a variety of ways including urination, defecation,

sweating, and exfoliating of old skin cells. Bleeding contributes to further loss of iron which is why women have a higher demand for iron than men.

If iron stores are low, normal haemoglobin production slows down, which means the transport of oxygen is diminished, resulting in symptoms such as fatigue, dizziness, lowered immunity or reduced ability for athletes to keep up with their training programs. Since our bodies can't produce iron itself, we need to make sure we consume sufficient amounts of iron as part of our daily diet. Spatone, natural liquid iron supplement can provide your body's daily absorbed iron needs whilst being extra gentle on the stomach.

2.13 IRON (FE) AND WATER:

Seawater contains approximately 1-3 ppb of iron. The amount varies strongly, and is different in the Atlantic and the Pacific Ocean. Rivers contain approximately 0.5-1 ppm of iron, and groundwater contains 100 ppm. Drinking water may not contain more than 200 ppb of iron. Most algae contain between 20 and 200 ppm of iron, and some brown algae may accumulate up to 4000 ppm. The bio concentration factor of algae in seawater is approximately $10^4 - 10^5$. Sea fish contain approximately 10-90 ppm and oyster tissue contains approximately 195 ppm of iron (all are dry mass).

Dissolved iron is mainly present as $Fe(OH)_2^+$ (aq) under acidic and neutral, <u>oxygen</u>-rich conditions. Under oxygen-poor conditions it mainly occurs as binary iron. Iron is part of many organic and inorganic chelation complexes that are generally water soluble.

Iron does not clearly alter in pure water or in dry air, but when both water and oxygen are present (moist air), iron corrodes. Its silvery colour changes to a reddish-brown, because hydrated oxides are formed. Dissolved electrolytes accelerate the reaction mechanism, which is as follows:

$4 \ Fe + 3 \ O_2 + 6 \ H_2O \rightarrow 4 \ Fe^{3+} + 12 \ OH^- \rightarrow 4 \ Fe(OH)_3$ or $4 \ FeO(OH) + 4 \ H_2O$ Usually the oxide layer does not protect iron from further corrosion, but is removed so more metal oxides can be formed. Electrolytes are mostly iron (II) sulphate, which forms during corrosion by atmospheric SO_2. In sea regions atmospheric salt particles may play an important role in this process.

Iron (II) hydroxide often precipitates in natural waters.

2.14 SOLUBILITY OF IRON AND IRON COMPOUNDS:

Elementary iron dissolves in water under normal conditions. Many iron compounds share this characteristic. Naturally occurring iron oxide, iron hydroxide, iron carbide and iron penta carbonyl are water insoluble. The water solubility of some iron compounds increases at lower pH values.

Other iron compounds may be more water soluble than the examples mentioned above. Iron carbonate has a water solubility of 60 mg/L, iron sulphide of 6 mg/L, and iron vitriol even of 295 g/L. Many iron chelation complexes are water soluble.

Usually there is a difference between water soluble Fe^{2+} compounds and generally water insoluble Fe^{3+} compounds. The latter are only water soluble in strongly acidic solutions, but water solubility increases when these are reduced to Fe^{2+} under certain conditions. The main naturally occurring iron minerals are magnetite, hematite, goethite and siderite. Weathering processes release the element into waters. Both mineral water and drinking water contain iron carbonate.

2.15 RISK ASSESSMENT:

In humans acute iron poisoning is associated with severe gastrointestinal damage which may include haemorrhagic gastroenteritis. Blood and other fluid loss may lead to shock and coma. In some cases, apparent recovery may take place, possibly due to a latency period during which the iron is distributed throughout the body. Systemic iron toxicity is characterised by multi-system damage, principally in the liver, metabolic acidosis, coagulopathies and cardiovascular collapse. Acute poisoning is relatively unusual in adults, the lethal dose being approximately 100 g, but is more common in children.

Iron overload as a result of dietary intake is unusual in the normal population and only a handful of case reports exist describing this phenomenon. This may be due to the reduction in iron absorption that occurs as exposure increases.

Individuals with conditions such as hereditary haemochromatosis (HHC) are particularly vulnerable to iron overload, which occurs as a result of enhanced uptake. In subjects heterozygous for the condition, a small increase in iron storage may occur. It has been suggested that heterozygous subjects (up to 1% of the population) may have an increased risk of cardiovascular disease but this remains controversial.

Similarly, the suggestion that high iron status may be associated with other chronic conditions remains unresolved.

Studies in rodents suggest a pattern of iron overload comparable with that seen in haemochromatosis, with cellular changes but not with fibrosis occurring. Reproductive studies in rodents have shown no significant evidence of iron transfer across the placenta. This is supported by a study in an ovine model where maternal iron poisoning did not result in increases in foetal serum iron levels. However one study reports that iron gluconate is teratogenic, causing exencephaly in mice following administration on the 8th and 9th days of gestation.

2.16 IRON TOXICITY:

Because intestinal absorption of iron is regulated by iron stores, iron toxicity is rare. Consuming large quantities of alcohol may increase the absorption of iron. Hemochromatosis, a genetic disorder, also increases iron absorption. Once iron is absorbed it is only excreted through blood loss. Excess iron will build up in tissues and organs, may increase the risk for certain cancers and may eventually lead to death.

The main concern with iron toxicity is overdoses in children. An overdose of iron supplements can cause toxicity in adults and children. However, in children as little as 20 to 60 mg of iron/kg body weight can cause toxicity and death. It is important to keep iron supplements away from children and tightly closed. The tolerable upper limits for iron as set by the Institute for medicine and the National Academy of Sciences is 40 mg/day for children under the age of 14 and 45 mg/day for anyone 14 years of age or older. This limit is set as the largest amount of iron a person can consume without risk of negative side effects.

2.17 IRON AND DISEASE:

Heart disease risk seems to be greater in societies that eat high amounts of red meat versus those that eat minimal amounts. The amount of iron stored in the body can influence a person's potential to develop heart disease. Excess iron is associated with the formation of free radicals, unstable molecules in the body that may injure vessels supplying blood to the heart. It has also been suggested that the incidence of heart disease rises dramatically in women once menstruation stops due to increased amounts of iron in the blood. There is no conclusive

evidence that excess iron increases coronary heart disease. It is not recommended to eliminate red meat or other iron rich foods from the diet.

2.18 Removing Iron from water:

Iron removal from water is mostly carried out in drinking water preparation, because mineral water contains high amounts of iron ions. These influence water colour ,odour and turbidity. iron is present in all wastewaters, it can be removed by oxidation of iron (II) to iron (III), hydrolysis subsequently causes flake formation, and flake can be removed by sand filtration , oxidation may by achieved by adding oxygen or other oxidants , values ,and is slower under acidic than alkalic conditions. To speed up the reaction under acidic conditions ,the water may be aerated for carbon dioxide removal and pH recovery . the total reaction causes acid formation and thereby diminishes itself . iron is often reduced together with manganese.

Applying ion exchangers for iron trace removal from drinking water and process water in another option , but this is not very suitable for removing high iron concentrations ,iron compounds are applied in wastewater treatment ,usually as coagulants . one example is iron sulphate application in phosphate removal .

2.19 IRON REMOVAL WITH WATER SOFTENERS:

More water softeners are used to remove iron from household water supplies than any other devices or systems. Many of these installations are successful and consistently remove both hardness and iron. At other installations, intermittent leakage of iron through the softener occurs, but the total water quality improvement is so great that the users are reasonably satisfied. In still other cases, softeners fail to do a satisfactory job, passing iron continuously or in "slugs", or gradually losing capacity due to fouling of the softener bed. Thus, we have several degrees of success with softeners in iron removal.

On some iron waters, it is immediately clear that a softener should not be used. Dissolved organic-iron compounds may simply pass through a softener, unaffected by either ion exchange or the filtering action of the softener bed. Solid organic matter particles frequently contain quantities of precipitated iron, and the combined solids can lead to rapid fouling of the bed. Iron

bacteria in water can rapidly foul softener beds, and worse, can grow and pass through the beds in slugs. When such materials are found in the water, softeners should not be applied.

