



بسم الله الرحمن الرحيم

Shendi University

College of Post Graduate Studies

and Scientific research

**Synthesis and Characterization of Some Schiff Bases Metal
Complexes and their applications in Analytical Chemistry**

تحضير و توصيف بعض معقدات قواعد شيفف الفلزية

وتطبيقاتها في الكيمياء التحليلية

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M.Sc. in Chemistry

By:

Alaa Mohamed Osman Ali Bakheet

B. Sc. Chemistry

Supervisor: Dr. Ahmed Mohamed Ahmed Emam

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الآية

بسم الله الرحمن الرحيم

قال تعالى:

(لَا يُكَلِّفُ اللَّهُ نَفْسًا إِلَّا وُسْعَهَا لَهَا مَا كَسَبَتْ وَعَلَيْهَا مَا اكْتَسَبَتْ رَبَّنَا لَا تُؤَاخِذْنَا
إِنْ نَسِينَا أَوْ أَخْطَأْنَا رَبَّنَا وَلَا تَحْمِلْ عَلَيْنَا إَصْرًا كَمَا حَمَلْتَهُ عَلَى الَّذِينَ مِنْ قَبْلِنَا رَبَّنَا
وَلَا تُحْمِلْنَا مَا لَا طَاقَةَ لَنَا بِهِ وَاعْفُ عَنَّا وَارْحَمْنَا أَنْتَ مَوْلَانَا فَانصُرْنَا عَلَى
الْقَوْمِ الْكَافِرِينَ)

صدق الله العظيم

سورة البقرة الآية (286)

Dedication

to

my family

Acknowledgment

First of all my sincere thanks to Allah almighty for helping me to complete this work.

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Abstract

Three Schiff's bases were synthesized, Benzylidene aniline (BA), Salicylidene aniline (SA), Benzophenone aniline (BPhA). The three compounds were synthesized by condensation of aniline with benzaldehyde, salicylaldehyde and benzophenone respectively, in methanol.

These Schiff's bases were identified using IR spectrum, nitrogen content, melting point, and their applications as analytical reagent were investigated using UV/VIS spectrophotometer. The following metal ions Cu(II), Cr(III), Co(II), Fe(III) and Zn(II) were scanned with these reagents

The optimum conditions of the practical analytical application of each Schiff's base with these metal ions were studied. These complexes gave higher absorbance in basic medium.

The effect of some foreign metal ions was studied. A serious interference was observed from Zn(II) in the determination of Cu(II)-BPhA.

On the other hand, it was found the minimum interference was observed from Co(II) in the determination of Cu(II)-BA, from Fe(II) in the determination of Co(II)-SA, from Fe(III) in the determination of Co(II)-BPhA.

No interference was observed from Cu(II) in the determination of Co(II)-BA, from Co(II) in the determination of Fe(III)-SA, from Cu(II) in the determination of Zn(II)-BPhA, from Co(II) in the determination of Fe(III)-BPhA, Cr(III) in the determination of Co(II)-SA and Co(II) in the determination of Cr(III)-SA.

ملخص البحث

تم تحضير ثلاثة مركبات من قواعد شيف، بنزالدين انلين، سلسلدين انلين، بنزوفينون انلين. هذه الثلاثة مركبات تم تحضيرها بتكاثف الانلين مع البنزالدهيد، سلسلدهيد وبنزوفينون في الميثانول.

وقد تم التعرف علي قواعد شيف عن طريق تحديد طيف الاشعة تحت الحمراء، نسبة النتروجين، درجة الانصهار وتم دراستها ككواشف تحليلية باستخدام مطيافية الاشعة فوق البنفسجية والمرئية.

ايونات المعادن التالية: النحاس (II) ، الكروم (III) ، الكوبالت (II) ، الحديد (III) ، والزنك (II) تم دراستها مع هذه المركبات.

تم دراسة الظروف المثالية للمركبات الثلاثة مع ايونات هذه المعادن. هذه المعقدات اعطت أعلى امتصاصية في وسط قاعدي.

تمت دراسة تأثير تداخلات بعض الايونات الخارجية. لوحظت تداخلات واضحة عند حساب معقد النحاس-بنزوفينون انيلين في وجود الخارصين.

و بعضها اظهرت تداخل قليل عند حساب معقد النحاس-بنزالدين انيلين في وجود الكوبالت، كوبالت-سلسلدين انيلين في وجود الحديد و كوبالت- بنزوفينون انيلين في وجود الحديد.

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Chapter One

Chapter One

Introduction

1.1 Coordination Chemistry

Coordination Chemistry is one of the most advanced and active research fields in inorganic Chemistry. This branch of Chemistry received much attention and offered fruitful results and hence this has become extremely attractive field of research. The first exploration of coordinated metal complexes dates back to the nineteenth century, during the days of Alfred Werner who is the father of coordination chemistry. Thereafter, the inorganic chemistry witnessed a great outflow of coordination compounds, with unique structural characteristics and diverse applications. The rapid development in the field of coordination chemistry has been dominating among the various research fields in inorganic chemistry. Many metal ions form aggregate with Lewis bases which are stable in solution, such species are known as coordination compounds or complex compounds. A complex may be positive ion, a negative ion or even neutral. It depends upon the charge of the metal ion and the donor ^[1].

Coordination compounds contain a central metal ion surrounded by a set of molecules or ions known as ligands and capable of existing independently. A ligand is a molecule or ion that can donate an electron pair to the central metal ion. The nature of the coordination compounds depends on the metal ion and donor atom, the structure of the ligand and the metal-ligand interaction ^[2].

1.2 Coordination number

The total number of points of attachment to the central element is termed the coordination number and this can vary from 2 to as many as 16. In simple terms, the coordination number of a complex is influenced by the relative sizes of the metal ion and the ligands and by electronic factors, such as charge which is dependent on the electronic configuration of the metal ion. These competing effects are described by the term ionic potential which is defined as the charge to radius ratio. Based on this, it can be seen that the bigger the charge on the central ion, the more attraction there will be for negatively charged ligands, however at the same time, the bigger the charge the smaller the ion becomes which then limits the number of groups able to coordinate^[3].

The most common coordination numbers are 2, 4 and 6. Odd coordination numbers (1, 3, 5, 7, and 9) are rare^[4].

1.2.1 Classification of structure in terms of coordination number:

i. Coordination number (2)

Two-coordinate bond directed at 180° angle, the structure is linear, examples: CuCl_2 , $[\text{Ag}(\text{NH}_3)_2]^+$ and $[\text{Au}(\text{CN})_2]^-$.

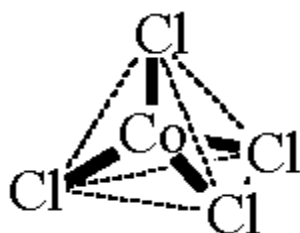


ii. Coordination number (4)

Four-coordinate bond, metal complexes may have either of two different geometries:-

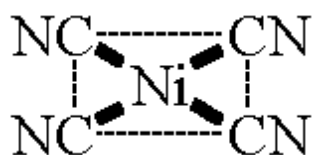
-**Tetrahedron:** Bonds direct towards the corners of regular tetrahedron.

Examples: $[\text{Zn}(\text{NH}_3)_4]^{+2}$ and $[\text{CoCl}_4]^{-2}$.



-**Square planar:** the four bonds direct towards the corners of the square.

Examples: $[\text{Pt}(\text{NH}_3)]^{+2}$ and $[\text{Ni}(\text{CN})_4]^{-2}$.



Geometric isomerism (cis and trans) can occur with square planar of the type Ma_2b_2 or Ma_2bc (where M refers to the central metal ion and a, b and c are different ligands). This does not occur in tetrahedral complex because all position of ligands equivalent.

iii. Coordination number (6)

The six ligands surrounding the central metal ion in a complex such as $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{Pt}(\text{Cl})_6]^{3-}$ and $[\text{Co}(\text{NH}_3)]^{+3}$ are located at corners of regular octahedron. Geometric isomerism can occur in octahedral complex such an example is $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ can exist in cis and trans. These two isomers differ in their physical and chemical properties.

The most striking difference is colour, the cis complex tend to be violet while trans is green ^[5].



1.3 Stability of Complexes

In recent years a number of attempts have been made to correlate the stability constants of metal chelates with various properties of either the metal ion or ligand in order to evaluate the factors affecting metal chelate stability. One of the most extensive is Pearson's classification into hard and soft ligand and metal ion. The metal ions are classified as hard or soft acids, and the ligand as hard or soft bases; the generalization about stabilities is then that soft ligands form stable complexes with soft metal ions; stable, hard-ligand hard-ion complexes are also stable. Mixtures of hard-ion soft-ligand or soft-ion hard-ligand are less stable. For metal complexes with multidentate ligands, the stability of the metal chelate is in part governed by the chelate structure. The type of the ligand has a distinct influence on the stabilities of complexes, in an extended form of the series, the stabilities of complexes by a particular chelating molecule with a series of metal atoms was first discovered by Mellor and Mally (1948), for the bivalent metals, they found an order, as, $\text{Cu} > \text{Ni} > \text{Co} > \text{Zn} > \text{Cd}$ ^[6].

1.4 The central metal ion

The central metal ion is the metal ion to which the ligands are attached at the centre of coordination sphere ^[7]. The bond between the metal ion and a ligand shows high dependency on the properties of the metal atom. The most important of these properties are the size of metal atom, its ionic charge, atomic number, electronic configuration, electro negativity and ionization potential. These properties govern the relative tendencies for various metal to combine with a given donor atom ^[8].

1.5 Transition metals

Transition metals may be strictly defined as those have partly filled d or f orbital's. Here the definition adopted is slightly broader and include also elements that have partly filled d or f shell in one of their commonly occurring oxidation states, this means that the coinage, Cu , Ag and Au treated as transition metals , since Cu^{+2} has $3d^9$ configuration , Ag^{+2} a $4d^9$ configuration and Au^{+3} a $5d^8$ configuration.^[9]

The large number of transition elements is subdivided into three main groups: (i) the main transition elements or d-block elements, (ii) the lanthanide elements and (iii) the actinide elements. ^[9]

Transition elements are metallic elements that serve as a bridge or transition between the two sides of periodic table S-block and P-block ^[10].

1.5.1 Transition metals properties

- Low ionization energies.
- Positive oxidation states.
- Multiple oxidation states, since there is a low energy gap between them.
- Very hard.
- Exhibit metallic luster.

- High melting points.
- High boiling points.
- High electrical conductivity.
- High thermal conductivity.
- Malleable.
- Form colored compounds, due to d-d electronic transitions.
- Five *d* orbital become more filled, from left to right on periodic table.

- Typically form paramagnetic compounds because of the unpaired d electrons.
- Typically exhibit high catalytic activity.
- Form stable complexes ^[11].

1.5.2 Effect of metal ions

Ions of the transition elements have a tendency towards the formation of complexes containing coordinate bonds, and these complexes are apparently more stable than those formed by electrostatic forces. The tendency to form coordinate compounds is indeed, one of the most fundamental inorganic properties of both organic and inorganic molecules. The radii of the transition metal cations are less than the radii of cations which are isoelectronic with inert gases. This may account, in part for the greater stability of the transition ion complexes.

According to Pauling the inner 3d orbitals of the transition elements have about the same energy as the 4s and 4p orbitals of the valence shell, and if they are not completely occupied by unshared electron pairs, they play a very important part in bond formation. The formation of complex ions by coordinate bonds appears to follow two general rules:

- i. The central ion tends to accept electrons to fill incomplete stable orbitals.
- ii. The central ion tends to accept sufficient coordinated molecules. Or ions to produce a symmetrical structure of molecules packed round the central ions ^[12].

1.6 The metals used

1.6.1 Copper (Cu)

Physical properties of Copper (Cu)

An important physical property of copper is its color. In fact, people often refer to anything with a reddish-brown tint as being copper colored. Copper metal is fairly soft and ductile. Ductile means capable of being drawn into wires. Both heat and electricity pass through copper very easily. The high electrical conductivity makes it ideal for many electrical purposes. Copper has a melting point of 1083 C° and a boiling point of 2595 C° . Its density is 8.96 grams per cubic centimetre.

Chemical properties of Copper (Cu)

Copper is a moderately active metal. It dissolves in most acids and in alkalis. An alkali is a chemical with properties opposite those of an acid. Sodium hydroxide, commonly found in bleach and drain cleaners, is an example of an alkali. An important chemical property of copper is the way it reacts with oxygen. In moist air, it combines with water and carbon dioxide. The product of this reaction is called hydrated copper carbonate ($\text{Cu}_2(\text{OH})_2\text{CO}_3$). This compound has a beautiful greenish color, called a patina. Copper roofs eventually develop this color ^[13].

Copper: It is having single electron outside the completed 3d shell, exhibits oxidation states of +1, +2 and +3. The most common oxidation state is +2. The $3d^9$ configuration makes Cu(II) susceptible to Jahn-Teller distortion when placed in environment of cubic symmetry i.e. regular octahedral or tetrahedral and this has performed effect on its stereochemistry. All the hexacoordinated Cu(II) complex structures of which have been established by X-ray technique are found to be affected from tetragonal distortion due to Jahn-Teller distortion ^[14].

1.6.2 Cobalt (Co)

Physical properties of Cobalt (Co)

Cobalt is a hard, gray metal that looks much like iron and nickel. It is ductile, but only moderately malleable. Malleable means capable of being hammered into thin sheets. Cobalt is one of only three naturally occurring magnetic metals. The other two are iron and nickel. The magnetic properties of cobalt are even more obvious in alloys. An alloy is made by melting and mixing two or more metals. The mixture has properties different from those of the individual metals.

The melting point of cobalt metal is 1493 C° , and the boiling point is about 3100 C° . The density is 8.9 grams per cubic centimetre.

Chemical properties of Cobalt (Co)

Cobalt is a moderately reactive element. It combines slowly with oxygen in the air, but does not catch fire and burn unless it is in a powder form. It reacts with most acids to produce hydrogen gas. It does not react with water at room temperatures ^[15].

Cobalt it exhibits various oxidation states ranging from +1 to +5. The most common oxidation states are +2 and +3. The cobalt compounds exhibits variable coordination number, geometry, stability etc. Literature survey reveals that Co(II) is basically associated with different type of stereo chemical configurations such as tetrahedral, octahedral and square planar ^[16].

1.6.3 Chromium (Cr)

Physical properties of Chromium (Cr)

Chromium is a hard, steel-gray, shiny, metal that breaks easily. It has a melting point of 1900 C° and a boiling point of 2642 C° . The density is 7.1 grams per cubic centimetre. One important property is that chromium can be polished to a high shine.

Chemical properties of Chromium (Cr)

Chromium is a fairly active metal. It does not react with water, but reacts with most acids. It combines with oxygen at room temperature to form chromium oxide (Cr_2O_3). Chromium oxide forms a thin layer on the surface of the metal, protecting it from further corrosion (rusting) ^[17].

1.6.4 Iron (Fe)

Physical properties of Iron (Fe)

Iron is a silvery-white or grayish metal. It is ductile and malleable. Ductile means capable of being drawn into thin wires. It is naturally occurring magnetic elements. Iron has a very high tensile strength. Tensile means it can be stretched without breaking. Iron is also very workable. Workability is the ability to bend, roll, hammer, cut, shape, form, and otherwise work with a metal to get it into a desired shape or thickness.

The melting point of pure iron is 1536 C° and its boiling point is about 3000 C° . Its density is 7.87 grams per cubic centimetre. The melting point, boiling point, and other physical properties of steel alloys may be quite different from those of pure iron.

Chemical properties of Iron (Fe)

Iron is a very active metal. It readily combines with oxygen in moist air. The product of this reaction, iron oxide (Fe_2O_3), is known as rust. Iron also reacts with very hot water and steam to produce hydrogen gas. It also dissolves in most acids and reacts with many other elements [18].

1.6.5 Zinc (Zn)

Physical properties of Zinc (Zn)

Zinc is a bluish-white metal with a shiny surface. It is neither ductile nor malleable at room temperature. At temperatures above 100 C° , however, zinc becomes somewhat malleable.

Zinc's melting point is 419.5 C° and its boiling point is 908 C° . Its density is 7.14 grams per cubic centimetre. Zinc is a fairly soft metal. Its hardness is 2.5 on the Mohs scale. The Mohs scale is a way of expressing the hardness of a material. It runs from 0 (for talc) to 10 (for diamond).

Chemical properties of Zinc (Zn)

Zinc is a fairly active element. It dissolves in both acids and alkalis. Zinc does not react with oxygen in dry air. In moist air, however, it reacts to form zinc carbonate. The zinc carbonate forms a thin white crust on the surface which prevents further reaction. Zinc burns in air with a bluish flame [19].

Zinc it shows oxidation states of +1 and +2. Zn(I) do not occur in the normal condition. Only spectroscopic species have been detected. Like Hg^{+2} , Zn^{+2} ions also exists. Zn(II) complexes are essentially diamagnetic due to filled d^{10} configuration. The complexes of Zn(II) can have coordination numbers 4, 5 and 6. It is invariably seen that Zinc forms only tetrahedral complexes with coordination number 4. Five coordinated complexes either possess square pyramidal or trigonal

bipyramidal structures with coordination number 5. Zn(II) complexes are octahedral when coordination number is 6 [20].

1.7 Ligand

In principle any molecule or anion with an unshared pair of electrons can donate them to a metal ion to form a coordinate covalent bond. The expected species, such as ammonia molecule, water molecule, hydroxide ion and the chloride ion to act as ligands [21].

Ligands that themselves can both donate or accept electrons, so that their own oxidation state is indistinct, make it difficult if not impossible to attribute unambiguous oxidation number to the metal atom. The extreme examples of such ligands are 1,2 dithiolene ligand, and many others such as NO, CO, CN and various phosphines are also capable of varying their net balance of donor and acceptor behavior toward a given metal atom, because of this the physical significance of the oxidation number assigned to the metal atom surrounded by such ligands becomes vague. A very cogent example is provided by the pair of ions $\text{Fe}(\text{CN})_6^{-3}$ and $\text{Fe}(\text{CN})_6^{-4}$, the formal oxidation state of the iron atoms are obviously +3 and +2 respectively, but detailed studies of Mossbauer and ESR spectra, coupled with molecular orbital treatment of the bonding, indicate that the effective charge residing on the metal atom is practically the same in the two cases [22].

1.7.1 Effect of Ligand

The nature of coordinating group varies considerably from inorganic to organic species. The hydroxide ion has strong coordinating tendency, partly because it has three pairs of unshared electrons, but chiefly because it is of negative charge. Many organic anions form stable coordination compounds, formate and acetate ions form strong bonds but monocarboxylic acids with longer chains show rapidly decreasing ability

to coordinate. The aliphatic monoamines coordinate less readily than does ammonia, the secondary amines coordinate less readily than the primary, and tertiary amines are almost devoid of ability to coordinate with metal ions. This is probably due to steric factors. Tertiary amines coordinate firmly with the hydrogen ion, that is they are strong bases ^[23].

1.7.2 Types of ligands

Ligands are classified, according to the number of electron pair donated to:

i. **monodentate ligands:**

Provide one electron pair per ligand molecule or ion. Monodentate (literally one toothed) because they bite the metal ion in only one place, typical monodentate ligands are:- F-, Cl-, I-, OH-, H₂O, NH₃. Such monodentate ligands form no chelate compounds ^[9].

ii. **Bidentate ligands** (two toothed):

That ligands furnish two electron pairs per molecule or ion ^[5]. For example ethylenediamine is bidentate ligand. It attaches to a metal by two nitrogen donor atoms.



iii. **Tridentate ligand:**

Diethylenetriamine



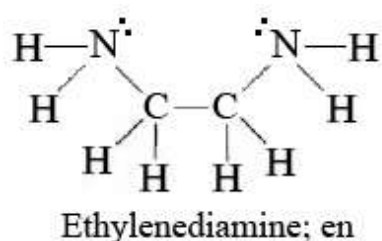
iv. **Hexadentate ligand:**

The general term polydentate is used for any ligand that supplies more than one pair of electrons.

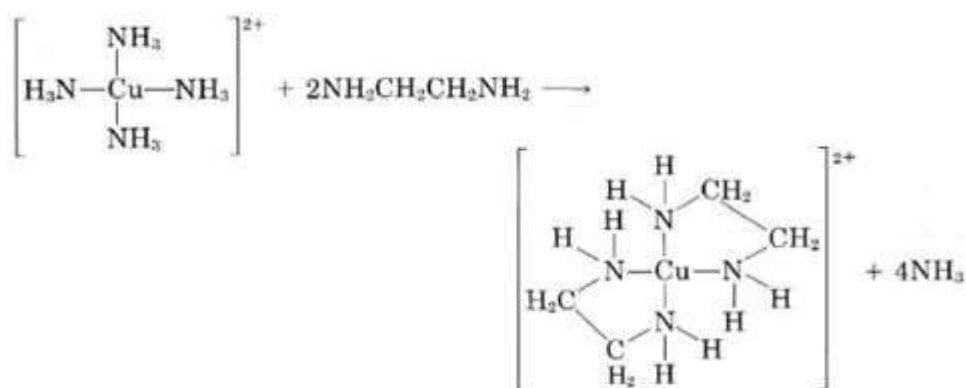
For example EDTA (Ethylenediaminetetraacetate)

1.7.3 Chelating agents

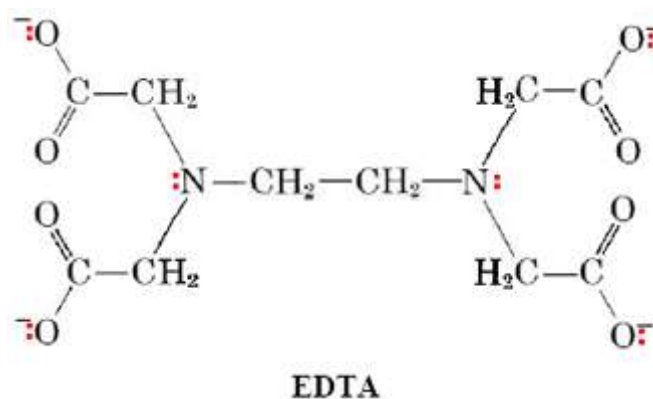
The complex form by polydentate ligands are often called chelate (Greek chela meaning crab's claw). For ligand to act as chelating agent it must have at least two pairs unshared of electrons, these two pairs must be far enough from one another to form a chelate ring with stable geometry ^[5] . One of the most common of these is 1,2-diaminoethane (usually called *ethylenediamine* and abbreviated *en*.)