Technically, industrial water softeners can remove dissolved ferrous iron by ion exchange, just as they remove calcium and magnesium. Further, precipitated iron can be removed by filtration. Problems arise, however, in getting the iron out of the softener bed during regeneration. Precipitated iron (ferric hydroxide), formed when soluble ferrous iron is oxidized by oxygen in air, is a gelatinous, sticky material which tends to adhere to the beads or particles in a softener bed. These strictly physical properties make it difficult to rid a softener bed of this material even with a thorough backwash, and it may gradually accumulate in the bed. After a period of this accumulation, slugs of iron may appear in the softened water immediately after regeneration or after abrupt increases in water flow through the softener. Since the materials may also clog the pores of the ion exchange material in the softener bed, it can gradually reduce the hardness removal capacity. Both of these effects create obvious problems for the user of the water.

Ideally, ferrous iron removed by ion exchange should be discharged with the hardness during the usual brine regeneration. In practice, however, it is usual for at least some of this iron to be converted to the ferric, insoluble state by oxygen in the regeneration water or brine. Thus, some of this iron is retained in the softener, and in time, may produce the slugs or fouling previously described above.

2.20 SPECTROSCOPY:

Spectroscopy is the method of choice in the determination of structure and function in chemical systems. Beyond the usual array of spectroscopic instrumentation (NMR, ESR, microwave, IR and Raman, UV/VIS, fluorescence, and X-Ray), many research groups in the Department are involved in the development of new methods of characterization and analysis of molecules in the gas and condensed phases. These include the development of nanostructures for optical sensing of chemical and biological transformations, determinations of the structures and dynamical properties of biologically relevant molecules using high resolution lasers, development of high resolution gas-phase separations of proteins and peptides based on ion mobility spectrometry, measuring distance constraints between two units on a macromolecule using pulsed ESR methods, new forms of spectroscopy for the detection of protein folding in real time,

femtosecond laser studies of metal surfaces and semiconductor interfaces, and ab initio computations for the prediction of spectra and chiroptical phenomena in complex systems.

The Light of Knowledge is an often used phrase, but it is particularly appropriate in reference to spectroscopy. Most of what we know about the structure of atoms and molecules comes from studying their interaction with light (electromagnetic radiation). Different regions of the electromagnetic spectrum provide different kinds of information as a result of such interactions. Realizing that light may be considered to have both wave-like and particle-like characteristics, it is useful to consider that a given frequency or wavelength of light is associated with a "light quanta" of energy we now call a photon. As noted in the following equations, frequency and energy change proportionally, but wavelength has an inverse relationship to these quantities.

$$\nu = c/\lambda \quad \nu = \text{frequency}, \lambda = \text{wavelength}, c = \text{velocity of light} \ (c = 3 \cdot 10^{10} \ \text{cm/sec})$$
$$\Delta E = h\nu \quad E = \text{energy}, \nu = \text{frequency}, h = \text{Planck's constant} \ (h = 6.6 \cdot 10^{-27} \ \text{erg sec})$$

In order to "see" a molecule, we must use light having a wavelength smaller than the molecule itself (roughly 1 to 15 angstrom units). Such radiation is found in the X-ray region of the spectrum, and the field of X-ray crystallography yields remarkably detailed pictures of molecular structures amenable to examination. The chief limiting factor here is the need for high quality crystals of the compound being studied. The methods of X-ray crystallography are too complex to be described here; nevertheless, as automatic instrumentation and data handling techniques improve, it will undoubtedly prove to be the procedure of choice for structure determination. The spectroscopic techniques described below do not provide a three-dimensional picture of a molecule, but instead yield information about certain characteristic features. A brief summary of this information follows:

- Mass Spectrometry: Sample molecules are ionized by high energy electrons. The mass to charge ratio of these ions is measured very accurately by electrostatic acceleration and magnetic field perturbation, providing a precise molecular weight. Ion fragmentation patterns may be related to the structure of the molecular ion.
- Ultraviolet-Visible Spectroscopy: Absorption of this relatively high-energy light

causes electronic excitation. The easily accessible part of this region (wavelengths of 200 to 800 nm) shows absorption only if conjugated pi-electron systems are present.

• Infrared Spectroscopy: Absorption of this lower energy radiation causes vibrational and rotational excitation of groups of atoms. within the molecule. Because of their characteristic absorptions identification of functional groups is easily accomplished.

• Nuclear Magnetic Resonance Spectroscopy: Absorption in the low-energy radio-frequency part of the spectrum causes excitation of nuclear spin states. NMR spectrometers are tuned to certain nuclei (e.g. ^{1}H, ^{13}C, ^{19}F & ^{31}P). For a given type of nucleus, high-resolution spectroscopy distinguishes and counts atoms in different locations in the molecule.

2.20.1 ULTRAVIOLET-VISIBLE (UV-VIS) SPECTROSCOPY – PRINCIPLE:

2.20.1.1 INTRODUCTION:

we have discussed the different wavelengths for ultraviolet and visible lights which range from 10 nm to 400nm and 400nm to 780 nm respectively. The following chapter discusses to a greater extent the principles involved in the utility of ultraviolet-visible spectroscopy (UV-Vis) and the Beer-Lambert law which is useful in quantitative analysis of samples.

2.20.1.2 PRINCIPLE OF ULTRAVIOLET-VISIBLE ABSORPTION:

The energy of the radiation can be calculated by the equation:

$E = h \cdot \nu$

Thus the energy of the radiation in the visible range is generally: 36 to 72 kcal/mole while that in the ultraviolet range goes as high as 143 kcal/mole. This energy irradiated on the molecules can result in changes in the electronic nature of the molecule i.e. changes between ground state and excited states of electrons within the system. As a result, UV-visible spectroscopy is also known as electronic spectroscopy.

Every time a molecule has a bond, the atoms in a bond have their atomic orbitals merged to form molecular orbitals which can be occupied by electrons of different energy levels. Ground state molecular orbitals can be excited to anti-bonding molecular orbitals.

The electrons in a molecule can be of one of three types: namely σ (single bond), π (multiple-bond), or non-bonding (n- caused by lone pairs). These electrons when imparted with energy in the form of light radiation get excited from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) and the resulting species is known as the excited state or anti-bonding state.

1. σ-bond electrons have the lowest energy level and are the most stable electrons. These would require a lot of energy to be displaced to higher energy levels. As a result these electrons generally absorb light in the lower wavelengths of the ultraviolet light and these transitions are rare.

2. π-bond electrons have much higher energy levels for the ground state. These electrons are therefore relatively unstable and can be excited more easily and would require lesser energy for excitation. These electrons would therefore absorb energy in the ultraviolet and visible light radiations.

3. n-electrons or non-bonding electrons are generally electrons belonging to lone pairs of atoms. These are of higher energy levels than π-electrons and can be excited by ultraviolet and visible light as well.

Most of the absorption in the ultraviolet-visible spectroscopy occurs due to π-electron transitions or n-electron transitions. Each electronic state is well defined for a particular system i.e. a double bond in 2-butene would have a particular energy level for the π-electons which when absorbs a specific (or quantized) amount of energy would get excited to the π* energy level for the electrons.

The figure below shows the different transitions between the bonding and anti-bonding electronic states.
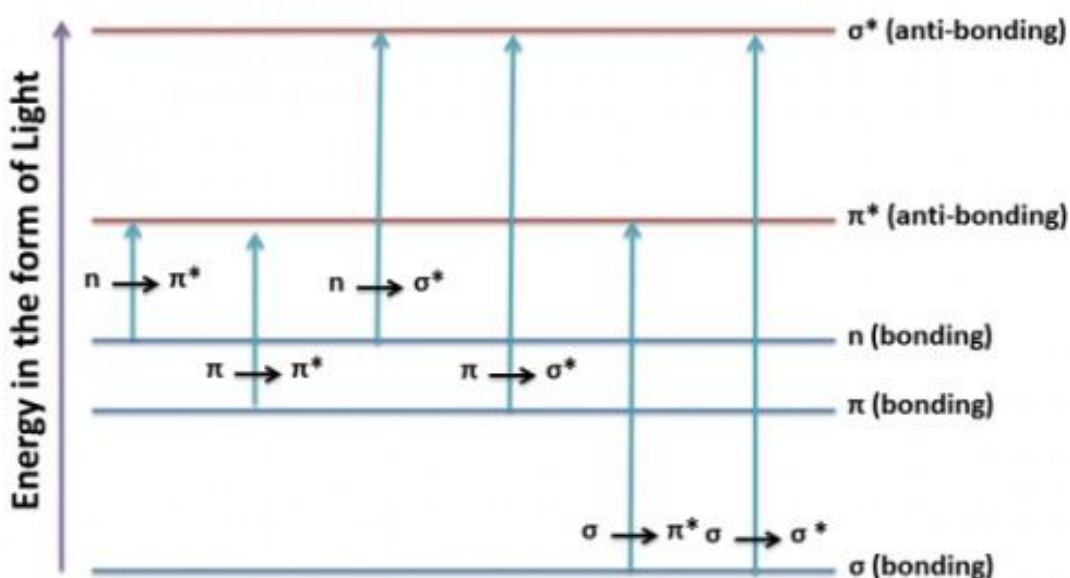
Different transitions between the bonding and anti-bonding electronic states when light energy is absorbed in UV-Visible Spectroscopy.