A chelating agent who forms several bonds to a metal without unduly straining its own structure is usually able to replace a similar simpler ligand. For example, although both form coordinate covalent bonds via >N: groups, ethylenediamine can readily replace ammonia from most complexes:



For metals which display a coordination number of 6, an especially potent ligand is *ethylenediaminetetraacetate* ion (abbreviated EDTA):



All six electron pairs marked in color are capable of coordinating to a metal ion, in which case the EDTA ion wraps completely around the metal and is very difficult to dislodge. EDTA is used to treat lead and mercury poisoning because of its ability to chelate these metals and aid their removal from the body ^[24].

1.7.4 Linkage isomers

This rise from ambidentate ligands which define as: ligands with two or more different donor sites only one of which is attached to single metal atom at a given time. Examples:-

For NO_2 : $\text{M}-\text{NO}_2$ nitro attached through N.

: $\text{M}-\text{ONO}$ nitrito attached through O.

CN^- : Cyano($\text{M}-\text{CN}$) and isocyano ($\text{M}-\text{NC}$) .

NCS^- : thiocyanato($\text{M}-\text{SCN}$) and isothiocyanato ($\text{M}-\text{NCS}$) .

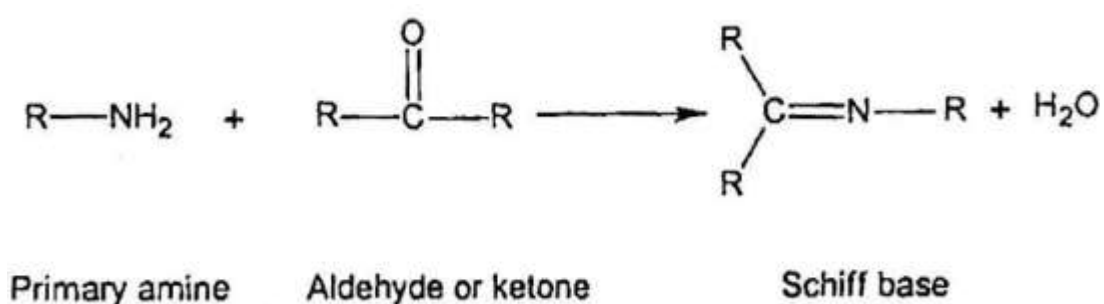
R_2SO : S-bond and O-bond.

If different donor atoms belong to the same ligand molecule the complex may be termed as mixed donor. If the different donor atoms belong to separate ligand molecules the complex may be termed mix ligand or ternary complex ^[25].

1.8 Schiff bases

Schiff bases are condensation products of primary amines and carbonyl compounds and they were discovered by a German chemist, Nobel Prize winner, Hugo Schiff in 1864 [26].

Structurally, Schiff base (also known as imine or azomethine) is an analogue of a ketone or aldehyde in which the carbonyl group (C=O) has been replaced by an imine or azomethine group (C=N-R) [27].

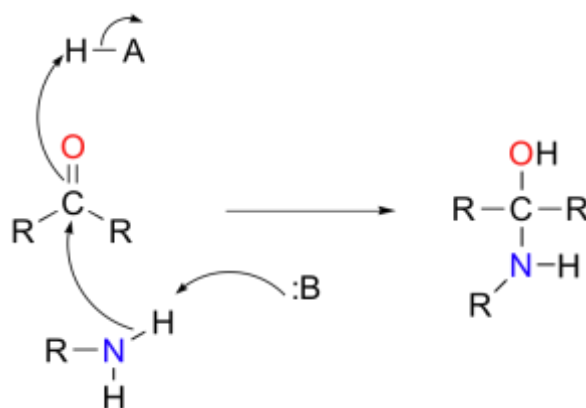


The resultant compound, R₁R₂C=NR₃ (Schiff base), where R₁ is an aryl group, R₂ is a hydrogen atom and R₃ is either an alkyl or aryl group. However, usually compounds where R₃ is an alkyl or aromatic group are also regarded as Schiff bases. Schiff bases that contain aryl substituent are substantially more stable and readily synthesised, while those which contain alkyl substituent are relatively unstable. Schiff bases of aliphatic aldehydes are relatively unstable and readily polymerisable [28].

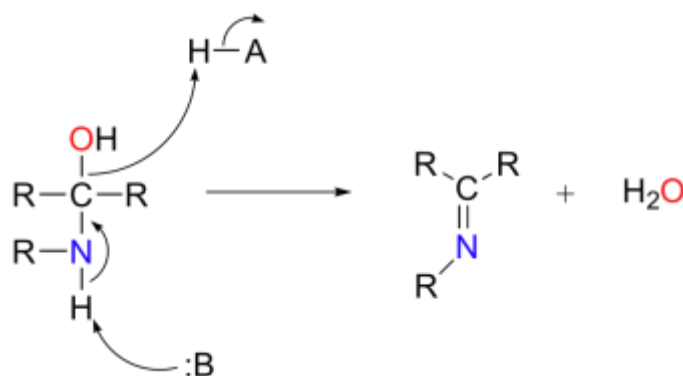
While those of aromatic aldehydes having effective conjugation are more stable. In general, aldehydes react faster than ketones in condensation reactions, leading to the formation of Schiff bases as the reaction centre of aldehydes are sterically less hindered than that of ketone. Furthermore, the extra carbon of ketone donates electron density to the azomethine carbon and thus makes the ketone less electrophilic compared to aldehydes [29].

1.8.1 Mechanism of reaction

Mechanistically, the formation of an imine involves two steps. First, the amine nitrogen acts as a nucleophile, attacking the carbonyl carbon.



The next step would be attack by a second amine to form a compound with a carbon bound to two amine groups – the nitrogen version of a ketal. Instead, what happens next is that the nitrogen is deprotonated, and the electrons from this N-H bond ‘push’ the oxygen off of the carbon, leaving us with a C=N double bond (an imine) and a displaced water molecule ^[30].



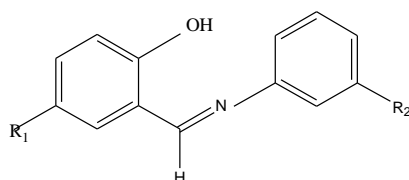
1.8.2 Classification of Schiff's bases

Schiff's bases are classified as monodentate, bidentate, tridentate, tetradentate and polydentate ligands containing O, N and S donor atoms.

Such type of donor site ligands have been tried for their complexation and the structures were deduced with the aid of analytical and spectral data.

1.8.2.1 Monodentate Schiff's bases

The basic strength of C=N group is not sufficient to obtain stable complexes by coordination of the imino nitrogen atom to the metal ion. Hence, the presence of at least one of the other group is required to stabilize metal-nitrogen bond. Aryl groups are attached to either O or N generally stabilizes the Schiff's base by resonance. Monoamine Schiff's base as *N*-Salicylidene -aniline derivatives [31].



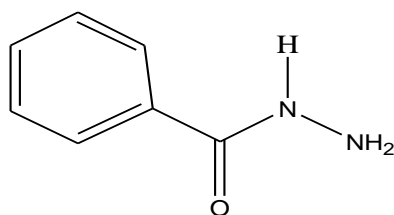
Monodentate Schiff's bases

1.8.2.2 Bidentate Schiff's bases

Bidentate Schiff's bases are the most useful ligands for preparing metal complexes. Potential bidentate ligands depending on their donor atom set has been given below.

N, O and N, N donor atom set

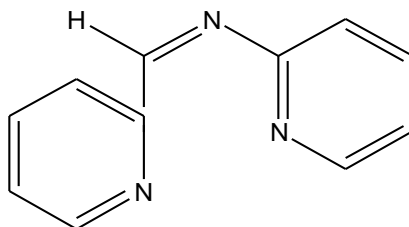
Numbers of metal complexes were synthesized by using Schiff's bases having N, O and N, N donor sets. Since in N, O donor set oxygen is often represented by OH group. These Schiff's bases generally act as chelating mono amines. Hydrazides have been synthesized and complexed with transition metals, both NH₂ and C=O groups are involved in the bond formation [32].



Bidentate Schiff's bases

1.8.2.3 Tridentate Schiff's bases

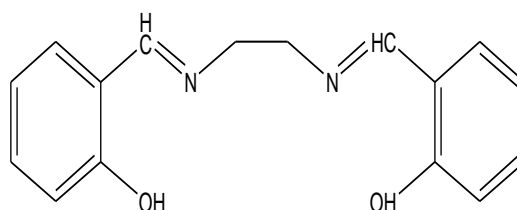
There are large number of tridentate Schiff's bases containing ONN, NNS, NOO and NSO donor sets. These may be generally derived from the bidentate analogous by the addition of another donor group. It must be pointed out that the oxygen donor atom of such ligands may often act as bridge between two metal centers giving polynuclear complexes of some tridentate ligands ^[33].



Tridentate Schiff's bases

1.8.2.4 Tetradentate Schiff's base

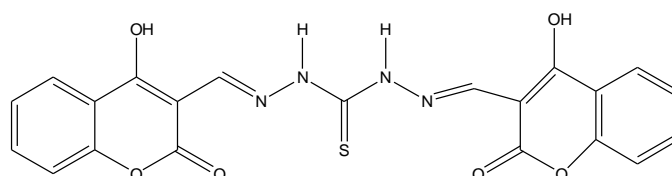
The Tetradentate Schiff's bases with N_2O_2 and N_2S_2 donor set have been studies for their ability to coordination with metal ions. The characterization of complexes obtained by their Schiff's base ligands are determined by electronic nature of the ligands as well as by their conformational behavior ^[34].



Tetradentate Schiff's base

1.8.2.5 polydentate Schiff's base

ligands containing O, N and S donor atoms.



polydentate Schiff's base

1.8.3 Applications of Schiff's bases

1.8.3.1 Applications of Schiff's bases in medicine and pharmacy

Imine complexes have a broad range of biological properties: antitumor, antiviral, antifungal, antibacterial ^[35]. They are also used in the treatment for diabetes and AIDS. As biological models, they help in understanding the structure of bio molecules and biological processes occurring in living organisms. They participate, interalia, in photosynthesis and oxygen transport in organisms. They are involved in the treatment of cancer drug resistance, and often tested as antimalarials. It also could be used for the immobilization of enzymes ^[36].

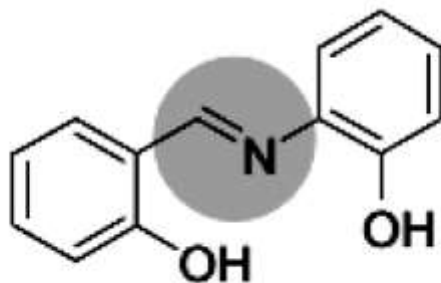
i. Biological activity

Schiff bases are characterized by an imine group -N=CH- , which helps to clarify the mechanism of transamination and racemisation reaction in biological system [26]. It exhibits antibacterial and antifungal effect in their biological properties. Metal-imine complexes have been widely investigated due to antitumor and herbicidal use. They can work as models for biologically important species [37].

ii. Antibacterial properties

Mortality increase caused by infectious diseases is directly related to the bacteria that have multiple resistances to antibiotics. The development of new antibacterial drugs enriched by innovatory and more effective mechanisms of action is clearly an urgent medical need [38].

Schiff bases are identified as promising antibacterial agents. For example, N-(Salicylidene)-2-hydroxyaniline is active against *Mycobacterium tuberculosis* [39].



N-(Salicylidene)-2-hydroxyaniline as the example of bioactive Schiff base

iii. Antifungal properties

Fungal infections usually are not only limited to the contamination of surface tissues. Recently, there was a considerable increase in the incidence of systemic fungal infections, which are potentially life threatening [40].

Exploration and development of more effective antifungal agents is necessity, and the individual Schiff bases are considered to be promising antifungal medicines ^[41].

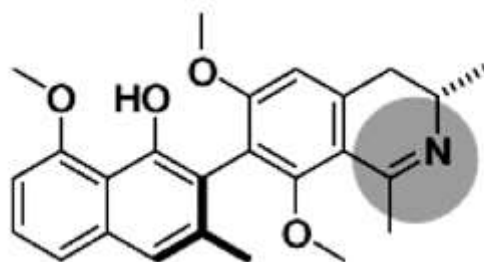
iv. Antiviral properties

The use of vaccines may lead to the eradication of pathogens known viruses, such as smallpox, poliomyelitis (polio), whether rubella. Although there are many therapeutic ways to work against viral infections, currently available antiviral agents are not fully effective, which is likely to cause a high rate of mutation of viruses and the possibility of side effects. Salicylaldehyde Schiff bases derived from 1-amino-3-hydroxyguanidine tosylate are good material for the design of new antiviral agents ^[42].

Isatin Schiff base ligands are marked by antiviral activity, and this fact is very useful in the treatment of HIV ^[43]. In addition, it was also found that these compounds have anticonvulsant activity and may be included in the anti-epileptic drugs ^[44]. Gossypol derivatives also present high antiviral activity. Increasingly, gossypol, often used in medical therapy is replaced by its derivatives, because of their much lower toxicity ^[45].

v. Antimalarial properties

Malaria is a disease which when is neglected causes serious health problems. Human malaria is largely caused by four species of the genus Plasmodium (P. falciparum, P. vivax, P. ovale and P. malariae). The search for new drugs, vaccines and insecticides for the prevention or treatment of this disease is a priority. Schiff bases are interesting compounds, which could be part of antimalarial drugs. For example, the compound with such effect is Ancistrocladidine which is a secondary metabolite produced by plants of the family Ancistrocladaceae and Dioncophyllaceae, and presenting an imine group in a molecular chain ^[42].



Ancistrocladaceae – antimalarial activity of bioactive Schiff base

vi. Anticancer properties

Some Schiff bases have a high antitumor activity. Imine derivatives of N-hydroxy-N'-aminoguanidine block ribonucleotide reductase in tumor cells, so that they are used in the treatment of leukaemia [46].

1.8.3.2 Applications of Schiff's bases chelates in classical analysis

Jungreis and Thabet have reported several applications for Schiff's bases in qualitative and quantitative classical analyses. All these applications did not cover a wide area in analytical chemistry.

Advances in analytical techniques and the development and application of new analytical reagents are as important in trace analyses as the development of analytical instruments. A number of Schiff's base chelating agents used for the detection of metal ions can also be applied for their quantitative determination. The procedures in most cases remain similar. The main step in the above applications is the complex formation which depends mainly on pH, temperature, cation size, and the structure of the ligand. Optimisation of these factors to enhance the stability of the complex leads to high selectivity of the developed analytical method [47].

i. Photometric methods

Developments in photometric methods have been extensive, particularly for the determination of trace amount of metals. A number of these procedures are based on color formation resulting from the reaction

between Schiff's base and the metal ion. For example, o-[N-(o-hydroxyphenyl)formimidoyl]phenol, known as Manganon, forms with manganese(II) at pH 9.1 to 11.6 a brown complex, the absorbance of which is measured at 428nm ^[48].

ii. Fluorometry

Fluorometric methods often provide excellent means for the detection and determination of inorganic ions. The reagents employed to produce fluorescence are often highly selective and very sensitive. In most cases a chelate is formed with the metal. There is often a dependence of fluorescence on the pH similar to that of acid-base fluorescence indicators. The analytical importance of such indicators lies in the fact that they make possible acid-base titrations in colored solutions when the use of conventional indicators would be precluded. Holzbecher reported that Schiff's bases obtained from salicylaldehyde and aniline fluoresce in the alkaline medium and therefore, can be used for titration of acids with bases ^[49].

iii. Schiff's bases as potentiometric sensors

Since the 1930s, potentiometric membrane sensors have found great practical applicability in different fields. The response mechanism of these sensors is based on the measurement of a potential under a zero current regime or a under a low electrical current flow. Potentiometric membrane sensors, which have been designed based on molecular recognition, contain a molecule that selectively recognizes another target species through various molecular interactions. As it is widely known, potentiometric electrodes possess as advantages the direct, simple, rapid, inexpensive and selective detection of ionic activities ^[50].

Ganjali et al. have prepared potentiometric sensors for Dy(III) based on a Bis-pyrrolidene Schiff's bases, the electrode has been also used in the

potentiometric determination of Fluoride ions in mouthwash by the titration against Dy(III) ^[51].

They also prepared a novel Bromide ion sensor based on Iron(III)-salen, this sensor has high Bromide selectivity over a wide variety of organic and inorganic anions, specially iodide, chloride and hydroxide ions ^[52].

iv. Schiff's bases as solvent extraction reagents

Solvent extraction separation is based on the differences in the solubility of elements and their compounds in two immiscible liquid phases. Usually, the initial phase is an aqueous solution and the second phase is an organic solvent immiscible with water. Extraction is usually fast and simple process; it demands only very simple equipments. Stripping (re-extraction, back-extraction or scrubbing) involves bringing the element from the organic extract back to the aqueous phase.

A solvent extraction using salophen was studied by Kim et al. and applied for trace determination of Ni(II), Co(II) and Cu(II) in water samples. The salophen is another type of salen derivative. Unlike the ethylenediamine of salen, salophen included a phenyldiamine as a backbone .

In another study the salophen has been used in solvent extraction for trace determination of Fe(II) and Fe(III) in water samples ^[53].

v. Schiff's bases as solid phase extraction (SPE) sorbents

The solid phase typically consists of small, porous particles of silica with a bonded organic phase or of an organic polymer, such as cross linked polystyrene. The extraction can take place in a batch mode in which the solid extractant is intimately mixed with liquid sample solution. In chemical analysis it is more common to pack the solid extractant into a small tube and pass the liquid sample through the tube ^[54].

The nature and properties of the sorbent are of prime importance for effective retention of metallic species. Careful choice of the sorbent is thus crucial to the development of SPE methodology.

Two approaches are used for loading the surface with specific organic compounds, chemical immobilization and physical adsorption. In the first case, a chemical bond is formed between the solid support surface groups and those of the organic compound (functionalized sorbent). In the second approach, the organic compound is directly adsorbed on the functional groups of the solid support surface (impregnated or loaded sorbent), either by passing the reagent solution through a column packed with the adsorbent, or by soaking the adsorbent in the reagent solution.

Ganjali et al. separated and pre-concentrated ultra-trace amounts of Cu(II) by solid phase extraction on octadecyl-bonded silica membrane disk modified with (Bis-(2 hydroxyacetophenone)-2,2-dimethyl-1,3-propanediimine) SBTD followed by elution and ICP-AES detection in environmental and biological samples, the concentration factor was 500 [55].

vi. Schiff's bases as High-Performance Liquid Chromatography (HPLC)

In the last few years the rapid development of high-performance (pressure) liquid chromatography (HPLC) has also extended the possibilities for chromatographic methods in inorganic analysis. In particular liquid chromatographic methods in columns are of great importance for those inorganic compounds which are not suitable for the usual gas chromatographic methods because of low volatility or low thermal stability [56].

Chromatographic methods are very suitable for the separation and determination of extractable metal chelates. Different types of ligands or groups of compounds are suitable for HPLC such Schiff base chelates, hydrazones, dithizonates, and metal dithiocarbamates. For these groups of substances principally reversed-phase and adsorption systems are

suitable; separations by reversed-phase systems are very well reproducible [57].

The separation of neutral copper and nickel chelates of two representative Schiff base ligands, N,N'-ethylenebis(acetylacetonimine) and N,N'-ethylenebis(salicylaldehyde) is reported on a column of 10 micrometer diameter silica. Both pairs of chelates are well resolved with good peak shape and efficiencies when the mobile phase is 4: 1 methylene chloride-acetonitrile [58].

1.9 UV/ VIS spectroscopy

UV spectroscopy is type of absorption spectroscopy in which light of ultra-violet region (200-400 nm.) is absorbed by the molecule. Absorption of the ultra-violet radiations results in the excitation of the electrons from the ground state to higher energy state. The energy of the ultra-violet radiation that are absorbed is equal to the energy difference between the ground state and higher energy states .

Generally, the most favoured transition is from the highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO). For most of the molecules, the lowest energy occupied molecular orbitals are s orbital, which correspond to sigma bonds. The p orbitals are at somewhat higher energy levels, the orbitals (nonbonding orbitals) with unshared paired of electrons lie at higher energy levels. The unoccupied or antibonding orbitals (π^* and σ^*) are the highest energy occupied orbitals. In all the compounds (other than alkanes), the electrons undergo various transitions. Some of the important transitions with increasing energies are: nonbonding to π^* , nonbonding to σ^* , π to π^* , σ to π^* and σ to σ^* .

1.9.1 Principle of UV/VIS spectroscopy

UV spectroscopy obeys the Beer-Lambert law, which states that: when a beam of monochromatic light is passed through a solution of an absorbing substance, the rate of decrease of intensity of radiation with thickness of the absorbing solution is proportional to the incident radiation as well as the concentration of the solution.

The expression of Beer-Lambert law is:

$$A = \log (I_0/I) = ECL$$

Where, A = absorbance

I_0 = intensity of light incident upon sample cell

I = intensity of light leaving sample cell

C = molar concentration of solute

L = length of sample cell (cm.)

E = molar absorptivity

From the Beer-Lambert law it is clear that greater the number of molecules capable of absorbing light of a given wavelength, the greater the extent of light absorption.

1.9.2 Instrumentation and working of UV/VIS spectroscopy

Instrumentation and working of the UV/VIS spectrometers can be studied simultaneously. Most of the modern UV/VIS spectrometers consist of the following parts:

Light Source: Tungsten filament lamps and Hydrogen-Deuterium lamps are most widely used and suitable light source as they cover the whole UV region. Tungsten filament lamps are rich in red radiations; more specifically they emit the radiations of 375 nm, while the intensity of Hydrogen-Deuterium lamps falls below 375 nm.

Monochromator: Monochromators generally composed of prisms and slits. The most of the spectrophotometers are double beam spectrophotometers. The radiation emitted from the primary source is dispersed with the help of rotating prisms. The various wavelengths of the light source which are separated by the prism are then selected by the slits such the rotation of the prism results in a series of continuously increasing wavelength to pass through the slits for recording purpose. The beam selected by the slit is monochromatic and further divided into two beams with the help of another prism.

Sample cells: One of the two divided beams is passed through the sample solution and second beam is passed through the reference solution. Both sample and reference solution are contained in the cells. These cells are made of either silica or quartz. Glass can't be used for the cells as it also absorbs light in the UV region.