When a sample is exposed to light energy that matches the energy difference between a possible electronic transition within the molecule, a fraction of the light energy would be absorbed by the molecule and the electrons would be promoted to the higher energy state orbital. A spectrometer records the degree of absorption by a sample at different wavelengths and the resulting plot of absorbance (A) versus wavelength (λ) is known as a spectrum. The wavelength at which the sample absorbs the maximum amount of light is known as λ_{max}. For example, shown below is the spectrum of isoprene. Isoprene is colorless as it does not absorb light in the visible spectrum, and has a λ_{max} of 222nm.
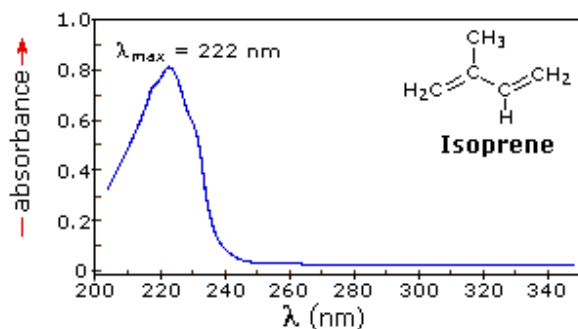
UV-visible spectrum of isoprene showing maximum absorption at 222 nm.
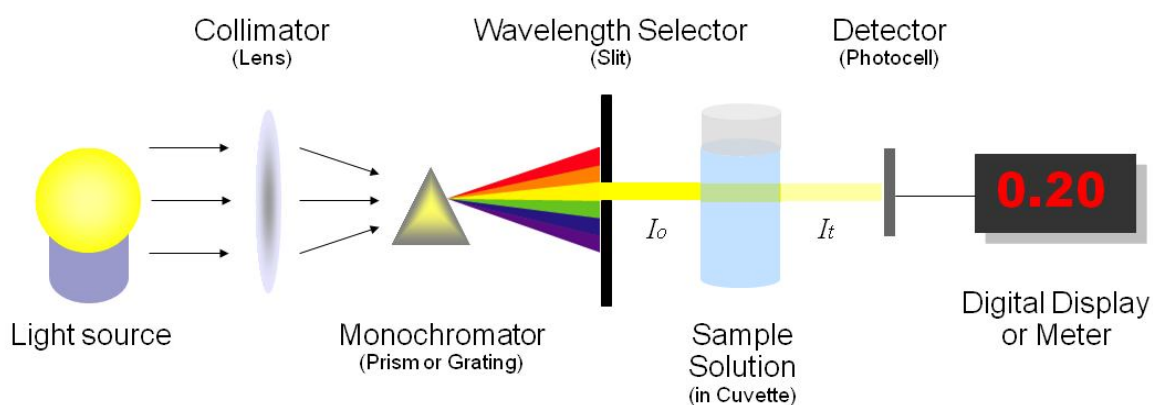
2.20.1.3 divices an mechanism:

Figure 1: Basic structure of spectrophotometers

A spectrophotometer, in general, consists of two devices; a spectrometer and a photometer. A spectrometer is a device that produces, typically disperses and measures light. A photometer indicates the photoelectric detector that measures the intensity of light.

- Spectrometer: It produces a desired range of wavelength of light. First a collimator (lens) transmits a straight beam of light (photons) that passes through a monochromator (prism)

to split it into several component wavelengths (spectrum). Then a wavelength selector (slit) transmits only the desired wavelengths, as shown in Figure 1.

- Photometer: After the desired range of wavelength of light passes through the solution of a sample in cuvette, the photometer detects the amount of photons that is absorbed and then sends a signal to a galvanometer or a digital display, as illustrated in Figure 1.

- You need a spectrometer to produce a variety of wavelengths because different compounds absorb best at different wavelengths. For example, p-nitrophenol (acid form) has the maximum absorbance at approximately 320 nm and p-nitrophenolate (basic form) absorb best at 400nm, as shown in Figure 3.
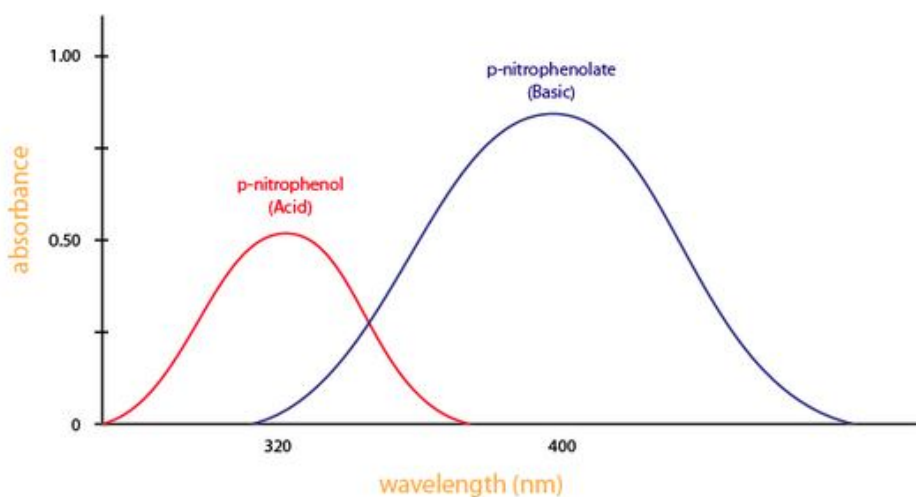
- Figure 2: Absorbance of two different compounds

- Looking at the graph that measures absorbance and wavelength, an isosbestic point can also be observed. An isosbestic point is the wavelength in which the absorbance of two or more species are the same. The appearance of an isosbestic point in a reaction demonstrates that an intermediate is NOT required to form a product from a reactant. Figure 4 shows an example of an isosbestic point.
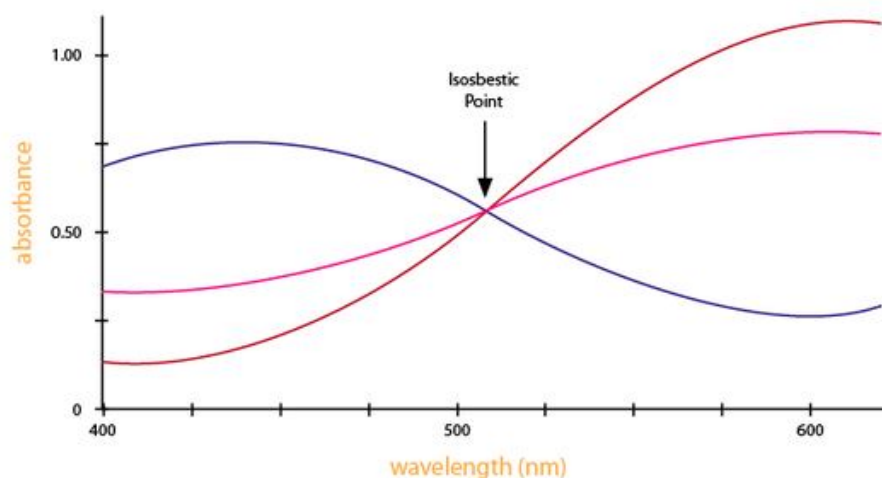
- Figure 3 : An example of isosbestic point