Detector: Generally two photocells serve the purpose of detector in UV spectroscopy. One of the photocell receives the beam from sample cell and second detector receives the beam from the reference. The intensity of the radiation from the reference cell is stronger than the beam of sample cell. This results in the generation of pulsating or alternating currents in the photocells.

Amplifier: The alternating current generated in the photocells is transferred to the amplifier. The amplifier is coupled to a small servometer. Generally current generated in the photocells is of very low intensity, the main purpose of amplifier is to amplify the signals many times so we can get clear and recordable signals.

Recording devices: Most of the time amplifier is coupled to a pen

recorder which is connected to the computer. Computer stores all the data generated and produces the spectrum of the desired compound.

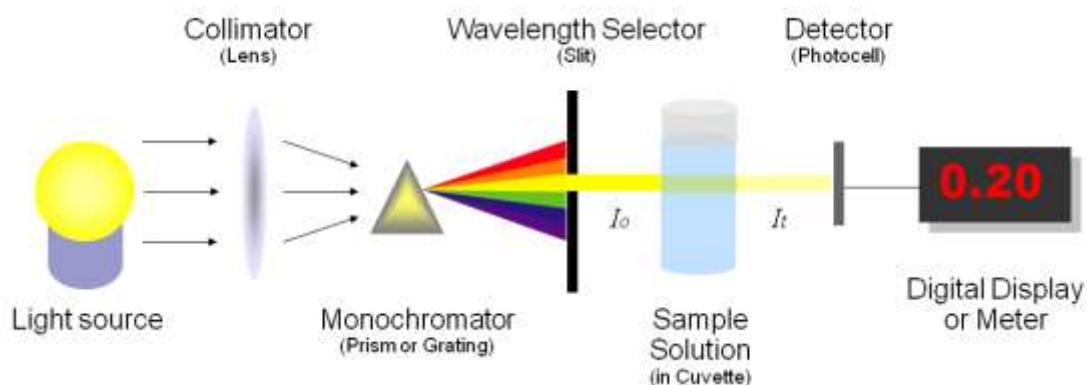


Fig. (1.1) Basic structure of UV/ VIS spectroscopy

1.9.3 Applications of UV/VIS spectroscopy

- Detection of functional groups- UV spectroscopy is used to detect the presence or absence of chromophore in the compound. This is technique is not useful for the detection of chromophore in complex compounds. The absence of a band at a particular band can be seen as an evidence for the absence of a particular group. If the spectrum of a compound comes out to be transparent above 200 nm than it confirms the absence of Conjugation , a carbonyl group , Benzene or aromatic compound , bromo or iodo atoms.

- Detection of extent of conjugation- The extent of conjugation in the polyenes can be detected with the help of UV spectroscopy. With the increase in double bonds the absorption shifts towards the longer wavelength.

- Identification of an unknown compound- An unknown compound can be identified with the help of UV spectroscopy. The spectrum of unknown compound is compared with the spectrum of a reference

compound and if both the spectrums coincide then it confirms the identification of the unknown substance.

- Determination of configurations of geometrical isomers- It is observed that cis-alkenes absorb at different wavelength than the trans-alkenes. The two isomers can be distinguished with each other when one of the isomers has non-coplanar structure due to steric hindrances. The cis-isomer suffers distortion and absorbs at lower wavelength as compared to trans-isomer.

- Determination of the purity of a substance- Purity of a substance can also be determined with the help of UV spectroscopy. The absorption of the sample solution is compared with the absorption of the reference solution. The intensity of the absorption can be used for the relative calculation of the purity of the sample substance^[59].

1.10 Aims of the study:

- Prepare schiff's compounds by Schiff reaction .
- Identification of compounds (by Nitrogen content, melting Point, IR) .
- Use these compounds as ligands with metal to form complexes .
- Characterize these complexes by UV spectrums .
- Use in chemical analysis to determine the concentration of metal .

Chapter Two

Chapter two

Experimental and Result

2.1 Instruments

- i. Melting point: Made in UK, BIBBY Sterilin L.T.D., and Serial No. R 000102810.
- ii. UV/ VIS spectrophotometer : Made in UK by Jenway, Model 6505, Serial NO. 2270.
- iii. IR spectrophotometer: Thermo Nicolet, 300 i.r, U.S.A .
- iv. Sensitive Balance: Made in Germany, Model PFB200-3 , Serial NO. WF1313413.
- v. Water bath: Model LWB-222A, Serial NO. DLCCCD1556C.

2.2 Chemicals

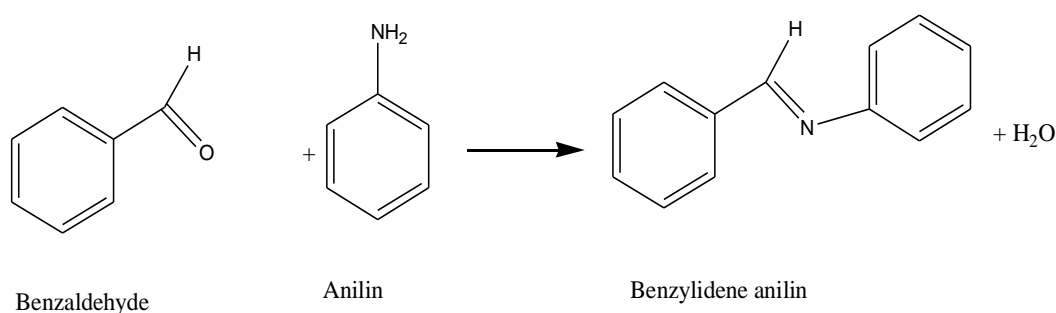
All chemical are analytical grade unless other wise stated. The water was distilled deionized water.

Benzaldehyde, Salicylaldehyde, Anilin, Benzophenone, Dichloromethane, methanol, Cobalt (II) chloride hexahydrate, Zinc Chloride, Cupric(II) chloride dehydrate, Chromium (III) chloride hexahydrate, Iron (III) chloride anhydrous , all were purchased from Merck (India).

2.3 Synthesis of reagents

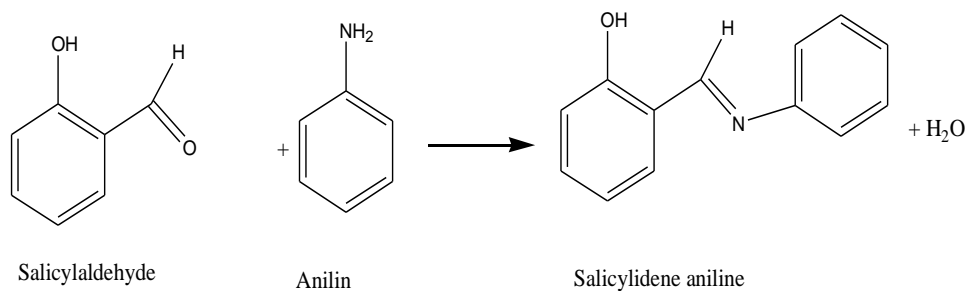
2.3.1 Synthesis of benzylidene aniline

The ligand was prepared by mixing 1 ml (0.01 mol) from Benzaldehyde and 0.9 ml (0.01 mol) from Aniline in 25 ml of absolute methanol and refluxing on a water bath for two hours, the condensation products(Beige) was filtered, recrystallized from methanol and dried, to give 1.54 g (85%).



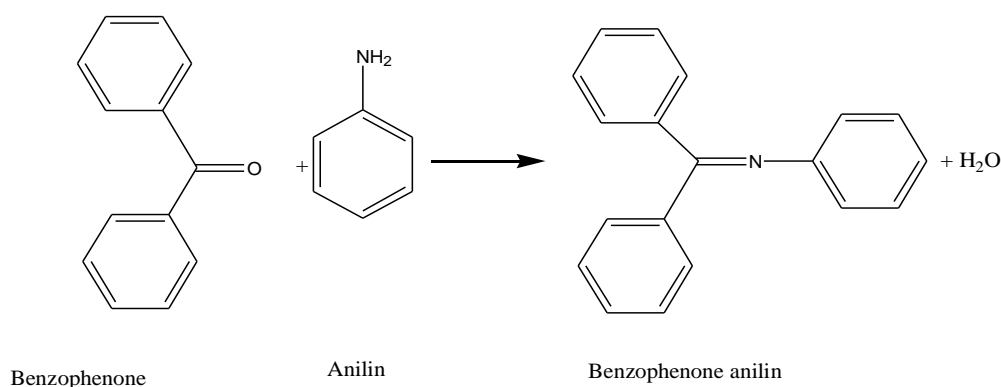
2.3.2 Synthesis of Salicylidene aniline

The ligand was prepared by mixing 1 ml (0.01 mol) from Salicylaldehyde and 0.9 ml (0.01 mol) from Aniline in 25 ml of absolute methanol and refluxing on a water bath for two hours, the condensation products (Yellow) was filtered, recrystallized form methanol and dried, to give 1.74 g (87%) .



2.3.3 Synthesis of Benzophenone aniline

The ligand was prepared by mixing 1.8g (0.01 mol) from Benzophenone dissolved in 25 ml of dichloromethane and add 0.9 ml (0.01 mol,) from Aniline and refluxing on a water bath for two hours, the condensation products (White) was filtered, recrystallized form methanol and dried, to give 1.93g (75 %) .



2.4 Identification of prepared reagents

2.4.1 Determiration of nitrogen content

This was carried out by kjeldal method as follows, 0.2g of the Benzylidene aniline were placed in a kjeldal flask and added one kjeldal tablet (copper sulphate - potassium sulphate catalyst) and digested with 3ml of concentrated sulphuric acid. The mixture was then heated until the organic matter was destroyed and the solution became clear. The contents were cooled and transferred quantitatively to a distillation apparatus, and the steam distillation of the ammonia was commenced the released ammonia was observed in 10ml of 2% boric acid. The distillation was continued until all the ammonia gas was absorbed by the acid as indicated by distillation of water. Added 20ml of sodium hydroxide solution to The

excess acid and titrated a ganist standard 0.1M hydrochloric acid solution using phenolphthalein as indicator.

The same procedure was repeated for all reagent and the results are shown in Table (2.1)

The nitrogen content percentage in the samples was calculated from the relation:

$$N\% = 0.014 * M * (\text{volume of titrant} - \text{volume of blank}) * 100 / \text{weight of sample}$$

Table (2.1) Nitrogen content of the reagents

Reagents	Nitrogen Content (%)
Benzylidene aniline	6.5
Salicylidene aniline	7.98
Benzophenone aniline	4.41

2.4.2 Melting points of the prepared reagent

It measured by using the Melting point device, the results are shown in Table (2.2)

Table (2.2) Melting points of the reagents

Reagents	Melting points (C^o)
Benzylidene aniline	62
Salicylidene aniline	52
Benzophenone aniline	55

2.4.3 IR spectrum of the reagents

Benzylidene aniline is mixed with a weighed amount of powdered potassium bromide and the mixture is admitted to a pressure of several tones in a die, to produce a highly transparent plate or disc which can be inserted into the spectrophotometer.

The same procedure was repeated for all reagent and the results are shown in Table (2.3)

Table (2.3) IR spectrum of the reagents

Ligand	C=N Cm^{-1} (1500-1900)	=C-H Cm^{-1} (3000-3100)	C=C Cm^{-1} (1600-1800)	C-C Cm^{-1} (600-1400)	C-H Cm^{-1} (690-900)	C-OH Cm^{-1} (600-1400)
BA	1581.92	3056.74	1624.84	757.43	865.16	–
SA	1576.75	3064.31	1616.40	750.56	829.67	1397.56
BPhA	1587.08	3050.69	1650.88	700.41	814.72	–

2.5 Preparation of solutions

1.0×10^{-2} M stock solutions of each benzylidene aniline, Salicylidene aniline and Benzophenone aniline were prepared by dissolving 1.81 g, 1.98 g, 2.57 g respectively, in Acetone in 1000 ml volumetric flask.

1000 ppm stock solutions of each of Cu (II) , Co (II) , Fe (III) ,Zn (II) and Cr (III) ions were prepared from the corresponding salt by dissolving the following weights in 1000 ml volumetric flask , 2.685g of Cupric(II) chloride dehydrate, 4.039g of Cobalt (II) chloride hexahydrate, 2.906g of Iron (III) chloride anhydrous, 2.083g of Zinc(II) Chloride, 5.125g of Chromium (III) chloride hexahydrate, respectively.

5 M stock solutions of Sodium hydroxide was prepared by dissolving 10g of Sodium hydroxide in deionized water in 50 ml volumetric flasks.

5 M stock solutions of Hydrochloric acid were prepared by 21.2 ml of Hydrochloric acid in deionized water in 50 ml volumetric flasks.

The working solutions were prepared by serial dilutions of the stock solutions with deionized water.

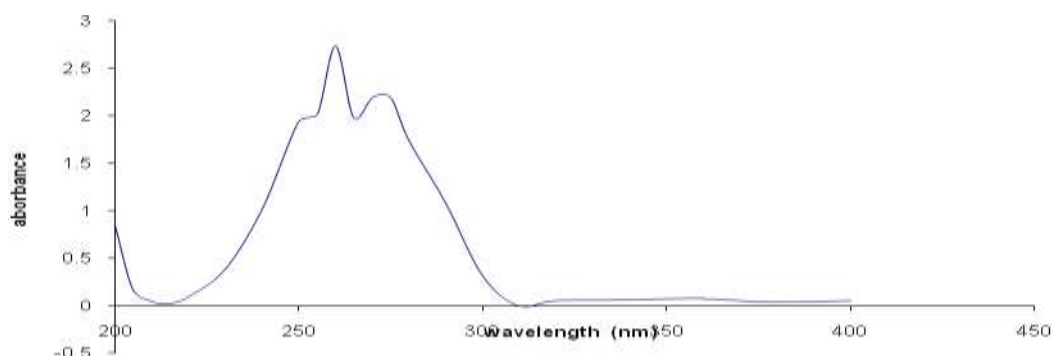
2.6 Analytical parameters for BA complexes with some metal ions

2.6.1 Scanning of the wavelength of maximum absorption

To locate the wavelengths of maximum absorbance, solutions of 1.0×10^{-4} M of reagent and 2.00 ppm of each of the metal ions was scanned. The wavelengths of maximum absorption (λ_{\max}) are shown in Table (2.4) and Fig. 2.1, 2.2, 2.3, 2.4, and 2.5 respectively.

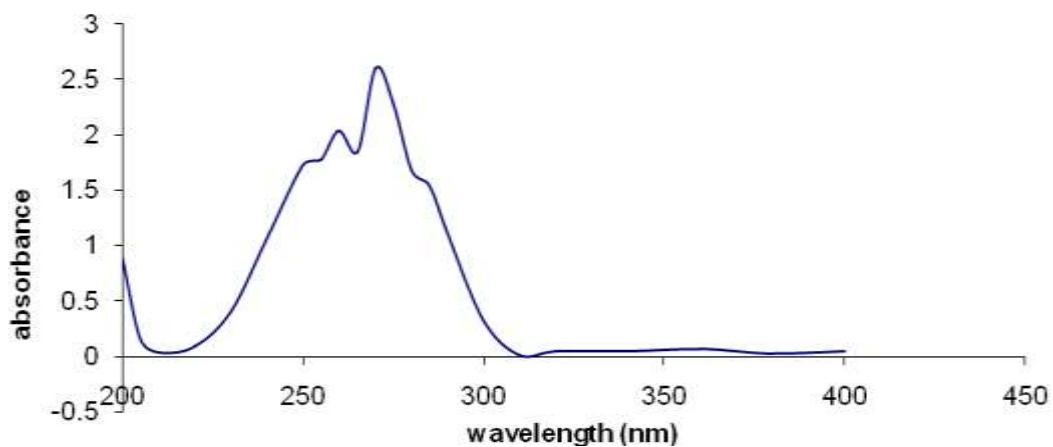
Table (2.4), wavelengths of maximum absorption (λ_{\max}) for metal ions complexes:

Metal ion	Wavelength (nm)	Absorbance
Cu(II)	260	2.737
Cr(III)	270	2.604
Co(II)	260	2.513
Fe(III)	265	2.641
Zn(II)	255	2.637



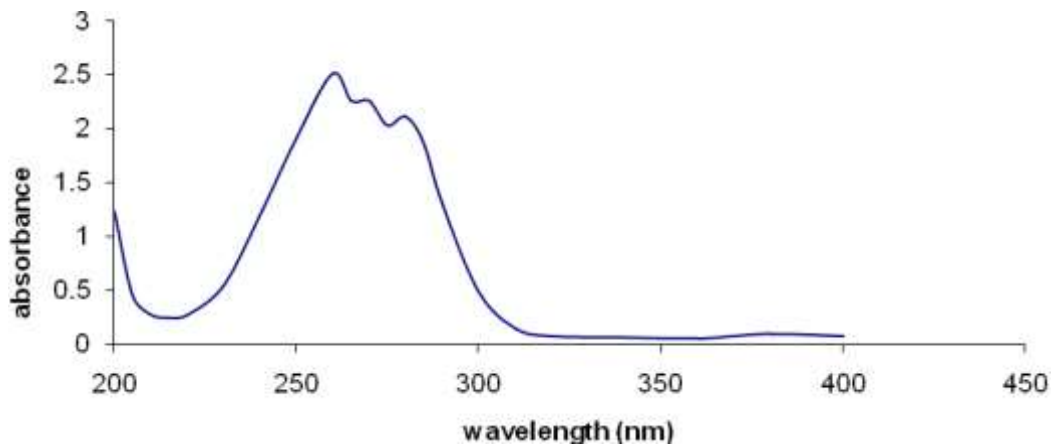
abs nm
2.737 260

Fig. (2.1). wavelengths of maximum absorption (λ_{\max}) for BA with Cu



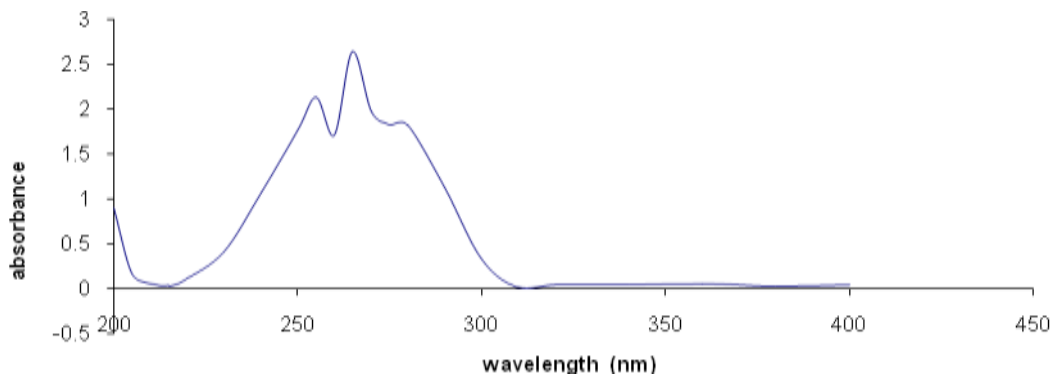
abs	nm
2.604	270

Fig.(2. 2). Wavelengths of maximum absorption (λ_{max}) for BA with Cr



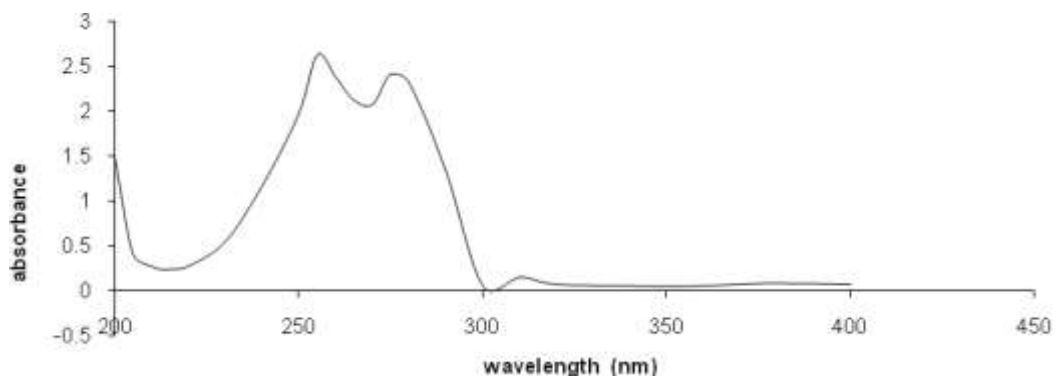
abs	nm
2.513	260

Fig. (2. 3). Wavelengths of maximum absorption (λ_{max}) for BA with Co



abs	nm
2.641	265

Fig. (2. 4). Wavelengths of maximum absorption (λ_{\max}) for BA with Fe



abs	nm
2.637	255

Fig.(2. 5). Wavelengths of maximum absorption (λ_{\max}) for BA with Zn

2.6.2 Effect of PH on the absorbance

Three sets of mixture were prepared by keeping the concentration of metal ions and ligand at 2.00 ppm and 1.00×10^{-4} M, respectively, to the first flask 1.0 ml of 0.10 M hydrochloric acid were added, and to the second 1.0 ml of 0.10 M sodium hydroxide were added, and the third was taken as reference. Absorbances at λ_{\max} of each metal ion were measured. The results are shown in Table (2. 5).