- Referring back to Figure 1 (and Figure 5), the amount of photons that goes through the cuvette and into the detector is dependent on the length of the cuvette and the concentration of the sample. Once you know the intensity of light after it passes through the cuvette, you can relate it to transmittance (T). Transmittance is the fraction of light that passes through the sample. This can be calculated using the equation:

- $Transmittance\ (T) = \dfrac{I_t}{I_o}$

- Where I_t is the light intensity after the beam of light passes through the cuvette and I_o is the light intensity before the beam of light passes through the cuvette. Transmittance is related to absorption by the expression:

- $Absorbance\ (A) = - \log(T) = - \log(\dfrac{I_t}{I_o})$

- Where absorbance stands for the amount of photons that is absorbed. With the amount of absorbance known from the above equation, you can determine the unknown concentration of the sample by using Beer-Lambert Law. Figure 5 illustrates transmittance of light through a sample. The length l is used for Beer-Lambert Law described below.
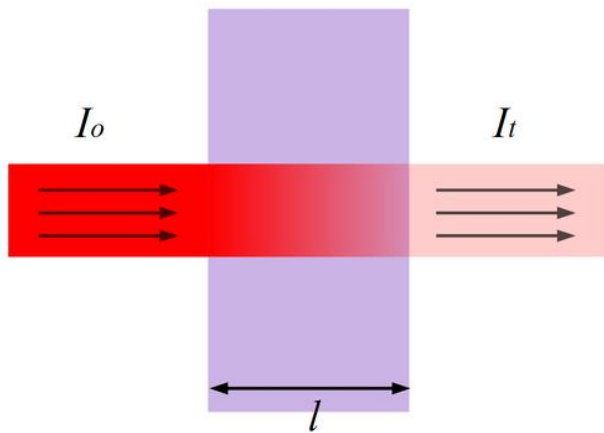
Figure 4: Transmittance

- *Beer-Lambert Law*
- Beer-Lambert Law (also known as Beer's Law) states that there is a linear relationship between the absorbance and the concentration of a sample. For this reason, Beer's Law can *only* be applied when there is a linear relationship. Beer's Law is written as:

- $A = \epsilon{lc}$

- where A is the measure of absorbance (no units), ϵ is the molar extinction coefficient or molar absorptivity (or absorption coefficient), l is the path length, and c is the concentration. The molar extinction coefficient is given as a constant and varies for each molecule. Since absorbance does not carry any units, the units for ϵ must cancel out the units of length and concentration. As a result, ϵ has the units: $L \cdot mol^{-1} \cdot cm^{-1}$. The path length is measured in centimeters. Because a standard spectrometer uses a cuvette that is 1 cm in width, l is always assumed to equal 1 cm. Since absorption, ϵ, and path length are known, we can calculate the concentration c of the sample.

2.21 ANALYSIS OF IRON:

2.21.1 COLORIMETRIC FE ANALYSIS:

In the colorimetric analysis for Mn the concentration of the Mn is determined using the characteristic color of the permanganate ion. However, few metal ions show such strong colors, particularly at low concentrations. Fortunately many highly colored complexes can be formed from metal ions and organic or inorganic complexing agents. These complexes are the result of the interaction of a Lewis acid (the metal ion) and a Lewis base (the complexing agent). The ideal color-forming reagent should be stable and selective (even specific) and react rapidly to form soluble, highly colored complexes. The colored complex should have a high absorptivity and be free from variations in color due to minor changes in pH or temperature. The application of colorimetric reagents is not a new technique but dates back nearly two thousand years. Around 60 A.D. Pliny the Elder in his "Natural History" recommended the use of nutgall as a reagent for the determination of iron in verdigris, which is a green pigment. Nutgall contains about 65-70% tannic acid which when combined with iron leads to the formation of a black irontannate complex.

In general organic colorimetric reagents are considerably more sensitive than are inorganic ones. They give more intense colors and are therefore frequently used for trace analyses. With many organic reagents, it is possible to determine concentrations at the ppm level. 2,2'-Bipyridyl (bipy), gfw = 156.20, forms an intensely red complex with iron(II) which may be exploited to determine iron concentrations in the ppm range. The reaction is:

$3bipy + Fe^{2+} <===> Fe(bipy)_3^{2+}$
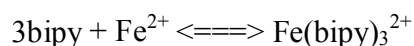
The figure below shows the structure of the reagent and the complex formed with Fe.
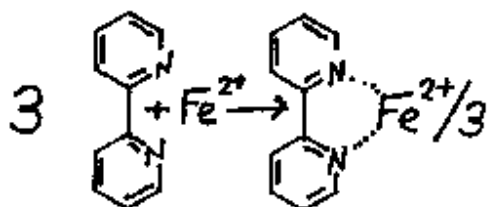
The complex conforms to an octahedral geometry with coordinate covalent bonds being

formed between the adjacent sp^3d^2 hybrid orbitals of the Fe^{2+}. The complex is chiral; there are left-handed and right-handed non-superimposable optically active forms. Can you draw the two? The molar absorptivity of the iron-bipyridyl complex is 8650 L/mol/cm at the wavelength of maximum absorbance. The complex forms rapidly, is stable over the pH range 3 to 9, and may be used to determine iron(II) concentrations in the range of 0.5 to 8 ppm.

Iron(III), if present, must be reduced to iron(II) to produce the colored species. A suitable reagent for this purpose is hydroxylamine hydrochloride, $HONH_3^+Cl^-$. The reaction for this reduction is shown below:

$$2HONH_3^+Cl^- + 2Fe^{3+} <===> 4H^+ + 2 H_2O + N_2 + 2Fe^{2+} + 2Cl^-$$

The concentration of iron in the sample could be calculated from Beer's Law however in this procedure we employ a different method. We will prepare a standard solution and compare absorbance readings of the sample and the standard solution. This technique minimizes the effects of instrument and solution variation. Spectrophotometric methods are normally accurate to about ± 1%, i.e. to about three significant figures. Even though higher accuracy and precision can be obtained with more sophisticated instruments, in most cases an accuracy of ± 1%, at concentration levels of parts per million, is quite sufficient. The ferrous ammonium sulfate standard that is used in the procedure is normally not considered a primary standard, however it is available in a purity greater than 99% and is therefore adequate for our purposes.
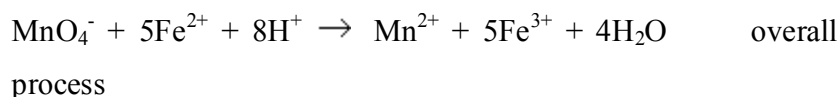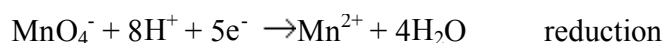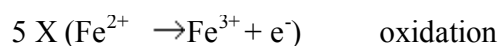
2.21.2 THE DETERMINATION OF IRON(II) BY REDOX TITRATION:

the method used an oxidation-reduction (redox) reaction as a means of analyzing an unknown sample for how much iron(II) the sample contains.

The experiment was performed over two weeks to give you a chance to take your time and get good results. During the first week of the experiment, you were given a solution of potassium permanganate, $KMnO_4$, of an approximate concentration which was to be used as the titrant (the solution in the buret). Potassium permanganate is highly reactive and is not available in a pure form. The solution you were given, therefore, could only be made up to an *approximate* concentration. Then, in the first week of the experiment, your goal was to determine the *exact*

concentration of the $KMnO_4$ solution by reacting it with a pure, stable iron compound of known composition, ferrous ammonium sulfate (FAS).

Potassium permanganate reacts with iron(II) salts according to the following oxidation-reduction equation

$$5 \text{ X } (Fe^{2+} \rightarrow Fe^{3+} + e^-) \qquad \text{oxidation}$$

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O \qquad \text{reduction}$$

———————————————————————————————————

$$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O \qquad \text{overall process}$$

By determining the exact mass of the FAS samples taken, and from the volume of $KMnO_4$ solution required to titrate those samples, the exact molarity of the $KMnO_4$ solutions could be calculate.