Table (2. 5) Effect of HCl , NaOH on the absorbance

Metal	Reference	HCl	NaOH
Cu(II)	1.884	1.870	1.923
Cr(III)	1.742	1.684	1.765
Co(II)	1.867	1.852	1.870
Fe(III)	2.640	2.634	2.736
Zn(II)	1.583	1.578	1.592

2.6.3 Analytical parameters for Cu(II)-BA

2.6.3.1 Effect of NaOH concentration on absorbance of Cu (II)-BA

A series of Cu(II)-BA solutions were prepared of 2.00 ppm of Cu(II) ion and 1.00×10^{-4} M of BA in different sodium hydroxide concentrations. The absorbance was measured at 260 nm and the results are shown in Table (2. 6) and Fig. 2. 6

Table (2.6). Effect of NaOH concentration on absorbance of Cu (II)-BA

NaOH (M)	Absorbance
0.00	1.884
0.10	1.923
0.30	1.914
0.50	1.898
0.70	1.910
0.90	1.891

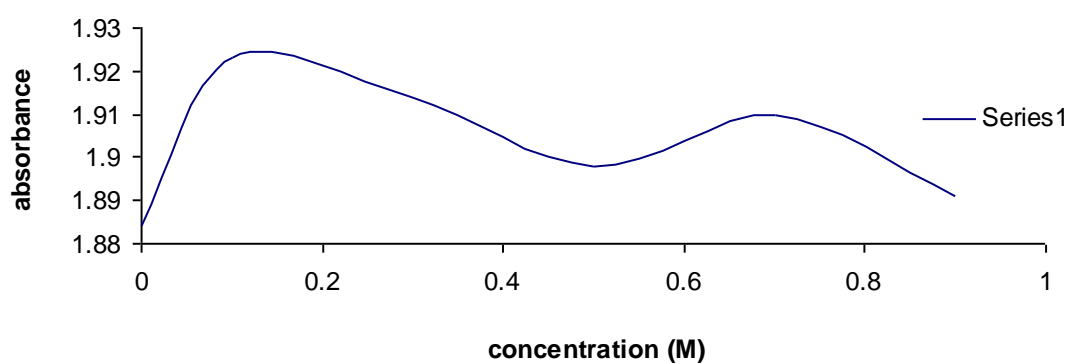


Fig. (2.6). Effect of NaOH concentration on absorbance of Cu (II)-BA

2.6.3.2 Effect of reagent concentration

The effect of the reagent concentration on the absorbance was studied by preparing solutions of 2.00 ppm of Cu(II) ion and 0.10 M of NaOH in different reagent concentrations. The absorbance was read at 260 nm and the results are shown in Table (2.7) and Fig. 2.7.

Table (2.7) Effect of reagent concentration on absorbance

Reagent (M)	Absorbance
1.00×10^{-4}	1.930
2.00×10^{-4}	1.912
4.00×10^{-4}	1.954
6.00×10^{-4}	1.942
8.00×10^{-4}	1.933

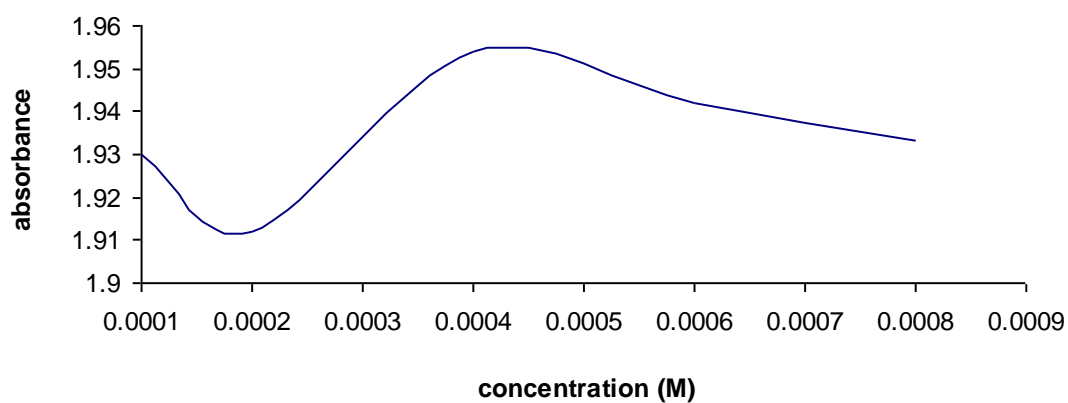


Fig.(2.7) Effect of reagent concentration on absorbance of Cu(II)-BA

2.6.3.3 Calibration curve for Cu(II)-BA

The Calibration curve for Cu(II)-BA was constructed using 0.10 M of NaOH , 4.00×10^{-4} M of the reagent and different concentrations of the metal ion. The absorbance was measured at 260 nm and the results are shown in Table (2.8) and Fig. 2.8.

Table (2.8) Calibration curve for Cu(II)-BA

Cu(II) (ppm)	Absorbance
2.00	1.949
4.00	1.956
6.00	1.968
8.00	1.981
10.00	1.997
12.00	2.014

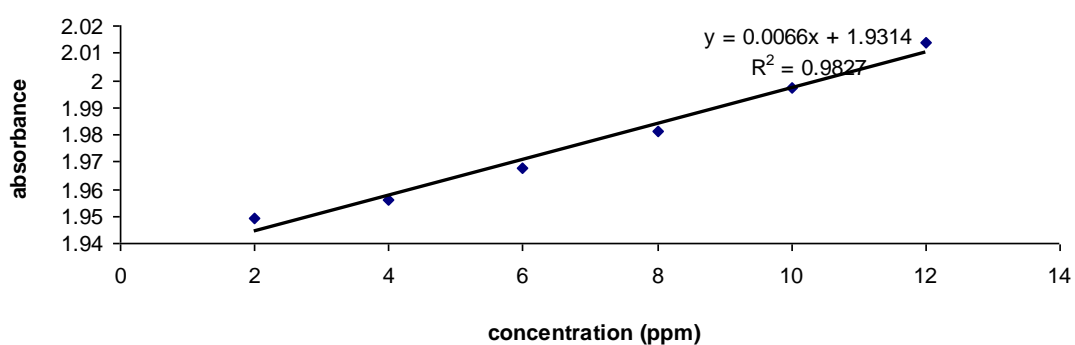


Fig.(2.8) Calibration curve for Cu(II)-BA

2.6.4 Analytical parameters for Cr(III)-BA

2.6.4.1 Effect of NaOH concentration on absorbance of Cr (III)-BA

A series of Cr(III)-BA solutions were prepared of 2.00 ppm of Cr(III) ion and 1.00×10^{-4} M of BA in different sodium hydroxide concentrations. The absorbance was measured at 270 nm and the results are shown in Table (2.9) and Fig. 2. 9.

Table (2.9) Effect of NaOH concentration on absorbance of Cr (III)-BA

NaOH (M)	Absorbance
0.00	1.742
0.10	1.765
0.30	1.751
0.50	1.744
0.70	1.736
0.90	1.731

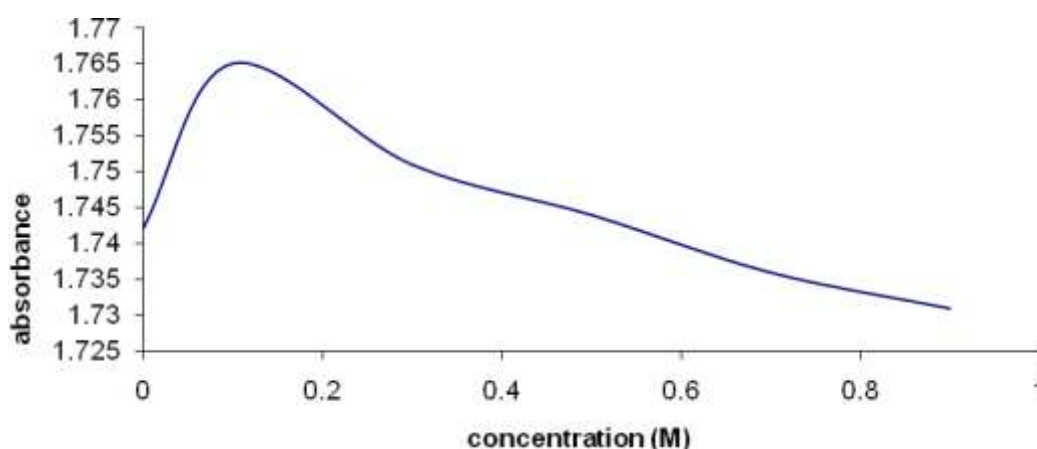


Fig. (2.9) Effect of NaOH concentration on absorbance of Cr (III)-BA

2.6.4.2 Effect of reagent concentration

The effect of the reagent concentration on the absorbance was studied by preparing solutions of 2.00 ppm of Cr(III) ion and 0.10 M of NaOH in different reagent concentrations. The absorbance was read at 270 nm and the results are shown in Table (2.10) and Fig. 2.10.

Table (2.10) Effect of reagent concentration on absorbance

Reagent (M)	Absorbance
1.00×10^{-4}	1.753
2.00×10^{-4}	1.732
4.00×10^{-4}	1.773
6.00×10^{-4}	1.765
8.00×10^{-4}	1.751

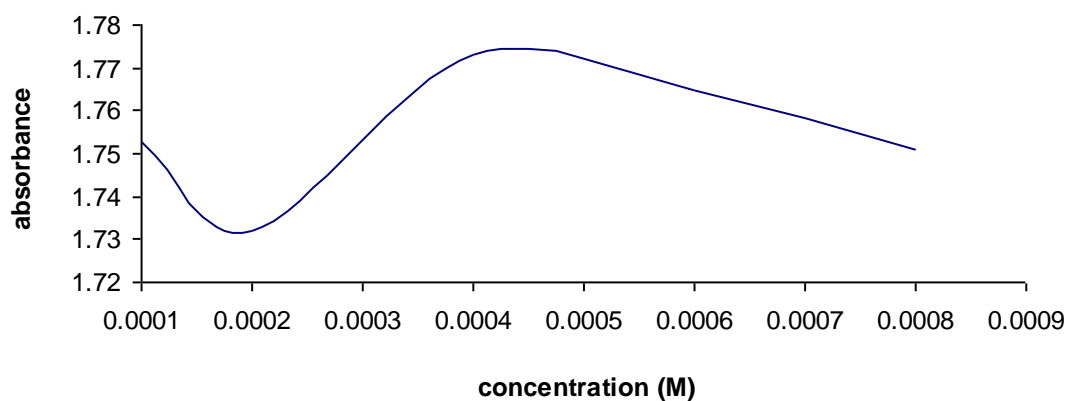


Fig. (2.10) Effect of reagent concentration on absorbance of Cr(III)-BA

2.6.4.3 Calibration curve for Cr(III)-BA

The Calibration curve for Cr(III)-BA was constructed using 0.10 M of NaOH , 4.00×10^{-4} M of the reagent and different concentrations of the metal ion. The absorbance was measured at 270 nm and the results are shown in Table (2.11) and Fig. 2.11.

Table (2.11) Calibration curve for Cr(III)-BA

Cr(III) (ppm)	Absorbance
2.00	1.782
4.00	1.789
6.00	1.796
8.00	1.809
10.00	1.821
12.00	1.839

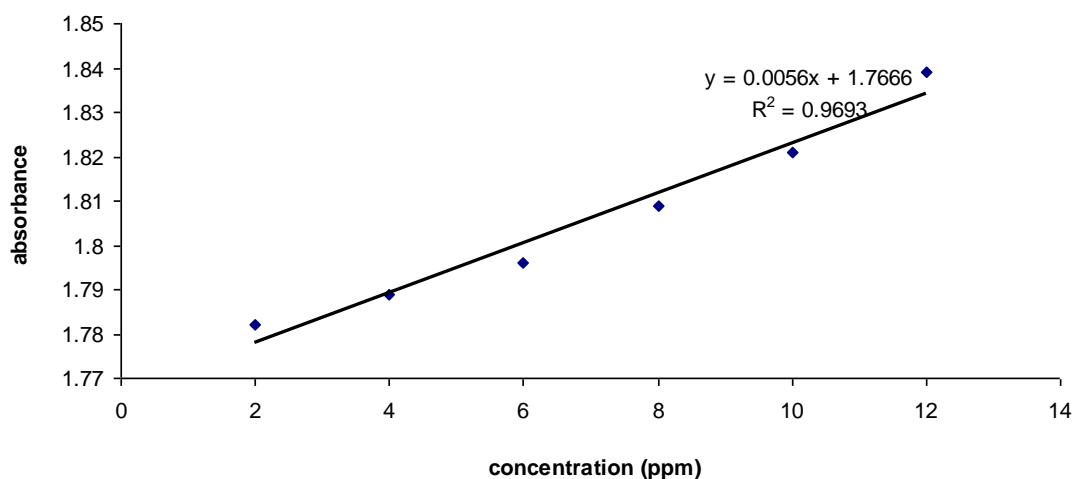


Fig. (2.11) Calibration curve for Cr(III)-BA

2.6.5 Analytical parameters for Co(II)-BA

2.6.5.1 Effect of NaOH concentration on absorbance of Co (II)-BA

A series of Co(II)-BA solutions were prepared of 2.00 ppm of Co(II) ion and 1.00×10^{-4} M of BA in different sodium hydroxide concentrations. The absorbance was measured at 260 nm and the results are shown in Table (2.12) and Fig. 2.12.

Table (2.12) Effect of NaOH concentration on absorbance of Co (II)-BA

NaOH (M)	Absorbance
0.00	1.867
0.10	1.870
0.30	1.859
0.50	1.840
0.70	1.862
0.90	1.855

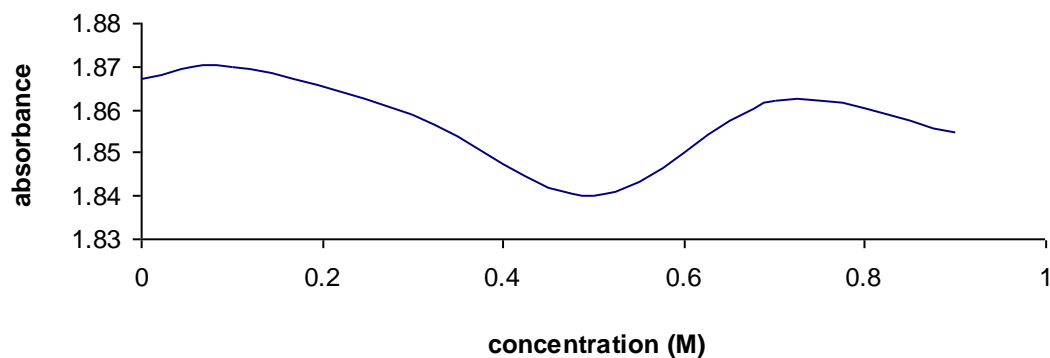


Fig. (2.12) Effect of NaOH concentration on absorbance of Co (II)-BA

2.6.5.2 Effect of reagent concentration

The effect of the reagent concentration on the absorbance was studied by preparing solutions of 2.00 ppm of Co(II) ion and 0.10 M of NaOH in different reagent concentrations. The absorbance was read at 260 nm and the results are shown in Table (2.13) and Fig. 2.13.

Table (2.13) Effect of reagent concentration on absorbance

Reagent (M)	Absorbance
1.00×10^{-4}	1.883
2.00×10^{-4}	1.875
4.00×10^{-4}	1.858
6.00×10^{-4}	1.898
8.00×10^{-4}	1.890

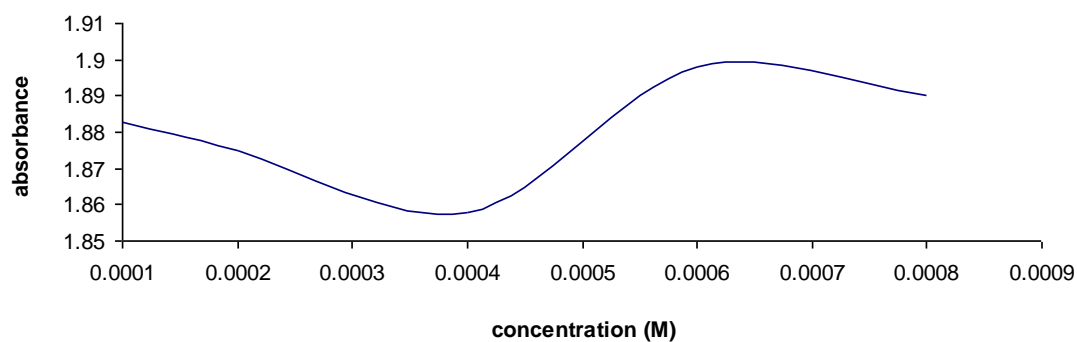


Fig. (2.13) Effect of reagent concentration on absorbance of Co(II)-BA

2.6.5.3 Calibration curve for Co(II)-BA

The Calibration curve for Co(II)-BA was constructed using 0.10 M of NaOH , 6.00×10^{-4} M of the reagent and different concentrations of the metal ion. The absorbance was measured at 260 nm and the results are shown in Table (2.14) and Fig. 2.14.

Table (2.14) Calibration curve for Co(II)-BA

Cu(II) (ppm)	Absorbance
2.00	1.894
4.00	1.910
6.00	1.922
8.00	1.939
10.00	1.951
12.00	1.963

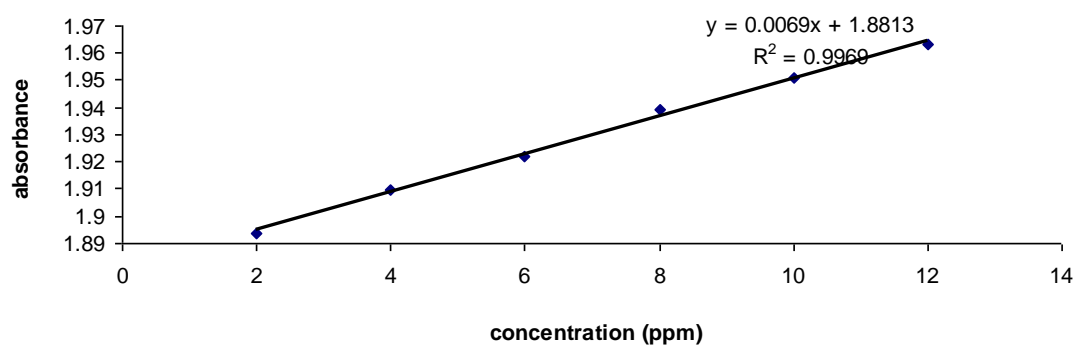


Fig. (2.14) Calibration curve for Co(II)-BA

2.6.6 Analytical parameters for Fe(III)-BA

2.6.6.1 Effect of NaOH concentration on absorbance of Fe (III)-BA

A series of Fe(III)-BA solutions were prepared of 2.00 ppm of Fe(III) ion and 1.00×10^{-4} M of BA in different sodium hydroxide concentrations. The absorbance was measured at 265 nm and the results are shown in Table (2.15) and Fig. 2.15.

Table (2.15) Effect of NaOH concentration on absorbance of Fe(III)-BA

NaOH (M)	Absorbance
0.00	2.640
0.10	2.762
0.30	2.650
0.50	2.637
0.70	2.626
0.90	2.618

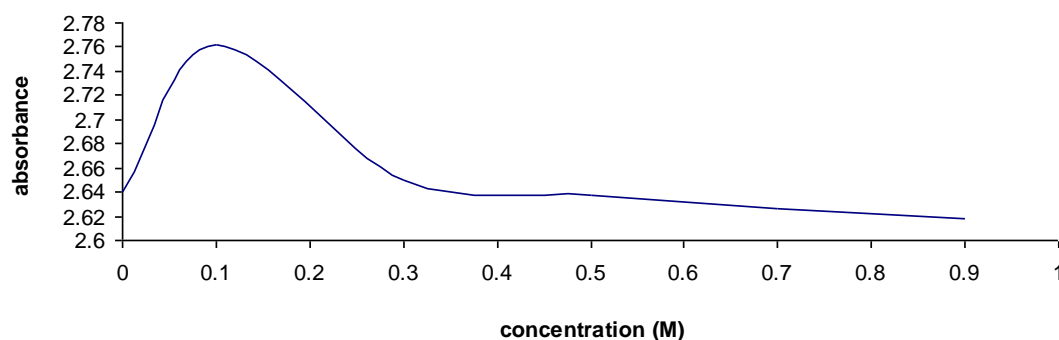


Fig. (2.15) Effect of NaOH concentration on absorbance of Fe (III)-BA

2.6.6.2 Effect of reagent concentration

The effect of the reagent concentration on the absorbance was studied by preparing solutions of 2.00 ppm of Fe(III) ion and 0.10 M of NaOH in different reagent concentrations. The absorbance was read at 265 nm and the results are shown in Table (2.16) and Fig. 2.16.

Table (2.16) Effect of reagent concentration on absorbance

Reagent (M)	Absorbance
1.00×10^{-4}	1.899
2.00×10^{-4}	1.885
4.00×10^{-4}	1.912
6.00×10^{-4}	1.878
8.00×10^{-4}	1.855

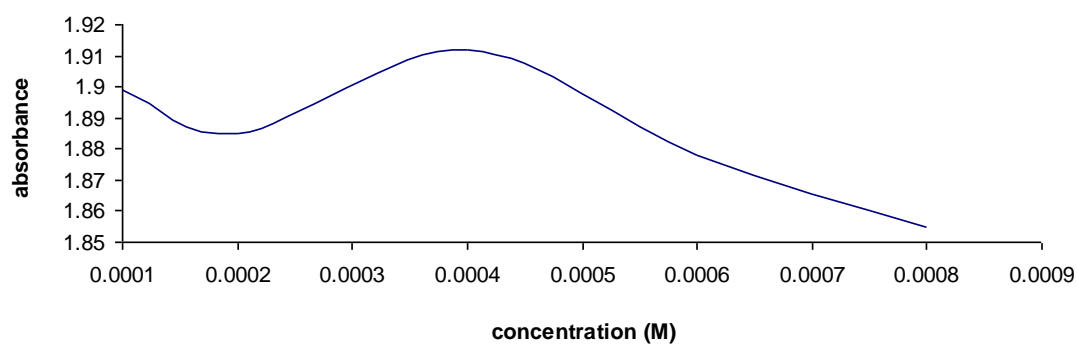


Fig. (2.16) Effect of reagent concentration on absorbance of Fe(III)-BA

2.6.6.3 Calibration curve for Fe(III)-BA

The Calibration curve for Fe(III)-BA was constructed using 0.10 M of NaOH , 4.00×10^{-4} M of the reagent and different concentrations of the metal ion. The absorbance was measured at 265 nm and the results are shown in Table (2.17) and Fig. 2.17.