In the second week of the experiment, you titrated samples of an "unknown" iron(II) salt with the same $KMnO_4$ solution, in order to determine what % by mass of Fe it contained. Knowing the volume of the $KMnO_4$ solution required to reach the endpoint enables you to calculate the number of moles of iron present in each sample and the mass of iron(II) present in each sample. Then, from the mass of iron(II) in a sample and from the mass of the sample itself, you can calculate the % of Fe in the sample.

2.21.3 DETERMINATION OF IRON BY ATOMIC AND MOLECULAR SPECTROSCOPY: BACKGROUND:

In this experiment, an unknown solid sample containing iron oxide (Fe2O3, FW=159.69)

will be analyzed by two spectroscopic techniques. Both are based on transmitting light through

the sample and measuring the fraction of light

absorbed. Mathematically, the measurement can

be expressed as:

$$T(\lambda) = P(\lambda) / P0(\lambda) \qquad (1)$$

In Eq. 1, T is termed the transmittance, P denotes the light intensity transmitted through the sample, and P0is the light intensity incident on the sample. The P0 value is measured by use of a blank solution that contains the sample matrix but contains no analyte. The values T, P, and P0 are all a function of λ, the wavelength of the light. The measured transmittance can be related to the analyte concentration through the Beer-Lambert law:

$$A(\lambda) = -\log 10(T(\lambda)) = \varepsilon bc \qquad (2)$$

In Eq. 2, A is termed the absorbance, c is the analyte concentration, and ε(absorptivity) and b (optical path length) are constants that define the linear relationship between A and c. Absorptivity is an intrinsic property of the analyte, and the path length is a characteristic of the

instrumental measurement. The value of εb is determined by a calibration procedure that employs a set of known standards that bracket the desired concentration range. Spectroscopic measurements are most easily performed with liquid samples. To convert the insoluble Fe_2O_3 in the unknown to a soluble species, an acid digestion will be performed. This will yield a solution of Fe^{3+}.
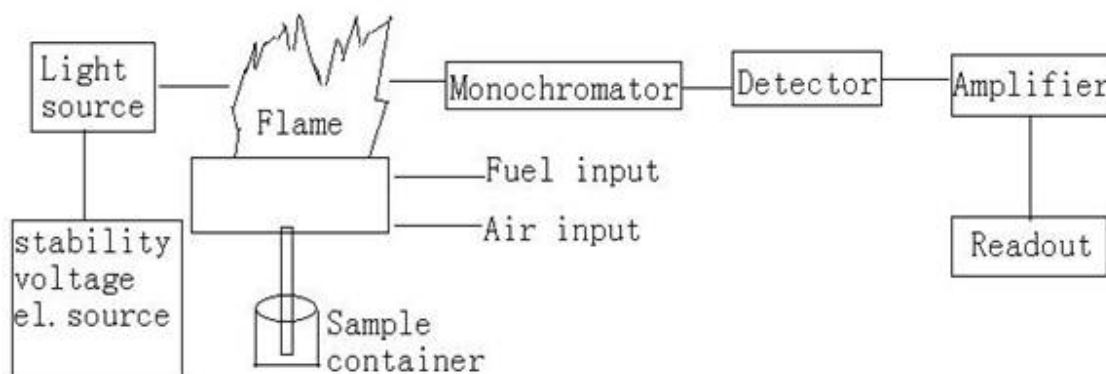

Figure 5: compound of AAS:

2.21.4 DETERMINATION OF IRON AS IRON(III) OXIDE BY INITIAL FORMATION OF BASIC IRON(III):

The precipitation of iron as iron(II1) hydroxide by ammonia solution yields a gelatinous precipitate which is rather difficult to wash and to filter. Iron(III) can, however, be precipitated from homogeneous solution as a dense basic formate by the urea hydrolysis method. The precipitate obtained is more readily filtered and washed and adsorbs fewer impurities than

that formed by other hydrolytic procedures. Ignition yields iron (III) oxide. The pH at which basic iron(III) formate begins to precipitate depends upon several factors, which include the initial iron and chloride concentration: a high concentration of ammonium chloride is essential to prevent colloid formation. It is important to use an optimum initial pH to avoid a large excess of free acid, which would have to be neutralised by urea hydrolysis, and yet there must be

present sufficient acid to prevent the formation of a gelatinous precipitate prior to boiling the solution: ideally, a turbidity should appear about 5-10 minutes after the solution has begun to boil. For iron contents of 5 mg to 55 mg per 100 mL, the optimum initial pH is between 2.00 and 1.70. Some reduction occurs during the precipitation (due to the presence of both formate and chloride): re-oxidation of iron(I1) to iron(II1) is easily effected by the addition of hydrogen

peroxide towards the end of the procedure. Precipitation as basic formate enables iron to be separated from manganese(II), cobalt, nickel, copper, zinc, cadmium, magnesium, calcium, and barium. When copper is present the solution must be cooled before hydrogen peroxide is added, otherwise the vigorous decomposition of the hydrogen peroxide may result in loss of some of the solution. Attention is directed to the fact that if ignition is carried out in a platinum crucible at a temperature above 1100 O C some reduction to the oxide iron (III), may occur, and at temperatures above 1200 O C some of the oxide may be reduced to the metal and alloy with the platinum. This accounts in part for the contamination of the platinum crucible by iron which sometimes occurs in analytical work. This oxide is not produced if silica crucibles are employed for the ignitions .

2.21.5 VOLUMETRIC METHODS TO DETARMINATION IRON :

Two procedures will be described - the thiocyanate and the 1,l0-phenanthroline

methods.

Iron (III) reacts with thiocyanate to give a series of intensely red-coloured compounds, which

remain in true solution:

iron(I1) does not react. Depending upon the thiocyanate concentration, a series of complexes can

be obtained; these complexes are red and can be formulated as [Fe(SCN),I3-", where n = 1,. . .

,6.   At low thiocyanate concentration the predominant coloured species is [Fe(SCN)I2+ {Fe3 +

+ SCN- + [Fe(SCN)I2+), at 0.1M thiocyanate concentration it is largely [Fe(SCN),] +, and at

very high thiocyanate concentration it is [Fe(SCN),I3-. In the colorimetric determination

a large excess of thiocyanate should be used, since this increases the intensity and also the

stability of the colour. Strong acids (hydrochloric or nitric acid - concentration 0.05-0.5M)

should be present to suppress the hydrolysis: Sulphuric acid is not recommended, because

sulphate ions have a certain tendency to form complexes with iron(II1) ions. Silver, copper,

nickel, cobalt, titanium, uranium, molybdenum, mercury (> 1 g L-'), zinc, cadmium, and

bismuth interfere. Mercury(1) and tin(I1) salts, if present, should be converted into the

mercury(I1) and tin(1V) salts, otherwise the colour is destroyed.

Phosphates, arsenates, fluorides, oxalates, and tartrates interfere, since they form fairly stable

complexes with iron(II1) ions; the influence of phosphates and arsenates is reduced by the

presence of a comparatively high concentration of acid.

When large quantities of interfering substances are present, it is usually best to proceed in either

of the following ways:

(1) remove the iron by precipitation with a slight excess of ammonia solution, and dissolve the

precipitate in dilute hydrochloric acid;

 (2) extract the 'iron(II1) thiocyanate' three times either with pure diethyl ether or, better, with a

mixture of pentan-1-01 and pure diethyl ether (5: 2) and employ the organic layer for the colour

comparison.

2.21.6 DETERMINATION OF IRON(III) WITH EDTA:

Salicylic acid and iron(II1) ions form a deep-coloured complex with a maximum absorption at

about 525 nm: this complex is used as the basis for the photometric titration of iron(II1) ion with

standard EDTA solution. At pH 2.4 the EDTA-iron complex is much more stable (higher

stability constant) than the iron-salicylic acid complex. In the titration of an iron salicylic acid solution with EDTA the iron-salicylic acid colour will therefore gradually disappear as the end point is approached. The spectrophotometric end point at 525 nm is very sharp. Considerable amounts of zinc, cadmium, tin(IV), manganese(II), chromium(III), and smaller amounts of aluminium cause little or no interference at pH 2.4: the main interferences are lead(II), bismuth, cobalt(II), nickel, and copper(I1).

2.21.7 DETERMINATION OF IRON(II1) IN THE PRESENCE OF ALUMINIUM:

Iron(II1) (concentration ca 50 mg per 100 mL) can be determined in the presence of up to twice the amount of aluminium by photometric titration with EDTA in the presence of 5-sulphosalicylic acid (2 per cent aqueous solution) as indicator at pH 1.0 at a wavelength of 510nm. The pH of a strongly acidic solution may be adjusted to the desired value with a concentrated solution of sodium acetate: about 8-10 drops of the indicator solution are required.

3.0 MATERIALS AND METHOD:

3.1 SAMPLE: A synthetic sample was prepared in the laboratory by dissolving in distilled water 7.01 g of ferrous ammonium sulphate hexahydrate , in 1000 ml of 0.2% sulfuric acid .

3.2 CHEMICALS:

- Nitric acid, HNO_3 , Conc .

- Sulphuric acid, HSO_4, Conc. 98%.

- 1,10-phenanthroline ,$C_{12}H_8N_2$.

- Sodium bicarbonate, $NaHCO_3$.

- Distilled water.

- Buffer solution, PH=2.4 ,4 ,7 ,10.

- Ethanol , C_2H_6O.

- Ferrous ammonium sulfate hexahydrate ,$Fe(NH_4)_2.6H_2O$.

- Calcium nitrate di hydrate , $CaNO_3.2H_2O$.

- Zinc ,Zn .

- Cobalt(II) chloride hexa hydrate , $CoCl_2.6H_2O$.

- Nickel(II) nitrate hexa hydrate , $Ni(NO_3)_2.6H_2O$.

- Manganese dioxide , MnO_2.

- Caber(II) chloride hexa hydrate , $CuCl_2.6H_2O$.

- Aluminum , AL .

3.3 PREPARATION OF SOLUTIONS:

3.3.1 PREPARATION OF 5-NITRO 1, 10-PHENANTHROLINE:

5g 1, 10-phenanthroline in 25ml oleum was heated to 110-115 C▯ and 7 ml nitric acid was added. The reaction mixture was then refluxed at 145 C▯ while 14 ml of nitric acid was being added over 30 minutes. at the end of addition the reaction temperature was reduced and maintained at 115 C▯ while stiring further for 45 min ,the mixture was cooled to room temperature and poured onto 1000 ml ice water. Upon neutralization with sodium hydrogen carbonate the solution turned pale yellow in color and subsequently,a pale yellow precipitate slowly settled down. The precipitate was removed by filtration, thoroughly washed with water and dried.

3.3.2 PREPARATION OF STOCK SOLUTION of iron :

Stock solution of iron (II) 1000 ppm was prepared by dissolving 7.01g of ferrous ammonium sulphate hexahydrate in distilled water and 2 ml of concentrated sulphuric acid were added then the volume was completed to 1L in volumetric fllask

3.3.3 PREPARATION OF STANDARD SOLUTION of iron:

The standard solution 100 ,50 ,10 ,1 ,0.1 ,and 0.01 ppm were prepared by dilution 10 ml of buffer solution pH 2.4 and 2ml of 5-nitro 1,10-phenanthroline which is prepared by dissolving 5.63g in ethanol were added.

3.3.4 THE LINEARITY OF CONCENTRATION:

The standard solution of iron (II) 50 ,40 ,30 ,20, and 10 ppm containing 10 ml buffer solution pH 2.4 and 2ml of 5-nitro 1,10- phenanthroline ,was measured at wave length 580 nm and calibration curve was prepared.

The same procdure was repeated by using another concentration rang 10 ,8 ,6 ,4 and 2 ppm and 1 ,0.8 ,0.6 ,0.4 and 0.2 ppm.

3.3.5 EFFECT OF THE PH ON COPLEX FORMATION :

standard solution of different concentration stander of iron (II) solutions 100 , 50 , 10 , 1 , 0.1, and 0.01 ppm were prepared by dilution .

2ml of 5-nitro 1, 10-phenanthroline and 10 ml of buffer solution at pH= 2.4 were added. This was repeated for pH 4 ,7 ,and 10 to test the effect of pH in complex formation .

The result were recovered in table 4.

3.3.6 DETERMINATION OF λ MAX :

The spectrophotometer was calibrated with blank solution (5-nitro 1, 10 -phenanthroline solution, buffer solution pH 2.4, and distilled water), then the absorbance of iron (II) solution (10ppm) was measured and λmax was determined .

The result were recovered in table 4.

3.3.7 THE EFFECT OF CONCENTRATION:

The absorbance's of different concentration of iron (II) solutions (100 ,50 ,10 ,1 ,0.1 ,0.01)ppm were measured at wave length 580 nm by spectrophotometer and calibration curve was prepared.

Results were tabulated in table 4..

3.3.8 THE INTERFERENCES EFFECT:

Standard solution's (0.1M) of calcium, cobalt, aluminum, manganese, copper, zinc, and nickel were prepared by dissolving their salts (calcium nitrate di hydrate ,coblalt (II) chloride hexa hydrate ,nickel (II) nitrate hexa hydrate , manganese di oxide ,aluminum ,and copper (II) chloride hexa hydrate) in distilled water, buffer solutions (pH= 2.4 , 4 , 7 and 10)and 5-nitro 1, 10-phenanthroline solution were added .

The complex formation for each metal was recorded.

4.1 RESULTS

Table (4.1)

The linearity of concentration:

In the rang between 0.1 and 0.6 ppm

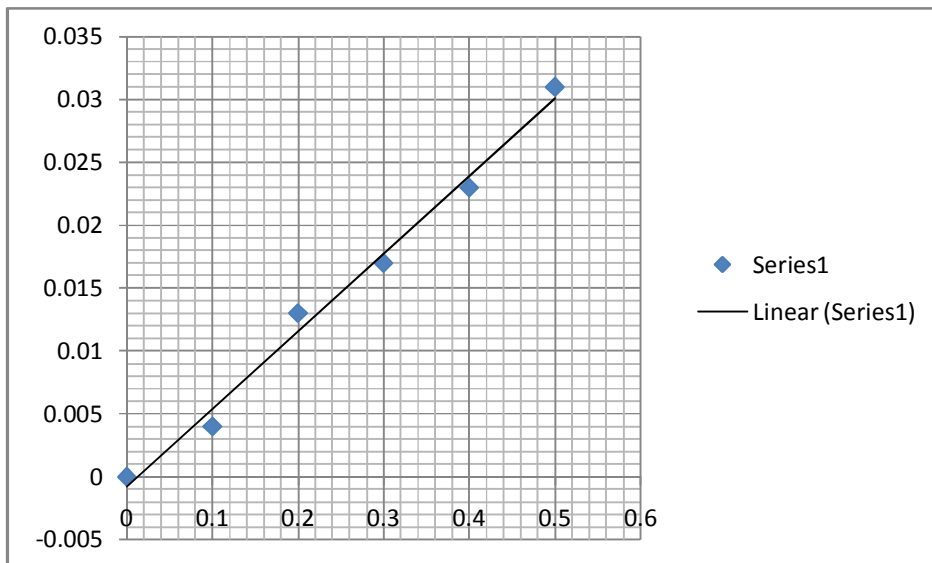| C/ppm	Abs
0.0	0.000
0.1	0.004
0.2	0.013
0.3	0.017
0.4	0.023
0.5	0.031
0.6	0.035

Fugure (6) shows relation between concentration & absorbance

Table (4.2)