Table (2.17) Calibration curve for Fe(III)-BA

Fe(III) (ppm)	Absorbance
2.00	1.824
4.00	1.832
6.00	1.843
8.00	1.851
10.00.	1.865
12.00	1.873

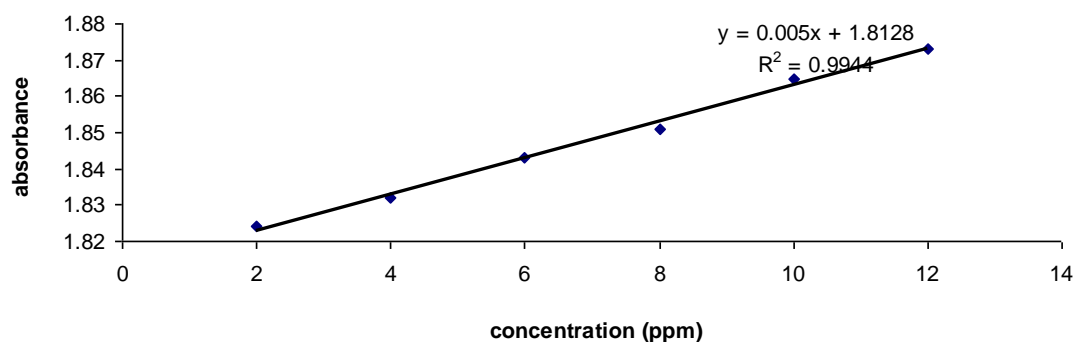


Fig. (2.17) Calibration curve for Fe(III)-BA

2.6.7 Analytical parameters for Zn(II)-BA

2.6.7.1 Effect of NaOH concentration on absorbance of Zn (II)-BA

A series of Zn(II)-BA solutions were prepared of 2.00 ppm of Zn (II) ion and 1.00×10^{-4} M of BA in different sodium hydroxide concentrations. The absorbance was measured at 255 nm and the results are shown in Table (2.18) and Fig. 2.18.

Table (2.18) Effect of NaOH concentration on absorbance of Zn (II)-BA

NaOH (M)	Absorbance
0.00	1.583
0.10	1.592
0.30	1.559
0.50	1.553
0.70	1.581
0.90	1.570

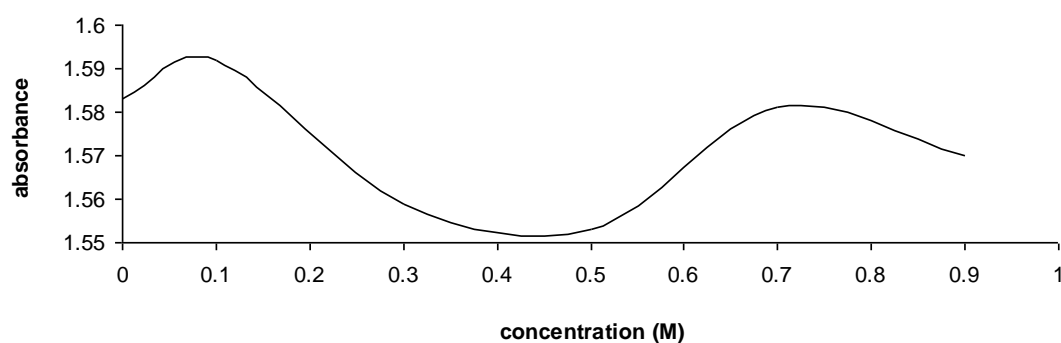


Fig. (2.18) Effect of NaOH concentration on absorbance of Zn (II)-BA

2.6.7.2 Effect of reagent concentration

The effect of the reagent concentration on the absorbance was studied by preparing solutions of 2.00 ppm of Zn(II) ion and 0.10 M of NaOH in different reagent concentrations. The absorbance was read at 255 nm and the results are shown in Table (2.19) and Fig. 2.19.

Table (2.19) Effect of reagent concentration on absorbance

Reagent (M)	Absorbance
1.00×10^{-4}	1.589
2.00×10^{-4}	1.609
4.00×10^{-4}	1.733
6.00×10^{-4}	1.635
8.00×10^{-4}	1.631

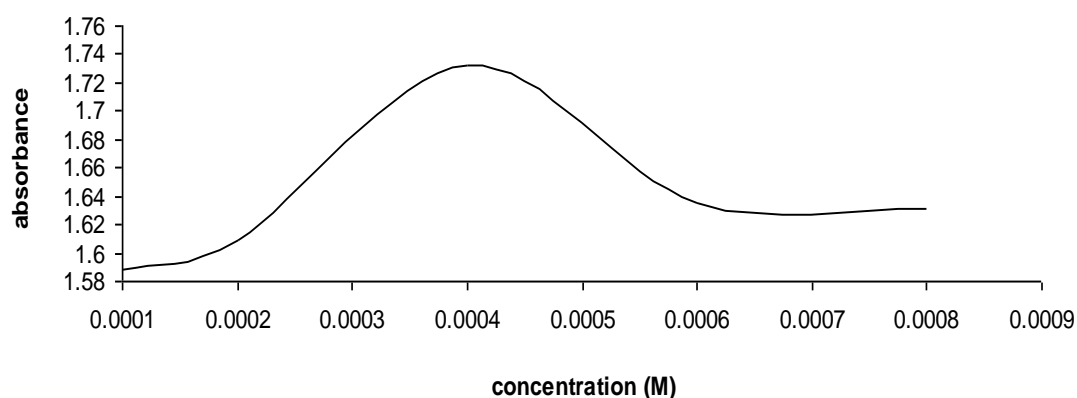


Fig. (2.19) Effect of reagent concentration on absorbance of Zn(II)-BA

2.6.7.3 Calibration curve for Zn(II)-BA

The Calibration curve for Zn(II)-BA was constructed using 0.10 M of NaOH , 4.00×10^{-4} M of the reagent and different concentrations of the metal ion. The absorbance was measured at 255 nm and the results are shown in Table (2.20) and Fig. 2.20.

Table (2.20) Calibration curve for Zn(II)-BA

Zn(II) (ppm)	Absorbance
2.00	1.749
4.00	1.769
6.00	1.784
8.00	1.810
10.00	1.942
12.00	2.020

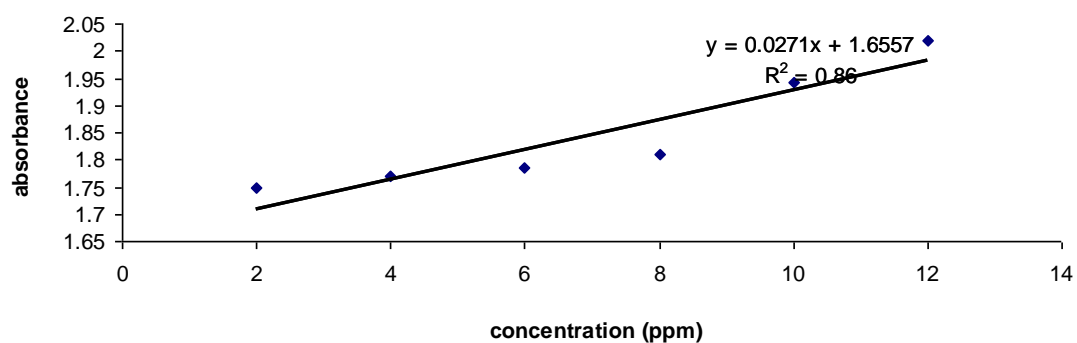


Fig. (2.20) Calibration curve for Zn(II)-BA

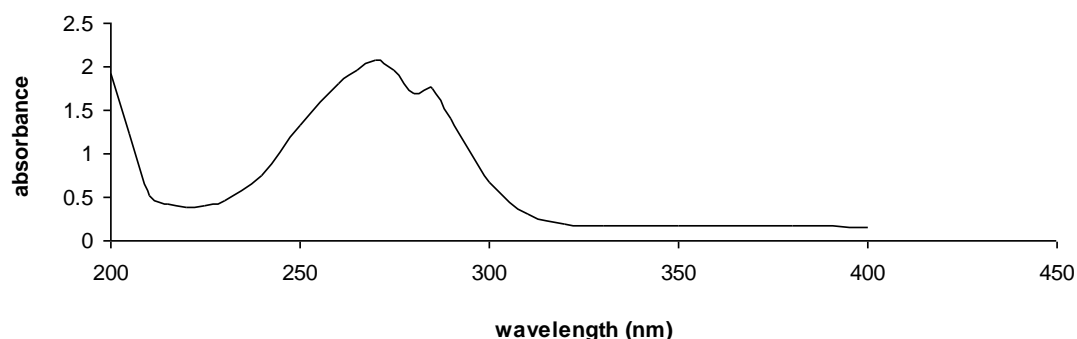
2.7 Analytical parameters for SA complexes with some metal ions

2.7.1 Scanning of the wavelength of maximum absorption

To locate the wavelengths of maximum absorbance, solutions of 1.0×10^{-4} M of reagent and 2.00 ppm of each of the metal ions was scanned. The wavelengths of maximum absorption (λ_{\max}) are shown in Table (2.21) and Fig. 2.21, 2.22, 2.23, 2.24, and 2.25 respectively.

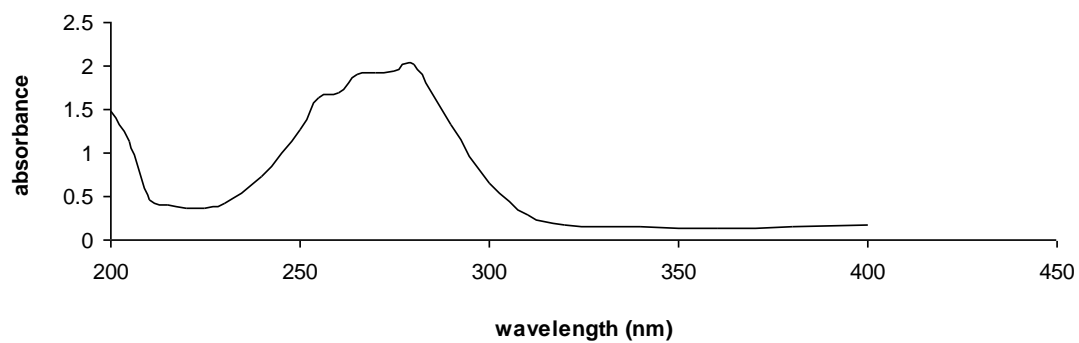
Table (2.21) wavelengths of maximum absorption (λ_{\max}) for metal ions complexes

Metal ion	Wavelength (nm)	Absorbance
Cu (II)	270	2.083
Cr (III)	280	2.022
Co (II)	265	2.233
Fe(III)	265	2.201
Zn(II)	275	2.007



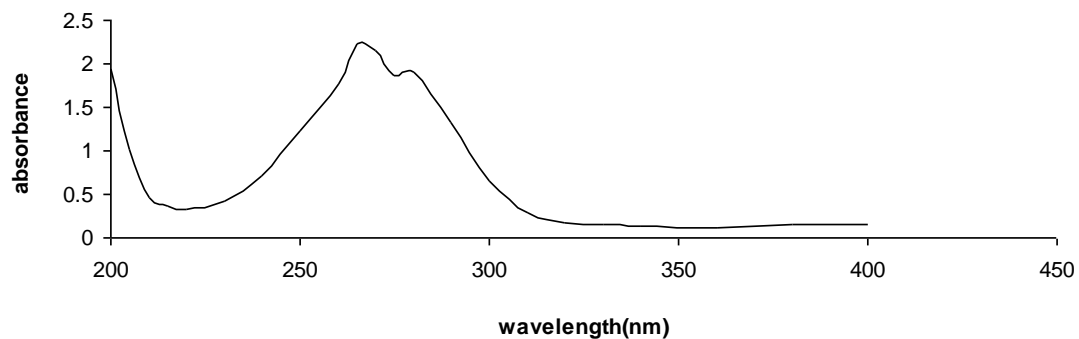
abs nm
2.083 270

Fig. (2.21) wavelengths of maximum absorption (λ_{\max}) for SA with Cu



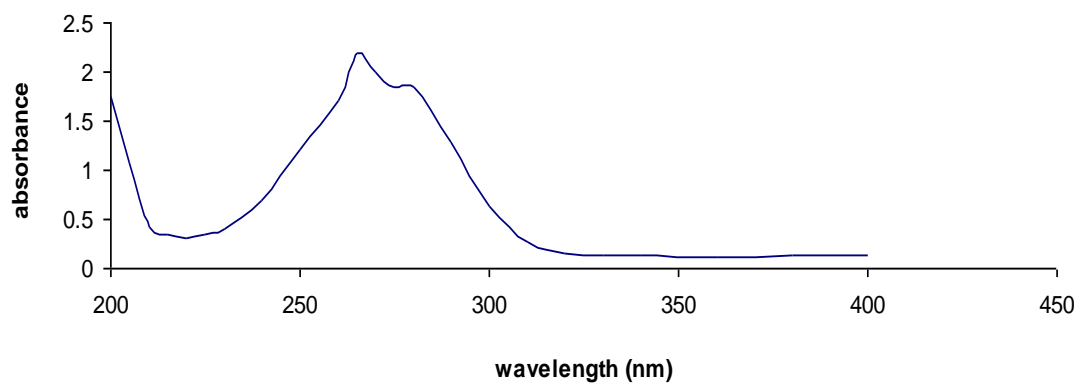
abs	nm
2.022	280

Fig. (2.22) wavelengths of maximum absorption (λ_{max}) for SA with Cr



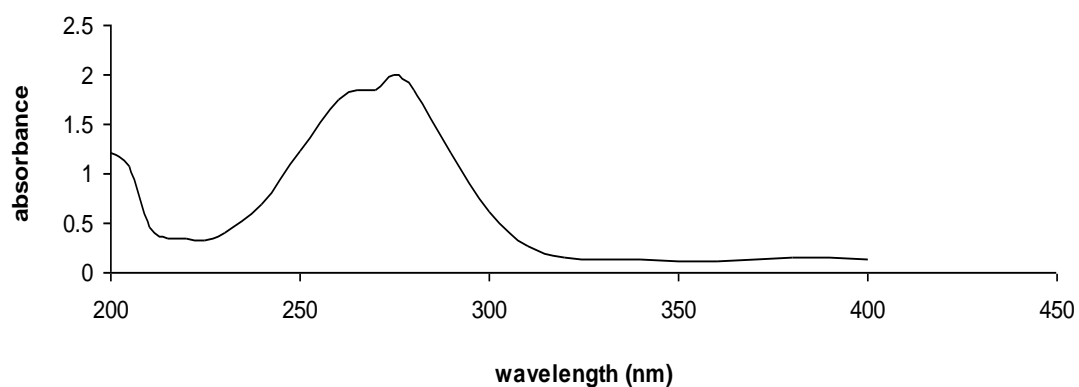
abs	nm
2.233	265

Fig. (2.23) wavelengths of maximum absorption (λ_{max}) for SA with Co



abs	nm
2.201	265

Fig. (2.24) wavelengths of maximum absorption (λ_{max}) for SA with Fe



abs	nm
2.007	275

Fig. (2.25) wavelengths of maximum absorption (λ_{max}) for SA with Zn

2.7.2 Effect of PH on the absorbance

Three sets of mixture were prepared by keeping the concentration of metal ions and ligand at 2.00 ppm and 1.00×10^{-4} M, respectively, to the first flask 1 ml of 0.10 M hydrochloric acid were added, and to the second 1 ml of 0.10 M sodium hydroxide were added, and the third was taken as reference. Absorbances at λ_{\max} of each metal ion were measured. The results are shown in Table (2.22).

Table (2.22) Effect of HCl , NaOH on the absorbance

Metal	Reference	HCl	NaOH
Cu(II)	1.830	1.825	1.860
Cr(III)	1.526	1.438	1.541
Co(II)	1.769	1.760	1.779
Fe(III)	1.772	1.765	1.783
Zn(II)	1.642	1.627	1.683

2.7.3 Analytical parameters for Cu(II)-SA

2.7.3.1 Effect of NaOH concentration on absorbance of Cu (II)-SA

A series of Cu(II)-SA solutions were prepared of 2.00 ppm of Cu(II) ion and 1.00×10^{-4} M of SA in different sodium hydroxide concentrations. The absorbance was measured at 270 nm and the results are shown in Table (2.23) and Fig. 2.26.

Table (2.23) Effect of NaOH concentration on absorbance of Cu (II)-SA

NaOH (M)	Absorbance
0.00	1.830
0.10	1.862
0.30	1.845
0.50	1.841
0.70	1.820
0.90	1.811

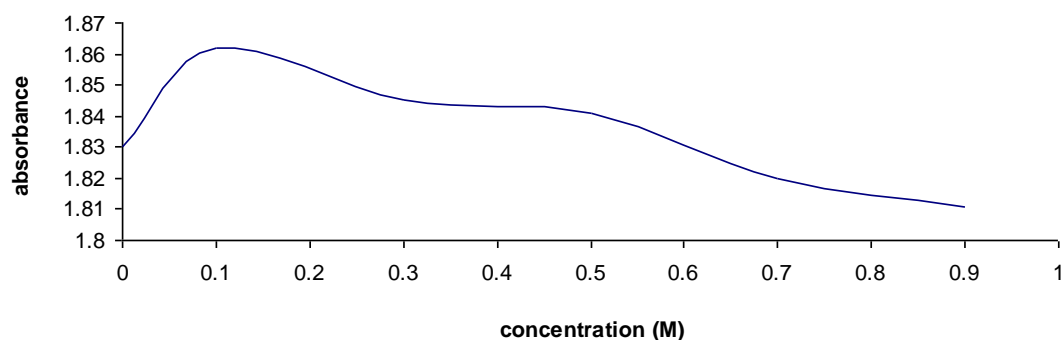


Fig. (2.26) Effect of NaOH concentration on absorbance of Cu (II)-SA

2.7.3.2 Effect of reagent concentration

The effect of the reagent concentration on the absorbance was studied by preparing solutions of 2.00 ppm of Cu(II) ion and 0.10 M of NaOH in different reagent concentrations. The absorbance was read at 270 nm and the results are shown in Table (2.24) and Fig. 2.27.

Table (2.24) Effect of reagent concentration on absorbance

Reagent (M)	Absorbance
1.00×10^{-4}	1.873
2.00×10^{-4}	1.845
4.00×10^{-4}	1.839
6.00×10^{-4}	1.879
8.00×10^{-4}	1.865

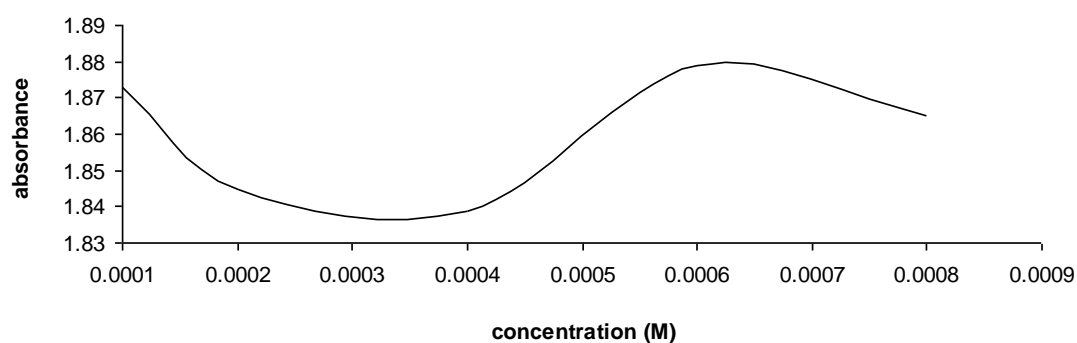


Fig. (2.27) Effect of reagent concentration on absorbance of Cu(II)-SA

2.7.3.3 Calibration curve for Cu(II)-SA

The Calibration curve for Cu(II)-SA was constructed using 0.10 M of NaOH , 6.00×10^{-4} M of the reagent and different concentrations of the metal ion. The absorbance was measured at 270 nm and the results are shown in Table (2.25) and Fig. 2.28.

Table (2.25) Calibration curve for Cu(II)-SA

Cu(II) (ppm)	Absorbance
2.00	1.652
4.00	1.657
6.00	1.660
8.00	1.665
10.00	1.671
12.00	1.680

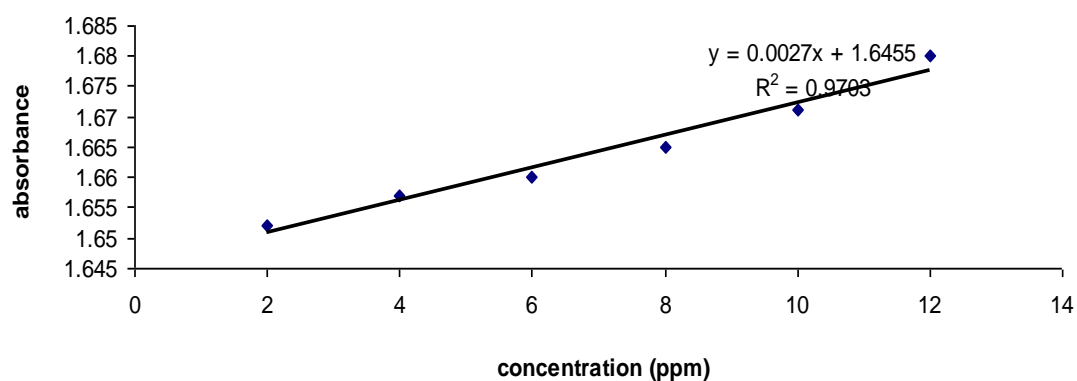


Fig. (2.28) Calibration curve for Cu(II)-SA

2.7.4 Analytical parameters for Cr(III)-SA

2.7.4.1 Effect of NaOH concentration on absorbance of Cr (III)-SA

A series of Cr(III)-SA solutions were prepared of 2.00 ppm of Cr(III) ion and 1.00×10^{-4} M of SA in different sodium hydroxide concentrations. The absorbance was measured at 280 nm and the results are shown in Table (2.26) and Fig. 2.29.

Table (2.26) Effect of NaOH concentration on absorbance of Cr (III)-SA

NaOH (M)	Absorbance
0.00	1.526
0.10	1.565
0.30	1.522
0.50	1.513
0.70	1.508
0.90	1.499

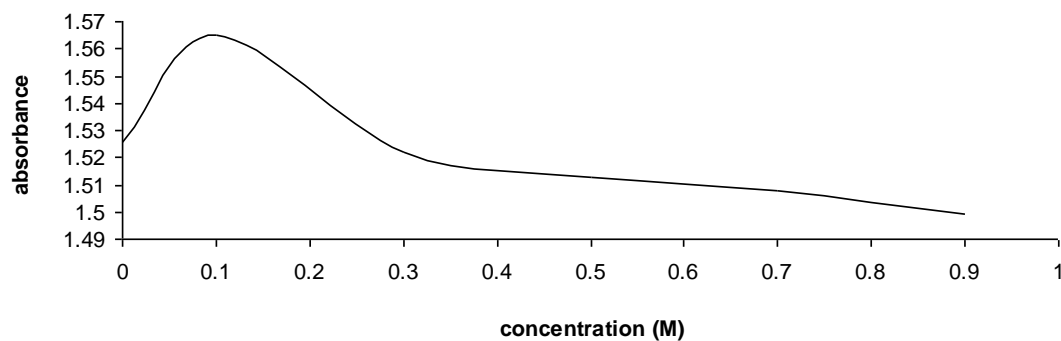


Fig. (2.29) Effect of NaOH concentration on absorbance of Cr (III)-SA

2.7.4.2 Effect of reagent concentration

The effect of the reagent concentration on the absorbance was studied by preparing solutions of 2.00 ppm of Cr(III) ion and 0.10 M of NaOH in different reagent concentrations. The absorbance was read at 280 nm and the results are shown in Table (2.27) and Fig. 2.30.