The rang between 0.1 & 1 ppm

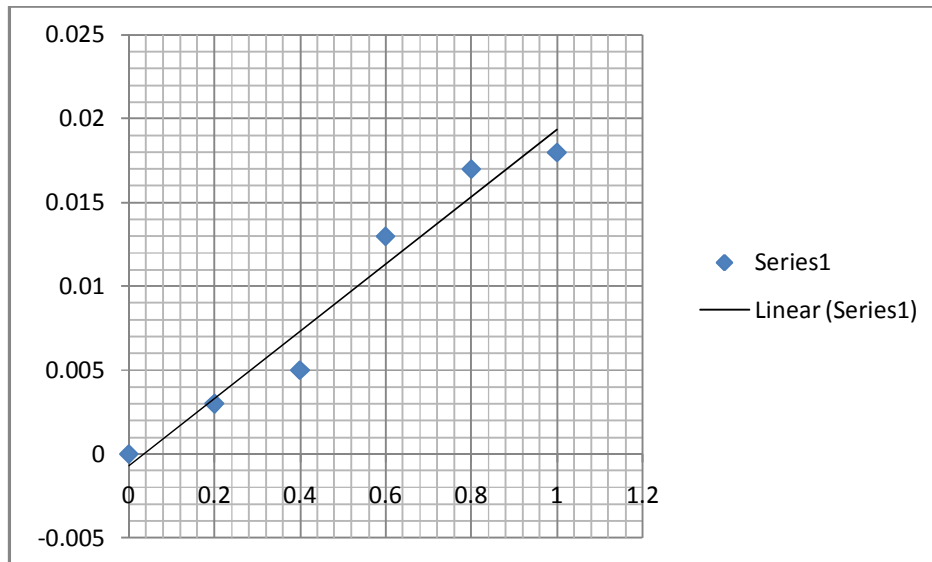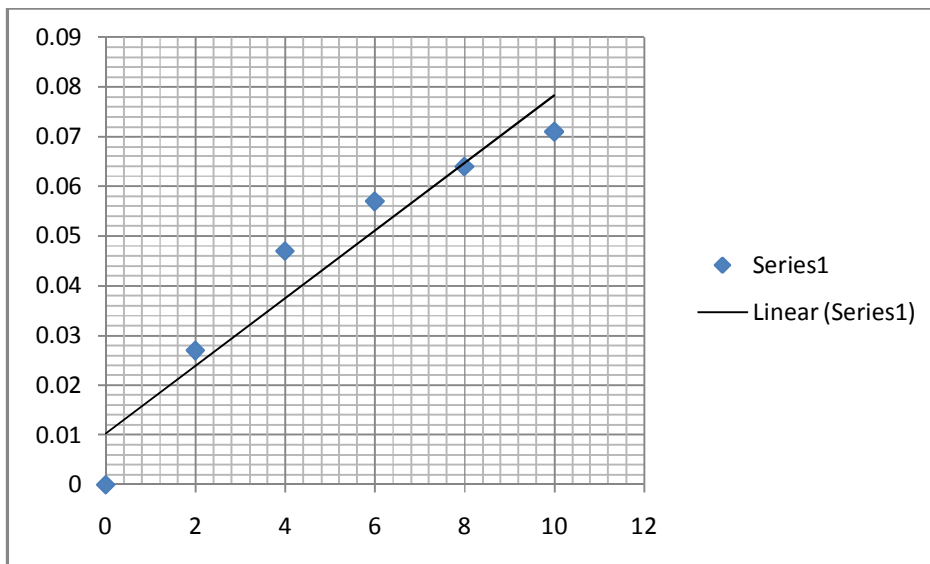| Concentration of iron /ppm	Abs
0.0	0.000
0.2	0.003
0.4	0.005
0.6	0.013
0.8	0.017
1.0	0.018

Figure (7) shows relation between concentration & absorbance

Table (4.3)

The rang of concentration from 1 to 10 ppm

Concentration of iron /ppm	Abs
0	0.000
2	0.027
4	0.047
6	0.057
8	0.064
10	0.071

Figure (8) shows relation between concentration & absorbance

Table (4.4)

The rang of concentration from 10 to 50 ppm

Concentration of iron /ppm	Abs
0	0.000
10	0.072
20	0.092
30	0.097
40	0.101
50	0.105
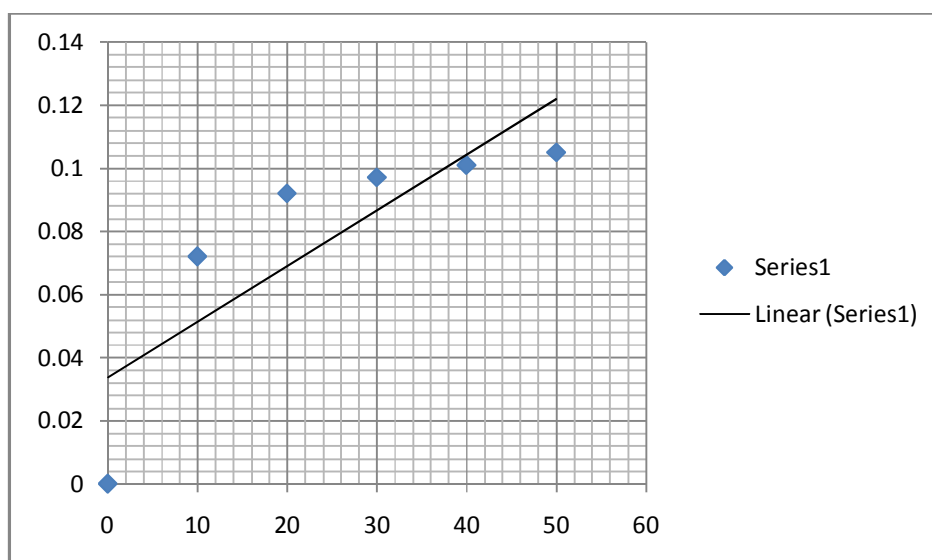
Figure (9) shows relation between concentration & abcorbance

Table (4.5)

pH effect on complex formation

PH	2.4	4	7	10
Result	Complex formation	Complex formation and precipitate in lower concentration	A precipitate was formed	A precipitate was formed

Table (4.6)

DETERMINATION OF λ MAX:

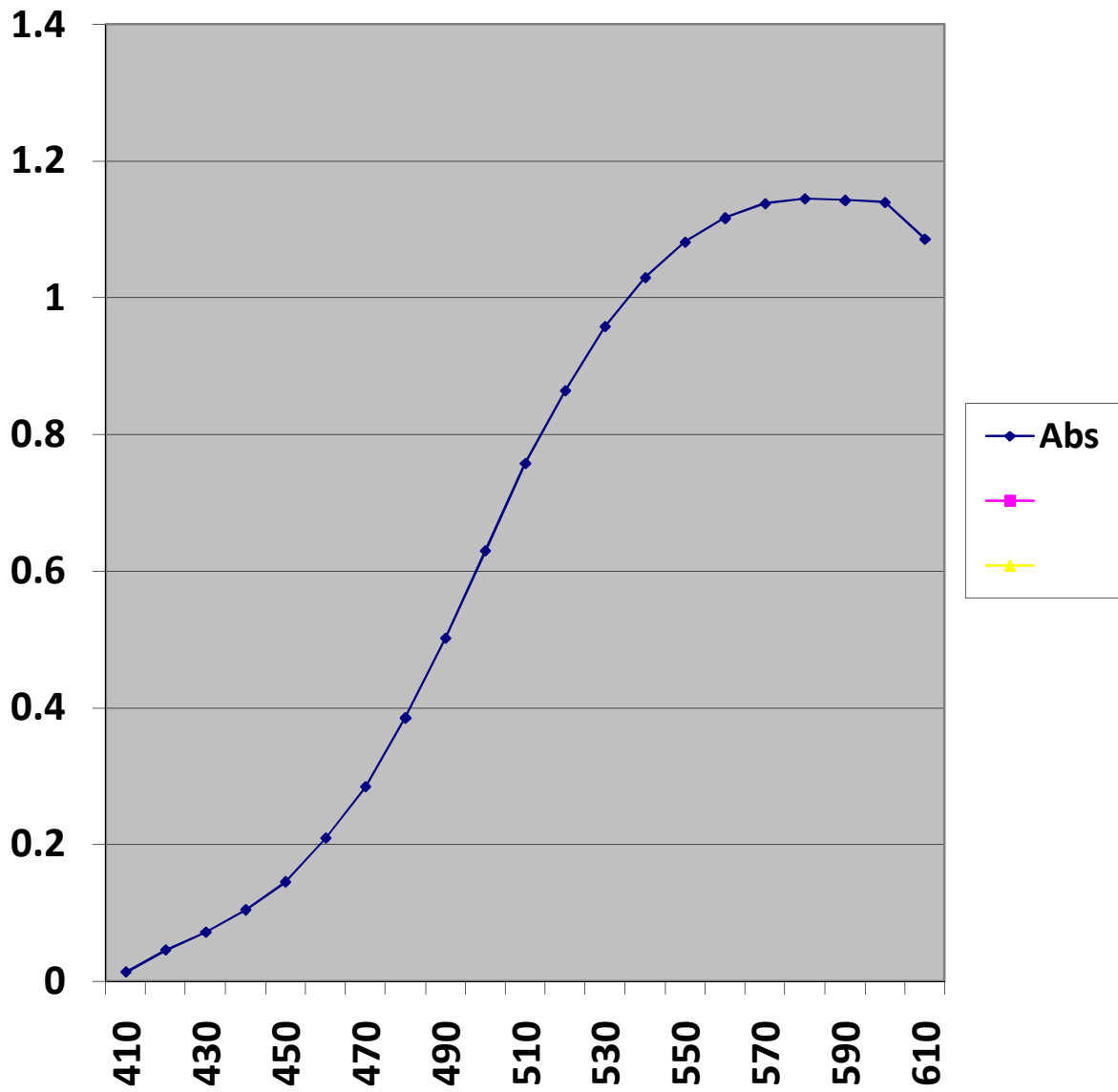| Wave length \nm	Abs	510	0.758
410	0.013	520	0.864
420	0.045	530	0.958
430	0.071	540	1.030
440	0.104	550	1.082
450	0.145	560	1.117
460	0.209	570	1.138
470	0.284	580	1.145
480	0.385	590	1.143
490	0.502	600	1.140
500	0.630	610	1.086