Table (2.27) Effect of reagent concentration on absorbance

Reagent (M)	Absorbance
1.00×10^{-4}	1.446
2.00×10^{-4}	1.467
4.00×10^{-4}	1.475
6.00×10^{-4}	1.499
8.00×10^{-4}	1.471

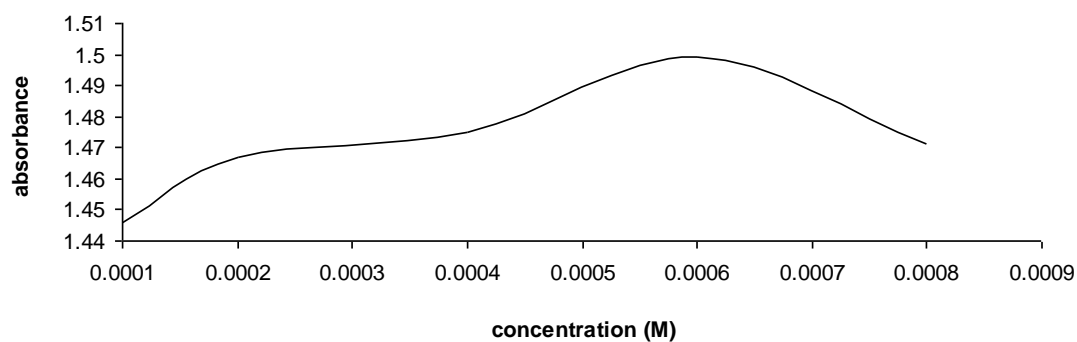


Fig. (2.30) Effect of reagent concentration on absorbance of Cr(III)-SA

2.7.4.3 Calibration curve for Cr(III)-SA

The Calibration curve for Cr(III)-SA was constructed using 0.10 M of NaOH , 6.00×10^{-4} M of the reagent and different concentrations of the metal ion. The absorbance was measured at 280 nm and the results are shown in Table (2.28) and Fig. 2.31.

Table (2.28) Calibration curve for Cr(III)-SA

Cr(III) (ppm)	Absorbance
2.00	1.495
4.00	1.512
6.00	1.523
8.00	1.532
10.00	1.540
12.00	1.554

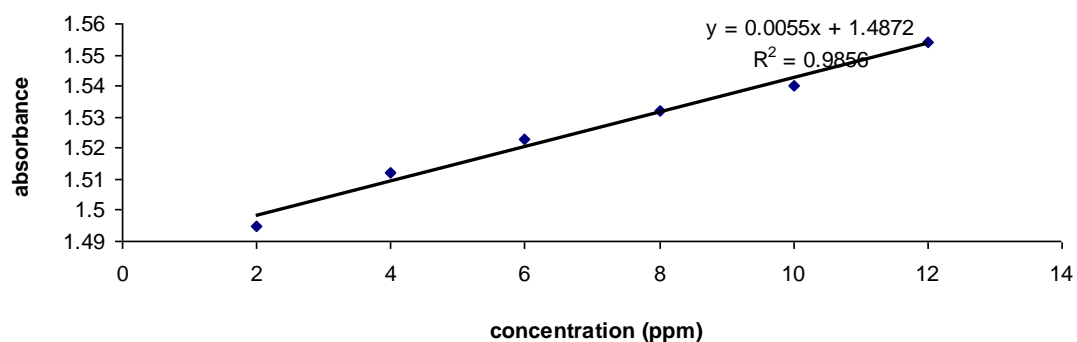


Fig. (2.31) Calibration curve for Cr(III)-SA

2.7.5 Analytical parameters for Co(II)-SA

2.6.5.1 Effect of NaOH concentration on absorbance of Co (II)-SA

A series of Co(II)-SA solutions were prepared of 2.00 ppm of Co(II) ion and 1.00×10^{-4} M of SA in different sodium hydroxide concentrations. The absorbance was measured at 265 nm and the results are shown in Table (2.29) and Fig. 2.32.

Table (2.29) Effect of NaOH concentration on absorbance of Co(II)-SA

NaOH (M)	Absorbance
0.00	1.769
0.10	1.773
0.30	1.745
0.50	1.739
0.70	1.732
0.90	1.726

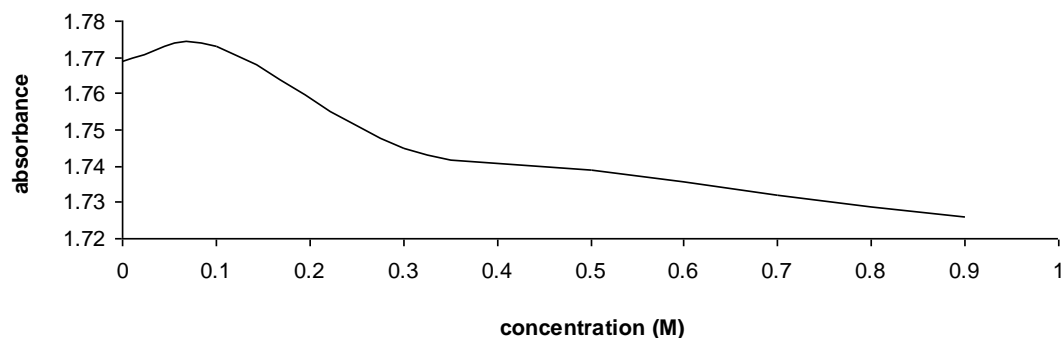


Fig. (2.32) Effect of NaOH concentration on absorbance of Co(II)-SA

2.7.5.2 Effect of reagent concentration

The effect of the reagent concentration on the absorbance was studied by preparing solutions of 2.00 ppm of Co(II) ion and 0.10 M of NaOH in different reagent concentrations. The absorbance was read at 265 nm and the results are shown in Table (2.30) and Fig. 2.33.

Table (2.30) Effect of reagent concentration on absorbance

Reagent (M)	Absorbance
1.00×10^{-4}	1.839
2.00×10^{-4}	1.832
4.00×10^{-4}	1.819
6.00×10^{-4}	1.863
8.00×10^{-4}	1.851

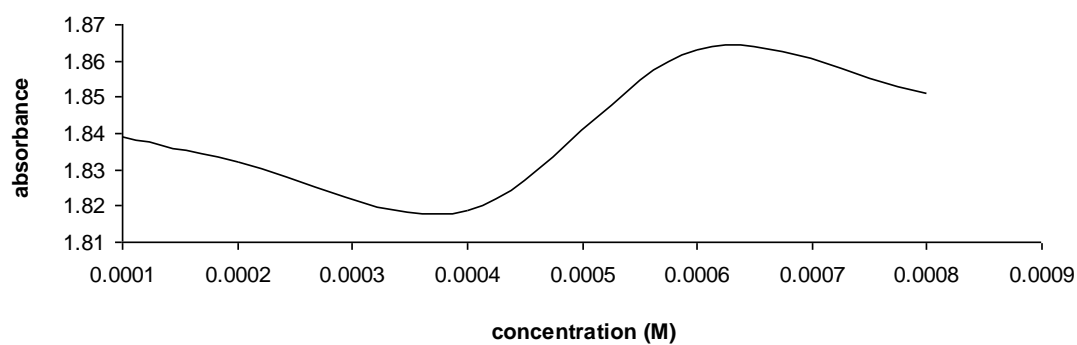


Fig. (2.33) Effect of reagent concentration on absorbance of Co(II)-SA

2.7.5.3 Calibration curve for Co(II)-SA

The Calibration curve for Co(II)-SA was constructed using 0.10 M of NaOH , 6.00×10^{-4} M of the reagent and different concentrations of the metal ion. The absorbance was measured at 265 nm and the results are shown in Table (2.31) and Fig. 2.34.

Table (2.31) Calibration curve for Co(II)-SA

Co(II) (ppm)	Absorbance
2.00	1.845
4.00	1.854
6.00	1.859
8.00	1.876
10.00	1.889
12.00	1.897

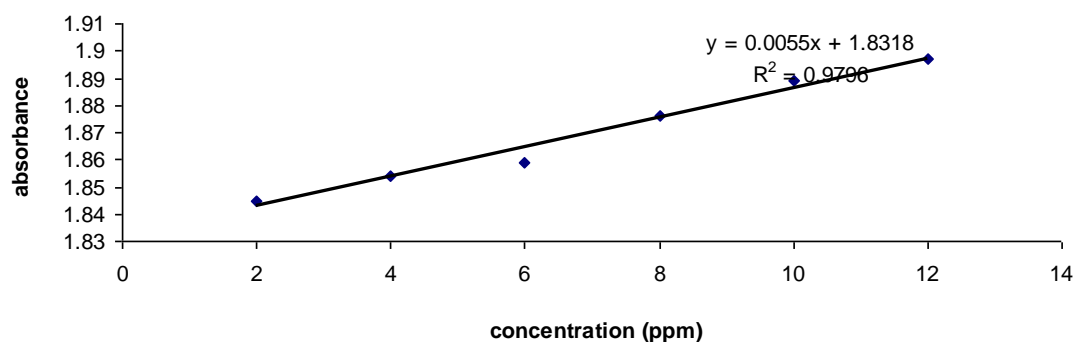


Fig. (2.34) Calibration curve for Co(II)-SA

2.7.6 Analytical parameters for Fe(III)-SA

2.7.6.1 Effect of NaOH concentration on absorbance of Fe (III)-SA

A series of Fe(III)-SA solutions were prepared of 2.00 ppm of Fe(III) ion and 1.00×10^{-4} M of SA in different sodium hydroxide concentrations. The absorbance was measured at 265 nm and the results are shown in Table (2.32) and Fig. 2.35.

Table (2.32) Effect of NaOH concentration on absorbance of Fe(III)-SA

NaOH (M)	Absorbance
0.00	1.772
0.10	1.799
0.30	1.778
0.50	1.757
0.70	1.739
0.90	1.715

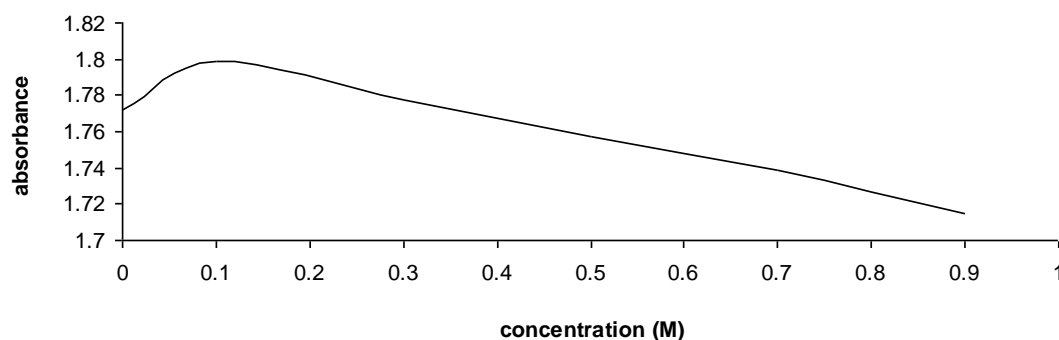


Fig. (2.35) Effect of NaOH concentration on absorbance of Fe (III)-SA

2.7.6.2 Effect of reagent concentration

The effect of the reagent concentration on the absorbance was studied by preparing solutions of 2.00 ppm of Fe(III) ion and 0.10 M of NaOH in different reagent concentrations. The absorbance was read at 265 nm and the results are shown in Table (2.33) and Fig. 2.36.

Table (2.33) Effect of reagent concentration on absorbance

Reagent (M)	Absorbance
1.00×10^{-4}	1.789
2.00×10^{-4}	1.773
4.00×10^{-4}	1.765
6.00×10^{-4}	1.812
8.00×10^{-4}	1.791

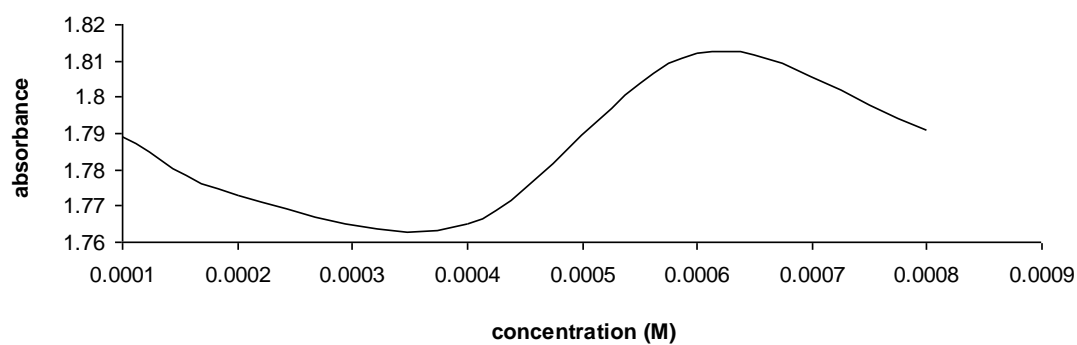


Fig.(2.36) Effect of reagent concentration on absorbance of Fe(III)-SA

2.7.6.3 Calibration curve for Fe(III)-SA

The Calibration curve for Fe(III)-SA was constructed using 0.10 M of NaOH , 6.00×10^{-4} M of the reagent and different concentrations of the metal ion. The absorbance was measured at 265 nm and the results are shown in Table (2.34) and Fig. 2.37.

Table (2.34) Calibration curve for Fe(III)-SA

Fe(III) (ppm)	Absorbance
2.00	1.782
4.00	1.793
6.00	1.813
8.00	1.820
10.00	1.834
12.00	1.846

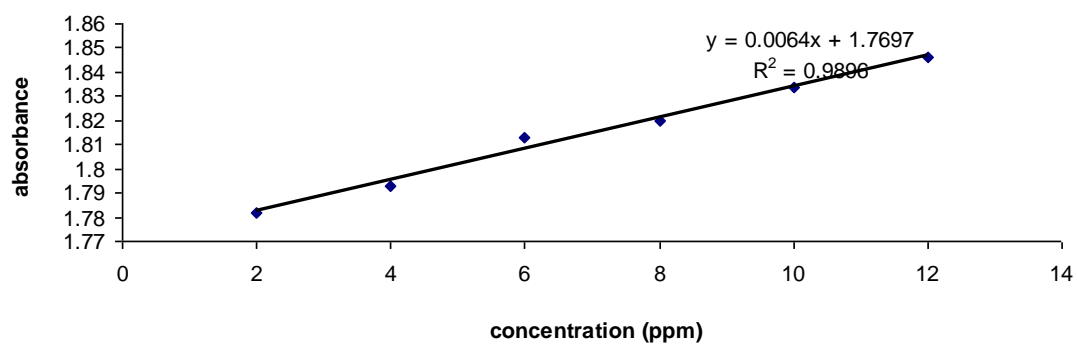


Fig. (2.37) Calibration curve for Fe(III)-SA

2.7.7 Analytical parameters for Zn(II)-SA

2.7.7.1 Effect of NaOH concentration on absorbance of Zn (II)-SA

A series of Zn(II)-SA solutions were prepared of 2.00 ppm of Zn (II) ion and 1.00×10^{-4} M of SA in different sodium hydroxide concentrations. The absorbance was measured at 275 nm and the results are shown in Table (2.35) and Fig. 2.38.

Table (2.35) Effect of NaOH concentration on absorbance of Zn(II)-SA

NaOH (M)	Absorbance
0.00	1.642
0.10	1.682
0.30	1.658
0.50	1.645
0.70	1.631
0.90	1.616

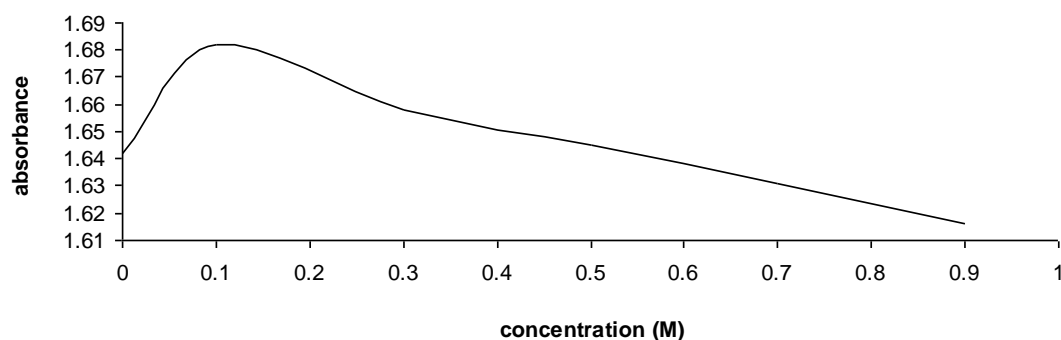


Fig. (2.38) Effect of NaOH concentration on absorbance of Zn(II)-SA

2.7.7.2 Effect of reagent concentration

The effect of the reagent concentration on the absorbance was studied by preparing solutions of 2.00 ppm of Zn(II) ion and 0.10 M of NaOH in different reagent concentrations. The absorbance was read at 275 nm and the results are shown in Table (2.36) and Fig. 2.39.

Table (2.36) Effect of reagent concentration on absorbance

Reagent (M)	Absorbance
1.00×10^{-4}	1.685
2.00×10^{-4}	1.650
4.00×10^{-4}	1.661
6.00×10^{-4}	1.694
8.00×10^{-4}	1.683

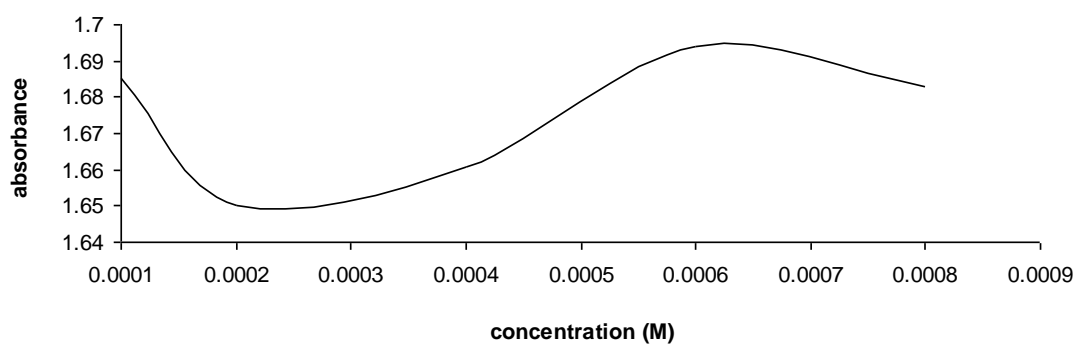


Fig. (2.39) Effect of reagent concentration on absorbance of Zn(II)-SA

2.7.7.3 Calibration curve for Zn(II)-SA

The Calibration curve for Zn(II)-SA was constructed using 0.10 M of NaOH , 6.00×10^{-4} M of the reagent and different concentrations of the metal ion. The absorbance was measured at 275 nm and the results are shown in Table (2.37) and Fig. 2.40.

Table (2.37) Calibration curve for Zn(II)-SA

Zn(II) (ppm)	Absorbance
2.00	1.647
4.00	1.654
6.00	1.660
8.00	1.667
10.00	1.674
12.00	1.681

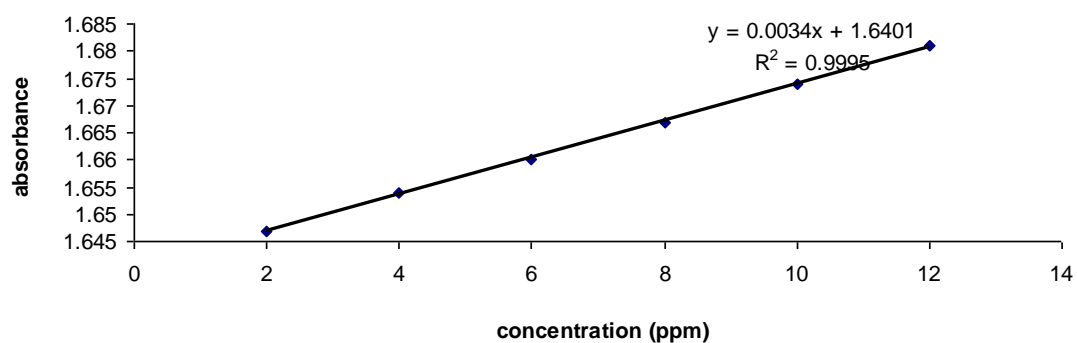


Fig. (2.40) Calibration curve for Zn(II)-SA

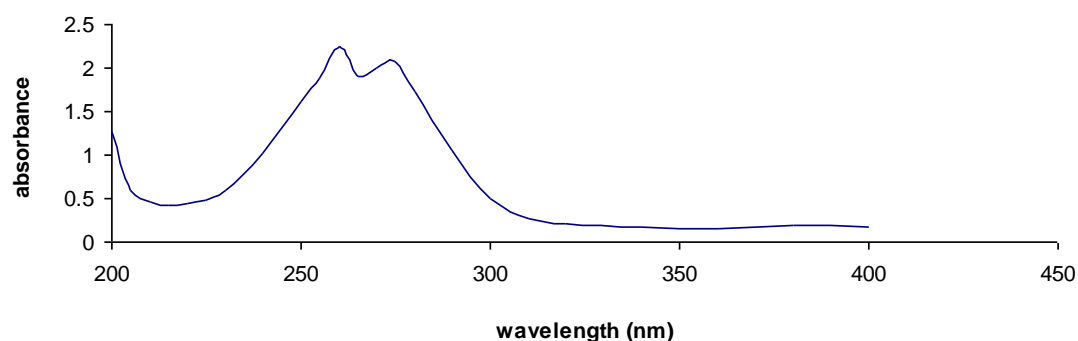
2.8 Analytical parameters for BPhA complexes with some metal ions

2.8.1 Scanning of the wavelength of maximum absorption

To locate the wavelengths of maximum absorbance, solutions of 1.0×10^{-4} M of reagent and 2.00 ppm of each of the metal ions was scanned. The wavelengths of maximum absorption (λ_{\max}) are shown in Table (2.38) and Fig. 2.41, 2.42, 2.43, 2.44, and 2.45 respectively.