figure (10) shows relation between wave length & absorbance

Table (4.7)

THE EFFECT OF CONCENTRATION on complex formation between Fe(II) & 5 NPT:

Concentration of iron /ppm	Abs
0.00	0.000
0.01	0.001
0.1	0.004
1	0.033
10	0.134
50	0.164
100	0.165
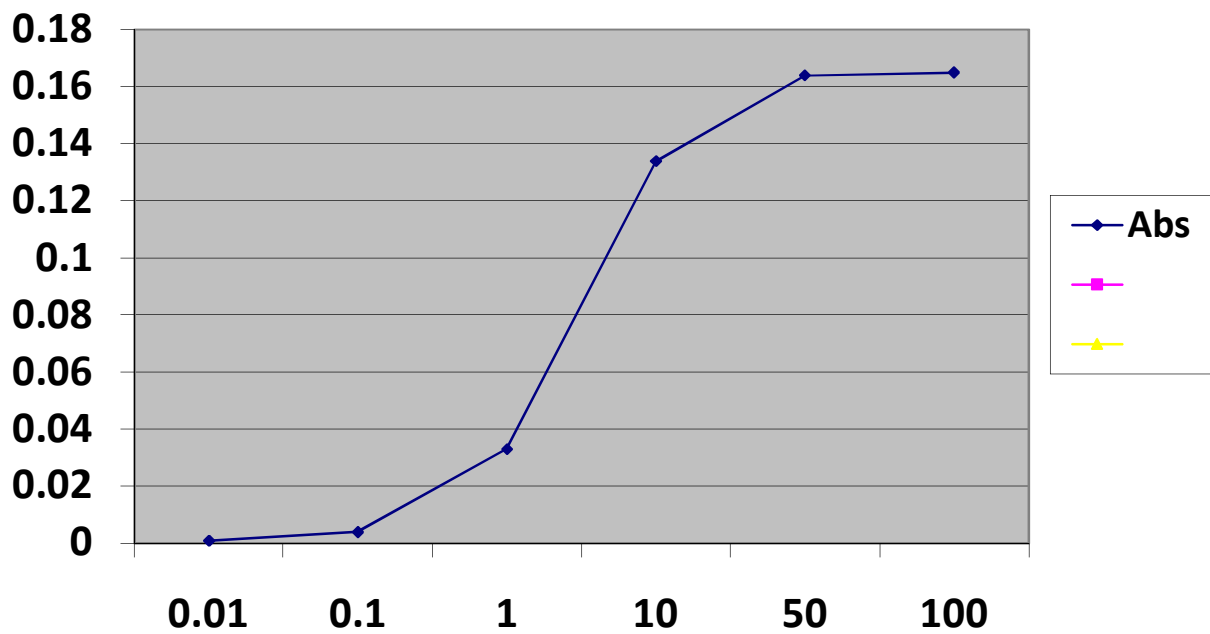
Figure (11) shows relation between concentration & absorbance

THE INTERFERENCES EFFECT:

Table (4.8)

    At PH=2.4

Ca	Zn	Co	Ni	Mn	Cu	Al
—	Complex Formation	—	—	—	—	—

Table (4.9)

    At PH=4

Ca	Zn	Co	Ni	Mn	Cu	Al
—	—	—	—	—	—	—

Table (4.10)

    At PH=10

Ca	Zn	Co	Ni	Mn	Cu	Al
—	—	—	—	—	—	—

4.1.1 PREPARATION OF 5-NITRO 1,10-PHENANTHROLINE:

The 5-nitro 1,10-phenanthroline was prepared with yield =4.25g (68%).

$HNO_3 + H_2SO_4$ -------- $NO_2 + H_2O$

NO₂ ₊
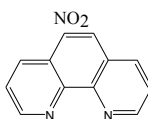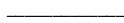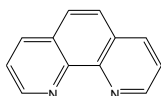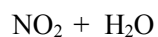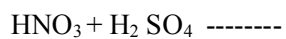
4.2 Results Discussions:

The complex formation between Fe (II) and 5-nitro1, 10-phenanthroline was performed in ethanol because the 5-nitro 1, 10-phnanthroline insoluble in water and it is soluble in ethanol.

The absorption spectrum of the product showed maximum at 580 nm.

4.2.1 Effect of the pH:

The procedure was repeated at different pH values between 2.4 and 10 with concentration of iron (II) solution, the complex is stable at PH=2.4 and at pH 4 a precipitate was formed, at pH 7 and 10 no complex formed.

The complex formed only at strong acidic medium.

4.2.2 Effect of concentration:

From the result it is clear that stable complex is formed at low concentration less than 1.0.ppm as this rang (0.2 – 0.6) ppm gives a linearity in this rang.

4.2.3 Interference study:

A number of transition earth alkaline and earth metal ion were studied for their possible interference in the determination of iron(II) .Zn(II) interfere weakly at pH2.4 only , the other ions Co, Cu, Al, Ca, Mn, Ni do not interfere in all tested pH method that refer to inductive effect of nitro group which decrees the reactivity of the cycle in chelating agent .

The conclusion, this method can be applied for the analysis of iron(II) even in presence of other ions as 5 NPT is selective for iron(II) .

5.1 Conclusion:

A new simple, sensitive and inexpensive method of iron complex was developed for the determination of iron in some industrial, biological, water, and environmental samples to control the levels of iron in different sample. It offers also a very efficient procedure for speciation analysis although many sophisticated techniques such as pulse plorography, HPLC, AAS, ICP-AES and ICP-MS are available for determination of iron at trace levels in numerous complex materials .Factors such as the low cost of the instrument, easy, handling, lack of requirement for consumable and almost no maintenance have caused spectrophotometry to remain a popular technique, particularly in laboratories in developing countries with limited budgets.

The sensitivity in terms of molar absorptivity and precision terms of present method are very reliable for determination of iron in real samples down to 0.01 ppm in aqueous medium at room temperature (25 ± 5 C□).

After all experiments and tests we had done during this project which concerned of analysis of iron with derivative of 1,10-phenanthroline using spectrophotometric method ,if we want to analysis iron using 1,10-phenanthroline derivative the optimum potential of hydrogen pH of medium must be acidic , exactly between 2.4 to 4 ,this value of pH will give us a stable complex to complete the analysis process.

The suitable wave length to the complex was found 580 nm , in this wave length we will gain an accurate results for absorbance of complex, we strongly advocate that before the analysis process we must separate any element which maybe formed any interference with iron complex such as Zinc (Zn).

5.2 Recommendation:

Further studies can be carried to test the selectivity of 5NPT for other metals such as Zn , Cd , Cr ,and pb.

The derivative was prepared but further studies can be carried for analysis of this derivative by using FTIR or other chromatograph techniques .

To study or solving the problem of precipitate formation at high pH .

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