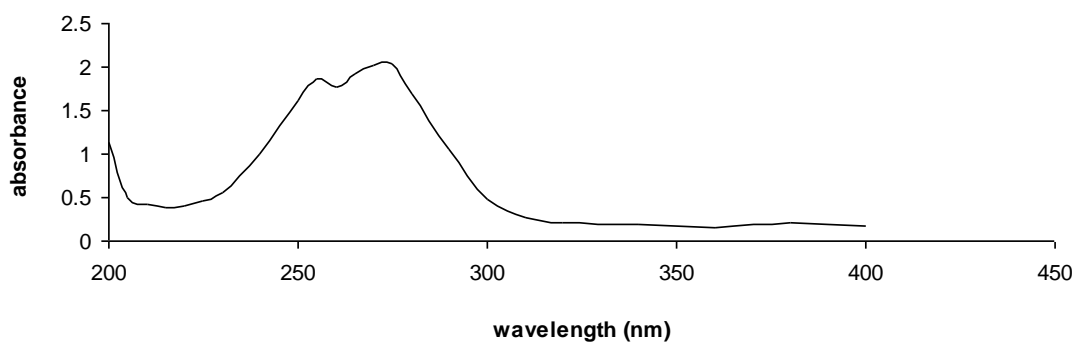
Table (2.38) wavelengths of maximum absorption (λ_{\max}) for metal ions complexes

Metal ion	Wavelength (nm)	Absorbance
Cu(II)	260	2.246
Cr(III)	275	2.036
Co(II)	265	2.346
Fe(III)	265	2.260
Zn(II)	260	2.509



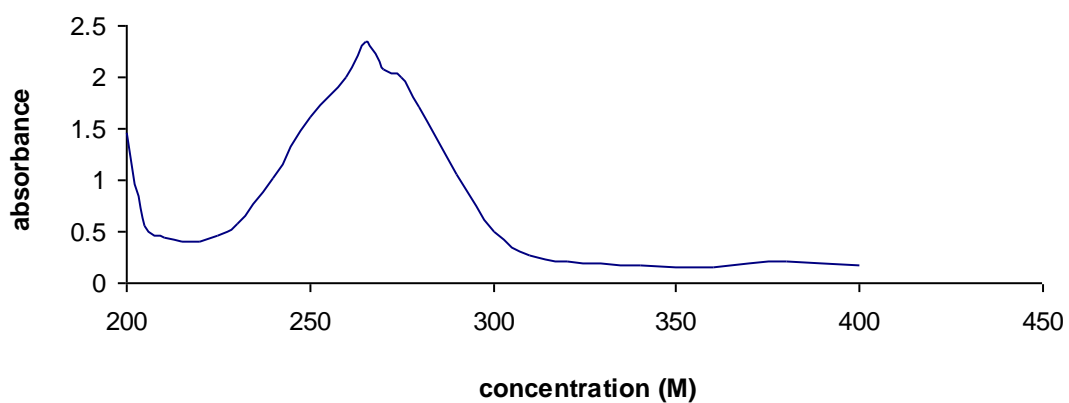
abs nm
2.246 260

Fig. (2.41).wavelengths of maximum absorption (λ_{\max}) for BPhA with Cu



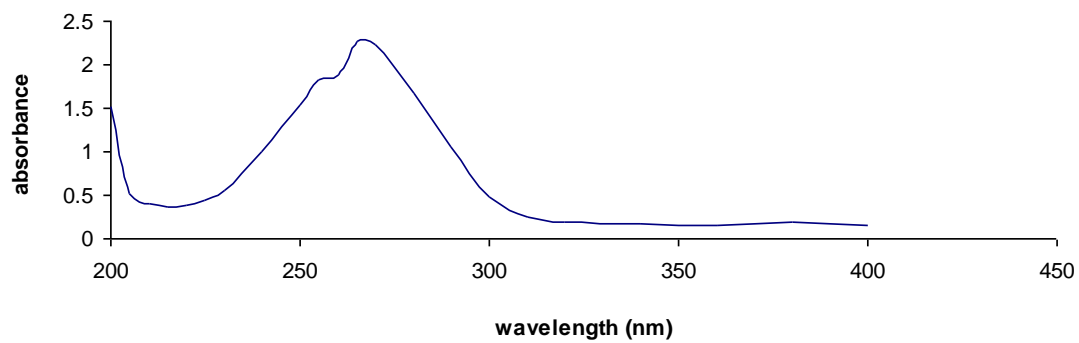
abs	nm
2.036	275

Fig. (2.42) wavelengths of maximum absorption (λ_{\max}) for BPhA with Cr



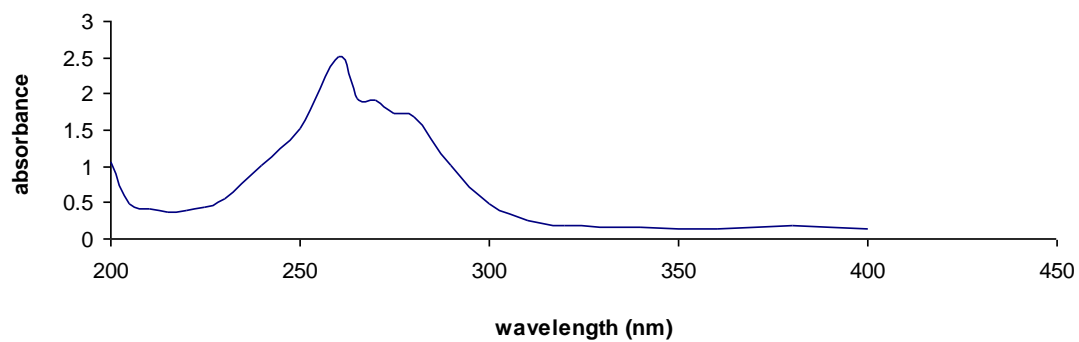
abs	nm
2.346	265

Fig. (2.43) wavelengths of maximum absorption (λ_{\max}) for BPhA with Co



abs	nm
2.260	265

Fig. (2.44) wavelengths of maximum absorption (λ_{\max}) for BPhA with Fe



abs	nm
2.509	260

Fig. (2.45) wavelengths of maximum absorption (λ_{\max}) for BPhA with Zn

2.8.2 Effect of PH on the absorbance

Three sets of mixture were prepared by keeping the concentration of metal ions and ligand at 2.00 ppm and 1.00×10^{-4} M, respectively, to the first flask 1 ml of 0.10 M hydrochloric acid were added, and to the second 1 ml of 0.10 M sodium hydroxide were added, and the third was taken as reference. Absorbance at λ_{max} of each metal ion were measured. The results are shown in Table (2.39).

Table (2.39) Effect of HCl , NaOH on the absorbance

Metal	Reference	HCl	NaOH
Cu(II)	1.633	1.592	1.671
Cr(III)	1.738	1.703	1.765
Co(II)	1.733	1.724	1.761
Fe(III)	1.765	1.758	1.845
Zn(II)	1.789	1.781	1.803

2.8.3 Analytical parameters for Cu(II)-BPhA

2.8.3.1 Effect of NaOH concentration on absorbance of Cu (II)-BPhA

A series of Cu(II)-BPhA solutions were prepared of 2.00 ppm of Cu(II) ion and 1.00×10^{-4} M of BPhA in different sodium hydroxide concentrations. The absorbance was measured at 260 nm and the results are shown in Table (2.40) and Fig. 2.46.

Table (2.40) Effect of NaOH concentration on absorbance of Cu (II) -BPhA

NaOH (M)	Absorbance
0.00	1.633
0.10	1.671
0.30	1.650
0.50	1.639
0.70	1.628
0.90	1.619

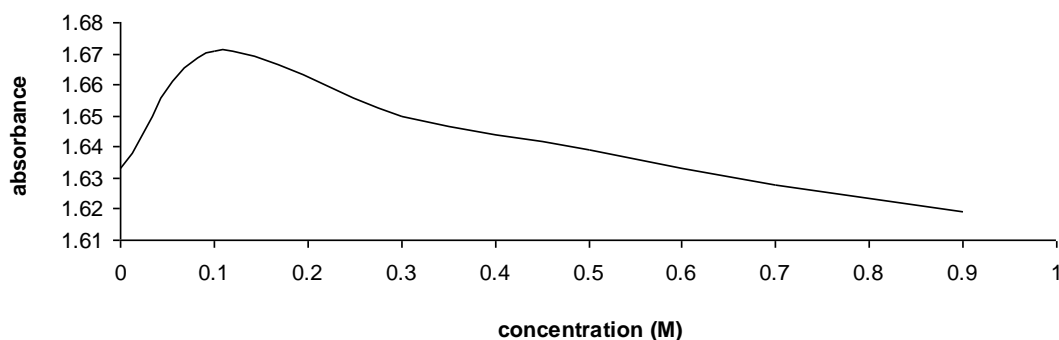


Fig. (2.46) Effect of NaOH concentration on absorbance of Cu (II)-BPhA

2.8.3.2 Effect of reagent concentration

The effect of the reagent concentration on the absorbance was studied by preparing solutions of 2.00 ppm of Cu(II) ion and 0.10 M of NaOH in different reagent concentrations. The absorbance was read at 260 nm and the results are shown in Table (2.41) and Fig. 2.47.

Table (2.41) Effect of reagent concentration on absorbance

Reagent (M)	Absorbance
1.00×10^{-4}	1.692
2.00×10^{-4}	1.671
4.00×10^{-4}	1.745
6.00×10^{-4}	1.724
8.00×10^{-4}	1.712

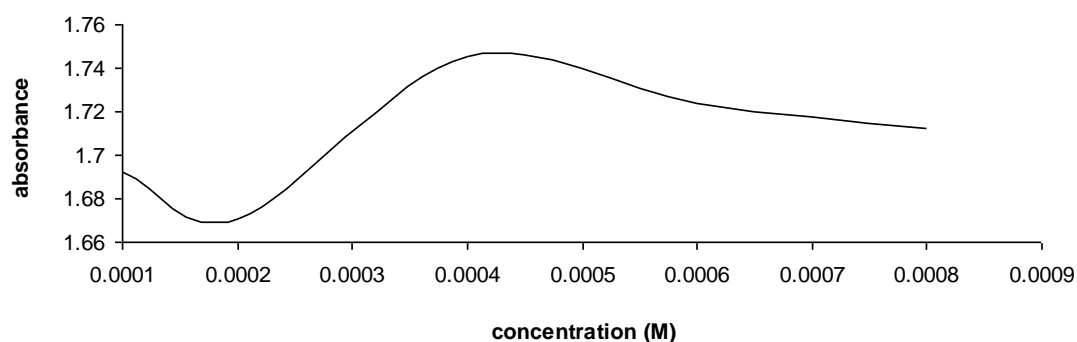


Fig.(2.47) Effect of reagent concentration on absorbance of Cu(II)-BPhA

2.8.3.3 Calibration curve for Cu(II)-BPhA

The Calibration curve for Cu(II)-BPhA was constructed using 0.10 M of NaOH , 4.00×10^{-4} M of the reagent and different concentrations of the metal ion. The absorbance was measured at 260 nm and the results are shown in Table (2.42) and Fig. 2.48.

Table (2.42) Calibration curve for Cu(II)-BPhA

Cu(II) (ppm)	Absorbance
2.00	1.771
4.00	1.785
6.00	1.820
8.00	1.834
10.00	1.846
12.00	1.858

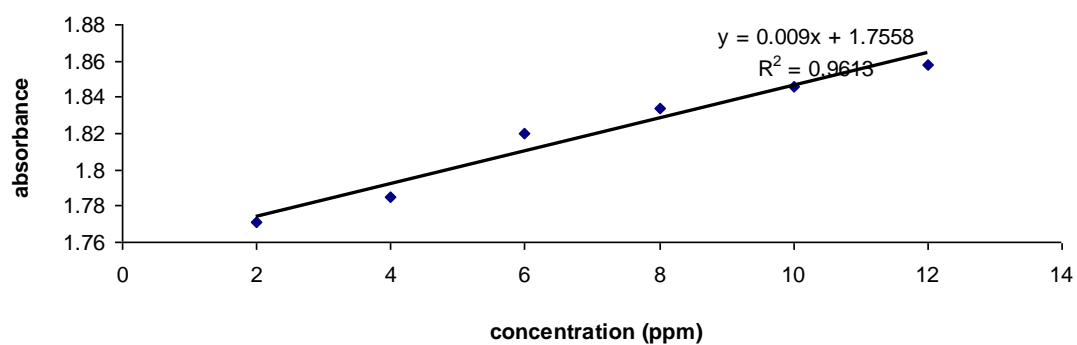


Fig. (2.48) Calibration curve for Cu(II)- BPhA

2.8.4 Analytical parameters for Cr(III)-BPhA

2.8.4.1 Effect of NaOH concentration on absorbance of Cr-(III)BPhA

A series of Cr(III)-BPhA solutions were prepared of 2.00 ppm of Cr(III) ion and 1.00×10^{-4} M of BPhA in different sodium hydroxide concentrations. The absorbance was measured at 275 nm and the results are shown in Table (2.43) and Fig. 2.49.

Table (2.43) Effect of NaOH concentration on absorbance of Cr (III)-BPhA

NaOH (M)	Absorbance
0.00	1.738
0.10	1.765
0.30	1.748
0.50	1.740
0.70	1.724
0.90	1.713

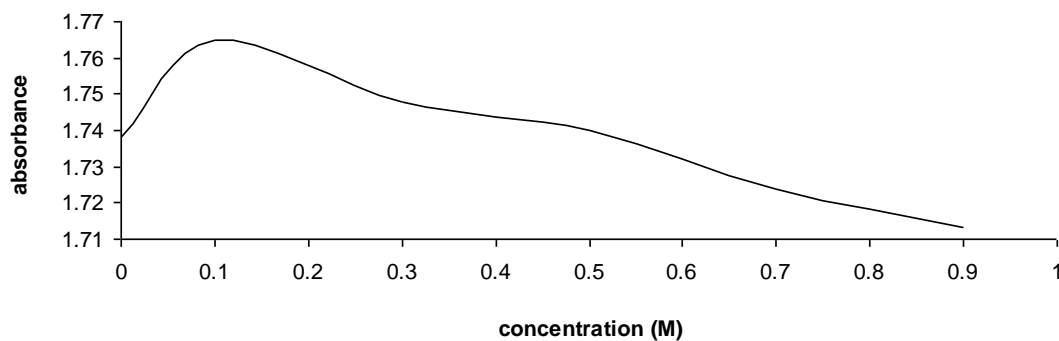


Fig. (2.49) Effect of NaOH concentration on absorbance of Cr (III)-BPhA

2.8.4.2 Effect of reagent concentration

The effect of the reagent concentration on the absorbance was studied by preparing solutions of 2.00 ppm of Cr(III) ion and 0.10 M of NaOH in different reagent concentrations. The absorbance was read at 275 nm and the results are shown in Table (2.44) and Fig. 2.50.

Table (2.44) Effect of reagent concentration on absorbance

Reagent (M)	Absorbance
1.00×10^{-4}	1.668
2.00×10^{-4}	1.740
4.00×10^{-4}	1.722
6.00×10^{-4}	1.693
8.00×10^{-4}	1.682

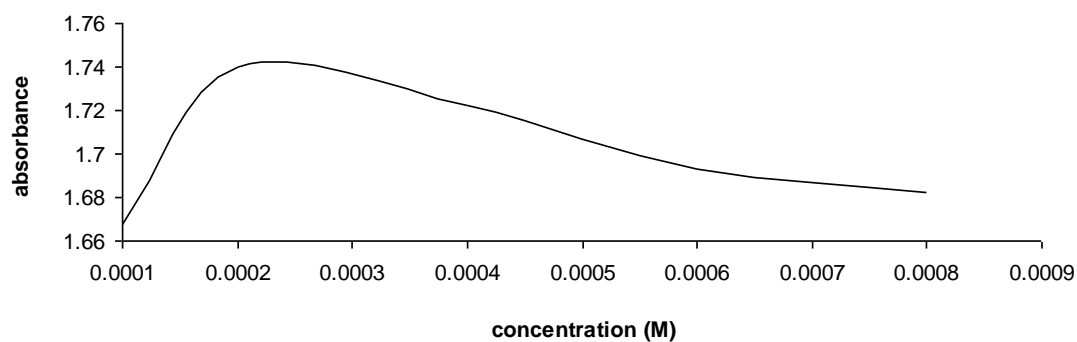


Fig. (2.50) Effect of reagent concentration on absorbance of Cr(III)-BPhA

2.8.4.3 Calibration curve for Cr(III)-BPhA

The Calibration curve for Cr(III)-BPhA was constructed using 0.10 M of NaOH , 2.00×10^{-4} M of the reagent and different concentrations of the metal ion. The absorbance was measured at 275 nm and the results are shown in Table (2.45) and Fig. 2.51.

Table (2.45) Calibration curve for Cr(III)-BPhA

Cr(III) (ppm)	Absorbance
2.00	1.732
4.00	1.758
6.00	1.776
8.00	1.791
10.00	1.815
12.00	1.827

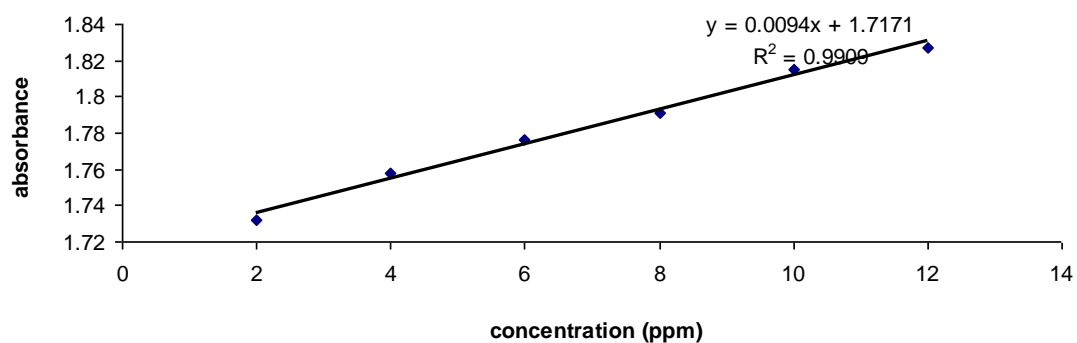


Fig. (2.51) Calibration curve for Cr(III)-BPhA

2.8.5 Analytical parameters for Co(II)-BPhA

2.8.5.1 Effect of NaOH concentration on absorbance of Co (II)-BPhA

A series of Co(II)-BPhA solutions were prepared of 2.00 ppm of Co(II) ion and 1.00×10^{-4} M of BPhA in different sodium hydroxide concentrations. The absorbance was measured at 265 nm and the results are shown in Table (2.46) and Fig. 2.52.

Table (2.46) Effect of NaOH concentration on absorbance of Co(II)-BPhA

NaOH (M)	Absorbance
0.00	1.733
0.10	1.761
0.30	1.748
0.50	1.729
0.70	1.719
0.90	1.708

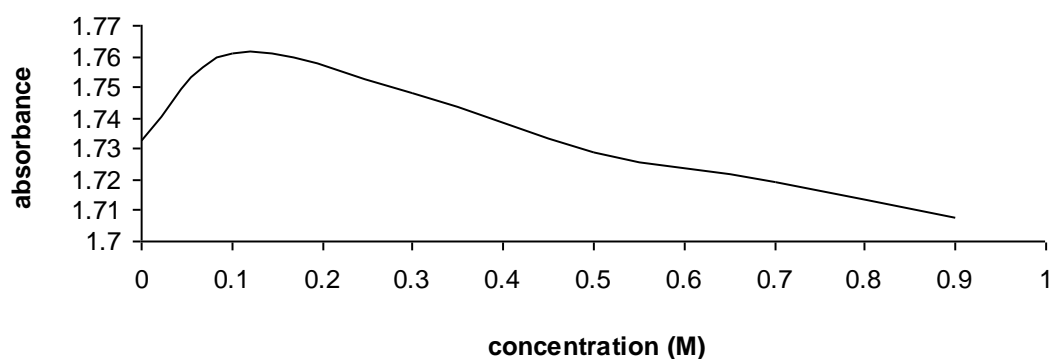


Fig. (2.52) Effect of NaOH concentration on absorbance of Co(II)-BPhA

2.8.5.2 Effect of reagent concentration

The effect of the reagent concentration on the absorbance was studied by preparing solutions of 2.00 ppm of Co(II) ion and 0.10 M of NaOH in different reagent concentrations. The absorbance was read at 265 nm and the results are shown in Table (2.47) and Fig. 2.53.

Table (2.47) Effect of reagent concentration on absorbance

Reagent (M)	Absorbance
1.00×10^{-4}	1.708
2.00×10^{-4}	1.694
4.00×10^{-4}	1.731
6.00×10^{-4}	1.682
8.00×10^{-4}	1.635

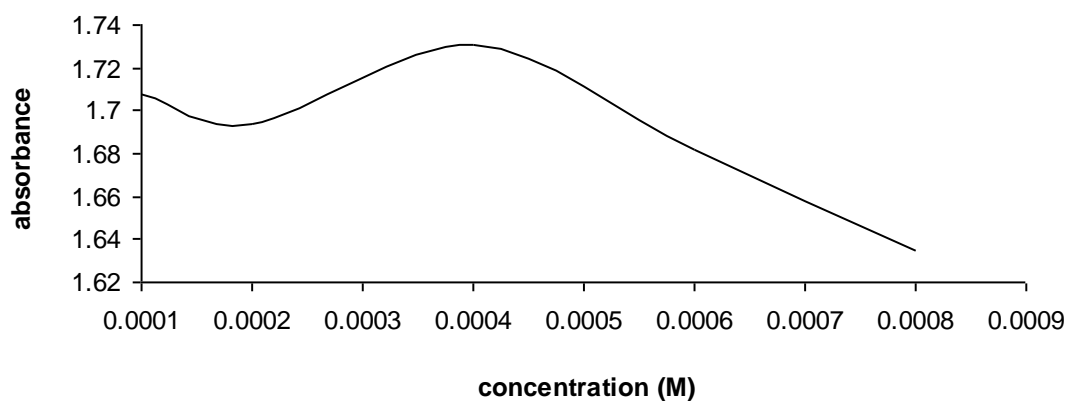


Fig. (2.53) Effect of reagent concentration on absorbance of Co(II)-BPhA

2.8.5.3 Calibration curve for Co(II)-BPhA

The Calibration curve for Co(II)-BPhA was constructed using 0.10 M of NaOH , 4.00×10^{-4} M of the reagent and different concentrations of the metal ion. The absorbance was measured at 265 nm and the results are shown in Table (2.48) and Fig. 2.54.

Table (2.48) Calibration curve for Co(II)-BPhA

Co(II) concentration (ppm)	Absorbance
2.00	1.758
4.00	1.771
6.00	1.786
8.00	1.806
10.00	1.823
12.00	1.841

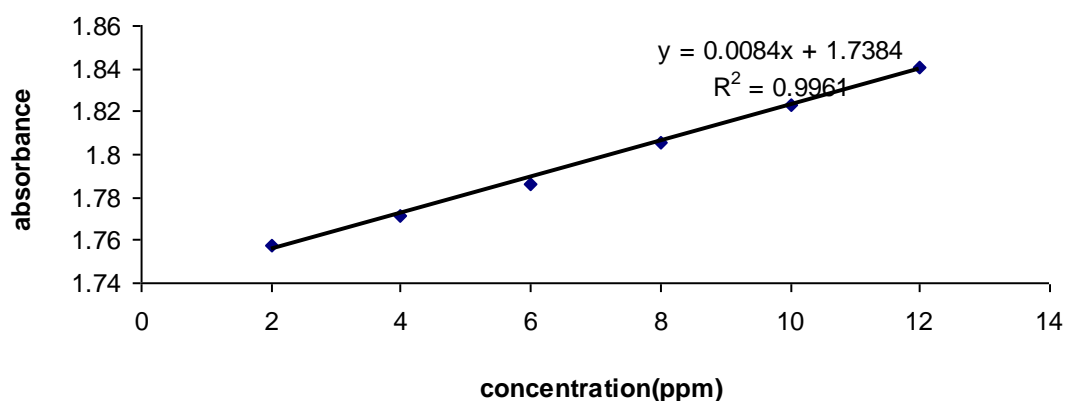


Fig. (2.54) Calibration curve for Co(II)-BPhA

2.8.6 Analytical parameters for Fe(III)-BPhA

2.8.6.1 Effect of NaOH concentration on absorbance of Fe (III)-BPhA

A series of Fe(III)-BPhA solutions were prepared of 2.00 ppm of Fe(III) ion and 1.00×10^{-4} M of BPhA in different sodium hydroxide concentrations. The absorbance was measured at 265 nm and the results are shown in Table (2.49) and Fig. 2.55.

Table (2.49) Effect of NaOH concentration on absorbance of Fe(III)-BPhA

NaOH (M)	Absorbance
0.00	1.765
0.10	1.845
0.30	1.785
0.50	1.763
0.70	1.728
0.90	1.711

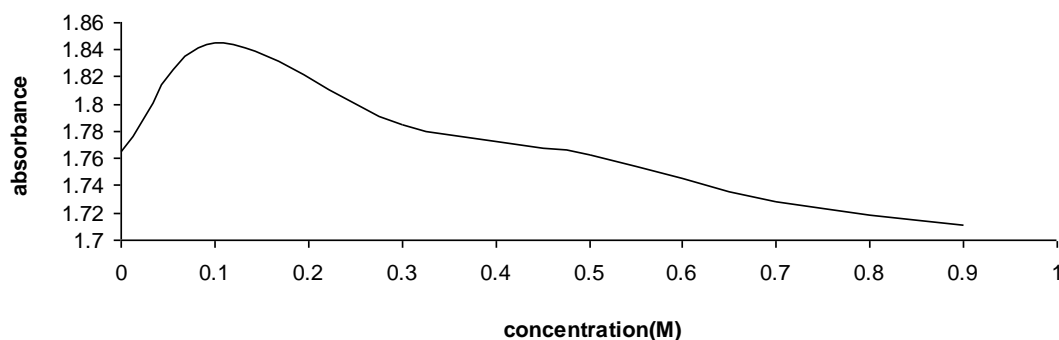


Fig. (2.55) Effect of NaOH concentration on absorbance of Fe (III)-BPhA

2.8.6.2 Effect of reagent concentration

The effect of the reagent concentration on the absorbance was studied by preparing solutions of 2.00 ppm of Fe(III) ion and 0.10 M of NaOH in different reagent concentrations. The absorbance was read at 265 nm and the results are shown in Table (2.50) and Fig. 2.56.

Table (2.50) Effect of reagent concentration on absorbance

Reagent (M)	Absorbance
1.00×10^{-4}	1.853
2.00×10^{-4}	1.836
4.00×10^{-4}	1.815
6.00×10^{-4}	1.895
8.00×10^{-4}	1.879

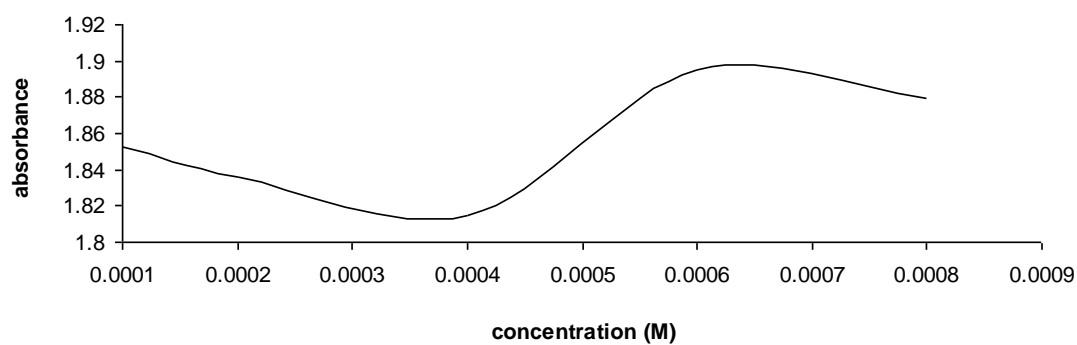


Fig. (2.56) Effect of reagent concentration on absorbance of Fe(III)-BPhA

2.8.6. 3 Calibration curve for Fe(III)-BPhA

The Calibration curve for Fe(III)-BPhA was constructed using 0.10 M of NaOH , 6.00×10^{-4} M of the reagent and different concentrations of the metal ion. The absorbance was measured at 265 nm and the results are shown in Table (2.51) and Fig. 2.57.

Table (2.51) Calibration curve for Fe(III)-BPhA

Fe(III) (ppm)	Absorbance
2.00	1.876
4.00	1.892
6.00	1.909
8.00	1.921
10.00	1.938
12.00	1.949

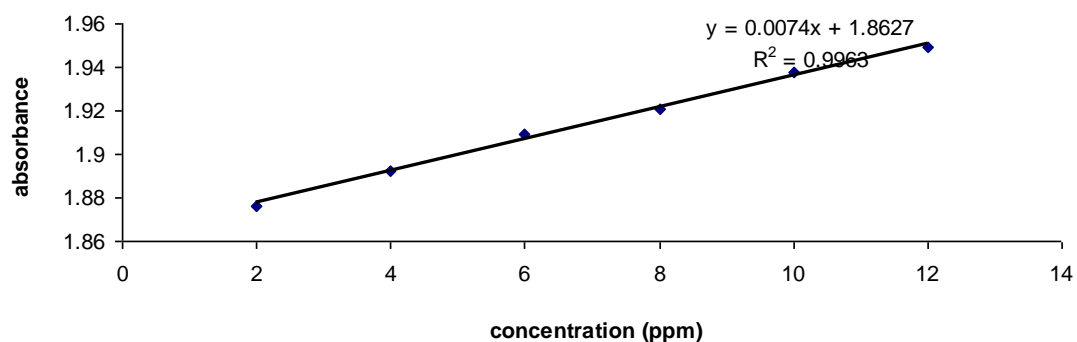


Fig. (2.57) Calibration curve for Fe(III)-BPhA

2.8.7 Analytical parameters for Zn(II)-BPhA

2.8.7.1 Effect of NaOH concentration on absorbance of Zn (II)-BPhA

A series of Zn(II)-BPhA solutions were prepared of 2.00 ppm of Zn (II) ion and 1.00×10^{-4} M of BPhA in different sodium hydroxide concentrations. The absorbance was measured at 260 nm and the results are shown in Table (2.52) and Fig. 2.58.

Table (2.52) Effect of NaOH concentration on absorbance of Zn(II)-BPhA

NaOH (M)	Absorbance
0.00	1.789
0.10	1.803
0.30	1.792
0.50	1.774
0.70	1.788
0.90	1.769

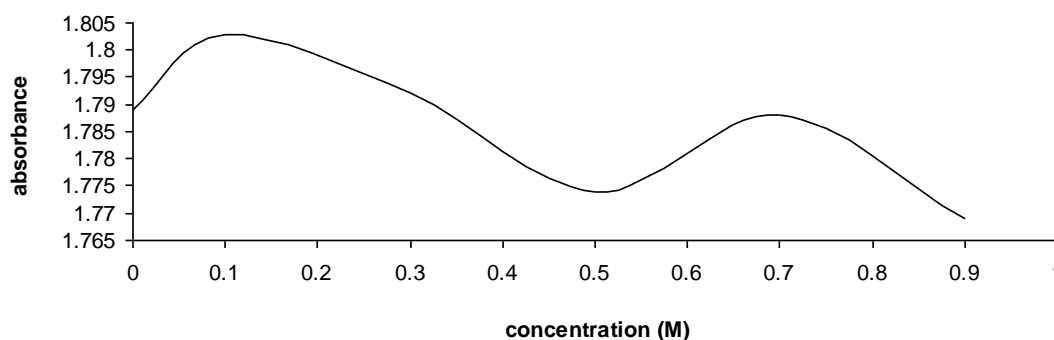


Fig. (2.58) Effect of NaOH concentration on absorbance of Zn(II)-BPhA

2.8.7.2 Effect of reagent concentration

The effect of the reagent concentration on the absorbance was studied by preparing solutions of 2.00 ppm of Zn(II) ion and 0.10 M of NaOH in different reagent concentrations. The absorbance was read at 260 nm and the results are shown in Table (2.53) and Fig. 2.59.

Table (2.53) Effect of reagent concentration on absorbance

Reagent (M)	Absorbance
1.00×10^{-4}	1.808
2.00×10^{-4}	1.822
4.00×10^{-4}	1.854
6.00×10^{-4}	1.913
8.00×10^{-4}	1.873

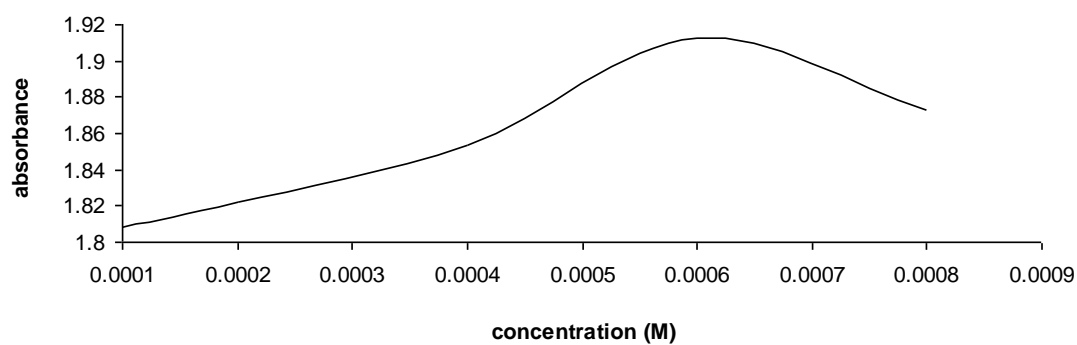


Fig. (2.59) Effect of reagent concentration on absorbance of Zn(II)-BPhA

2.8.7.3 Calibration curve for Zn(II)-BPhA

The Calibration curve for Zn(II)- BPhA was constructed using 0.10 M of NaOH , 6.00×10^{-4} M of the reagent and different concentrations of the metal ion. The absorbance was measured at 260 nm and the results are shown in Table (2.54) and Fig. 2.60.

Table (2.54) Calibration curve for Zn(II)-BPhA

Zn(II) (ppm)	Absorbance
2.00	1.843
4.00	1.856
6.00	1.869
8.00	1.883
10.00	1.899
12.00	1.912

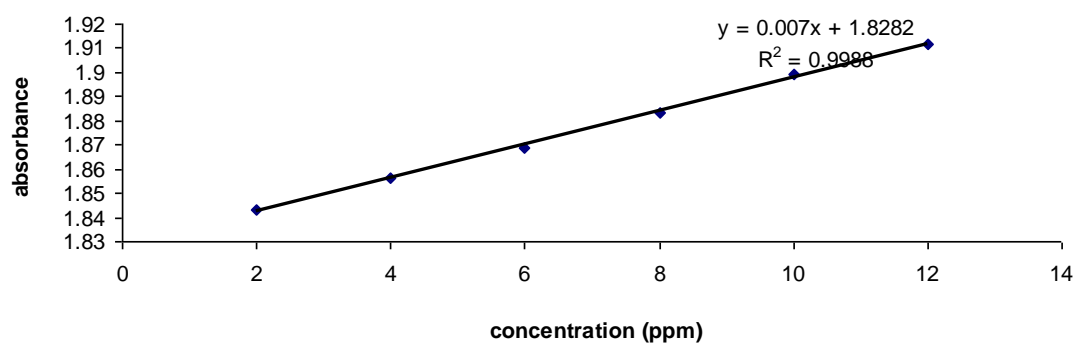


Fig. (2.60) Calibration curve for Zn(II)-BPhA

2.9 Effect of foreign metal ions

In order to assess the possible analytical of these complexes, the effect of some foreign metal ions was determined.

2.9.1 Effect of metal ions that have same maximum wavelength

2.9.1.1 Effect of Co(II) on determination of Cu(II)

To study the effect of foreign metal ion on the determination of Cu(II) under the optical conditions, 2.00 ppm of Cu(II) , 2.00 ppm of Co(II) , 4.00×10^{-4} M of the reagent (BA) and 0.10 M of NaOH . The absorbance was read at 260 nm (λ_{\max} of Cu(II)-BA). The results are shown in Table (2.55).

Table (2.55) Effect of Co(II) on determination of Cu(II)

Complex	Absorbance
Cu	1.776
Cu + Co	1.887

2.9.1.2 Effect of Cu(II) on determination of Co(II)

To study the effect of foreign metal ion on the determination of Cu(II) under the optical conditions, 2.00 ppm of Cu(II) , 2.00 ppm of Co(II) , 6.00×10^{-4} M of the reagent (BA) and 0.10 M of NaOH . The absorbance was read at 260 nm (λ_{\max} of Co(II)-BA). The results are shown in Table (2. 56).

Table (2.56) Effect of Cu(II) on determination of Co(II)

Complex	Absorbance
Co	1.815
Co +Cu	1.843

2.9.1.3 Effect of Co(II) on determination of Fe(III)

To study the effect of foreign metal ion on the determination of Fe(III) under the optical conditions, 2.00 ppm of Fe(III) , 2.00 ppm of Co(II) , 6.00×10^{-4} M of the reagent (SA) and 0.10 M of NaOH . The absorbance

was read at 265 nm (λ_{max} of Fe(III)-SA). The results are shown in Table (2.57).

Table (2.57) Effect of Co(II) on determination of Fe(III)

Complex	Absorbance
Fe	1.934
Fe + Co	1.961

2.9.1.4 Effect of Fe(III) on determination of Co(II)

To study the effect of foreign metal ion on the determination of Co(II) under the optical conditions, 2.00 ppm of Fe(III) , 2.00 ppm of Co(II) , 6.00×10^{-4} M of the reagent (SA) and 0.10 M of NaOH . The absorbance was read at 265 nm (λ_{max} of Fe(III)-SA). The results are shown in Table (2.58).

Table (2.58) Effect of Fe(III) on determination of Co(II)

Complex	Absorbance
Co	1.885
Co +Fe	1.961

2.9.1.5 Effect of Cu(II) on determination of Zn(II)

To study the effect of foreign metal ion on the determination of Zn(II) under the optical conditions, 2.00 ppm of Zn(II) , 2.00 ppm of Cu(II) , 6.00×10^{-4} M of the reagent (BPhA) and 0.10 M of NaOH . The absorbance was read at 260 nm (λ_{max} of Zn(II)-BPhA). The results are shown in Table (2.59).

Table (2.59) Effect of Cu(II) on determination of Zn(II)

Complex	Absorbance
Zn	1.855
Zn +Cu	1.873

2.9.1.6 Effect of Zn (II) on determination of Cu (II)

To study the effect of foreign metal ion on the determination of Cu(II) under the optical conditions, 2.00 ppm of Zn(II) , 2.00 ppm of Cu(II) ,

4.00*10⁻⁴ M of the reagent (BPhA) and 0.10 M of NaOH . The absorbance was read at 260 nm (λ_{max} of Cu (II)-BPhA). The results are shown in Table (2.60).

Table (2.60) Effect of Zn(II) on determination of Cu(II)

Complex	Absorbance
Cu	1.892
Cu +Zn	2.523

2.9.1.7 Effect of Co(II) on determination of Fe(III)

To study the effect of foreign metal ion on the determination of Fe(III) under the optical conditions, 2.00 ppm of Fe(III) , 2.00 ppm of Co(II) , 6.00*10⁻⁴ M of the reagent (BPhA) and 0.10 M of NaOH . The absorbance was read at 265 nm (λ_{max} of Fe(III)-BPhA). The results are shown in Table (2.61).

Table (2.61) Effect of Co(II) on determination of Fe(III)

Complex	Absorbance
Fe	1.925
Fe +Co	1.979

2.9.1.8 Effect of Fe(III) on determination of Co(II)

To study the effect of foreign metal ion on the determination of Co(II) under the optical conditions, 2.00 ppm of Fe(III) , 2.00 ppm of Co(II) , 4.00*10⁻⁴ M of the reagent (BPhA) and 0.10 M of NaOH . The absorbance was read at 265 nm (λ_{max} of Co(II)-BPhA). The results are shown in Table (2.62).

Table (2.62) Effect of Fe(III) on determination of Co(II)

Complex	Absorbance
Co	1.992
Co + Fe	2.009

2.9.2 Effect of metal ions that have different maximum wavelength

2.9.2.1 Effect of Cr(III) on determination of Co(II)

To study the effect of foreign metal ion on the determination of Co(II) under the optical conditions, 2.00 ppm of Cr(III) , 2.00 ppm of Co(II) , 6.00×10^{-4} M of the reagent (SA) and 0.10 M of NaOH . The absorbance was read at 265 nm (λ_{\max} of Co(II)-SA) . The results are shown in Table (2.63).

Table (2.63) Effect of Cr(III) on determination of Co(II)

Complex	Absorbance
Co	1.850
Co + Cr	1.853

2.9.2.2 Effect of Co(II) on determination of Cr(III)

To study the effect of foreign metal ion on the determination of Cr(III) under the optical conditions, 2.00 ppm of Cr(III) , 2.00 ppm of Co(II) , 6.00×10^{-4} M of the reagent (SA) and 0.10 M of NaOH . The absorbance was read at 280 nm (λ_{\max} of Cr(II)-SA). The results are shown in Table (2.64).

Table (2.64) Effect of Co(II) on determination of Cr(III)

Complex	Absorbance
Cr	1.542
Cr + Co	1.545

Chapter Three

Chapter Three

Discussion and Conclusion

3.1 Discussion

Three Schiff's bases were synthesized, Benzylidene aniline (BA), Salicylidene aniline (SA), Benzophenone aniline (BPhA). The three compounds were synthesized by condensation of aniline with benzaldehyde, salicylaldehyde and benzophenone respectively, in methanol.

These Schiff's bases were identified using IR spectrum, nitrogen content, melting point, and their applications as analytical reagent were investigated using UV/VIS spectrophotometer. The following metal ions Cu(II), Cr(III), Co(II), Fe(III) and Zn(II) were scanned with these reagents.

The optimum conditions of the practical analytical application of each Schiff's base with these metal ions were studied. The complexes of Cu(II), Cr(III), Co(II), Fe(III) and Zn(II) with BA, SA and BPhA respectively, gave a higher absorbance in basic medium (NaOH). While in the acidic medium (HCl) the absorbance are lowered.

Cu(II)-BA, Cr(III)-BA, Co(II)-BA, Fe(III)-BA and Zn(II)-BA absorbances increased by 2.07% , 1.32% , 0.16% , 3.6% and 0.56% respectively, in the presence of 0.10 M NaOH.

Cu(II)-SA, Cr(III)-SA, Co(II)-SA, Fe(III)-SA, and Zn(II)-SA absorbances increased by 1.6% , 0.98% , 0.56% , 0.62% and 2.49% respectively, in the presence of 0.10 M NaOH.

Cu(II)-BPhA, Cr(III)-BPhA, Co(II)-BPhA, Fe(III)-BPhA, and Zn(II)-BPhA absorbances increased by 2.32% , 1.55% , 1.61% , 4.53% and 0.78% respectively, in the presence of 0.10 M NaOH.

In order to assess the possible analytical applications of these types of complexes, the effect of some foreign metal ions was studied.

A serious interference was observed from Zn(II) in the determination of Cu(II) with BPhA.

On the other hand, it was found the minimum interfere was observed from Co(II) in the determination of Cu(II) with BA , from Fe(II) in the determination of Co(II) with SA, from Fe(III) in the determination of Co(II) with BPhA.

No interference was observed from Cu(II) in the determination of Co(II) with BA , from Co(II) in the determination of Fe(III) with SA, from Cu(II) in the determination of Zn(II) with BPhA, from Co(II) in the determination of Fe(III) with BPhA, Cr(III) in the determination of Co(II) with SA and Co(II) in the determination of Cr(III) with SA.

A survey of the literature reveals that most of the Schiff's bases synthesised were used for inorganic studies and few are used for analytical purposes. However, no work has been done on the transition metal complexes of the Schiff's base derived from BA, SA, and BPhA.

3.2 Conclusion

In conclusion it can be seen from this work that BA can be used for determination of Cu(II), Cr(III), Co(II),Fe(III) and Zn(II) , SA can be used for determination of Cu(II), Cr(III), Co(II),Fe(III) and Zn(II) , BPhA can be used for determination of Cu(II), Cr(III), Co(II),Fe(III) and Zn(II).

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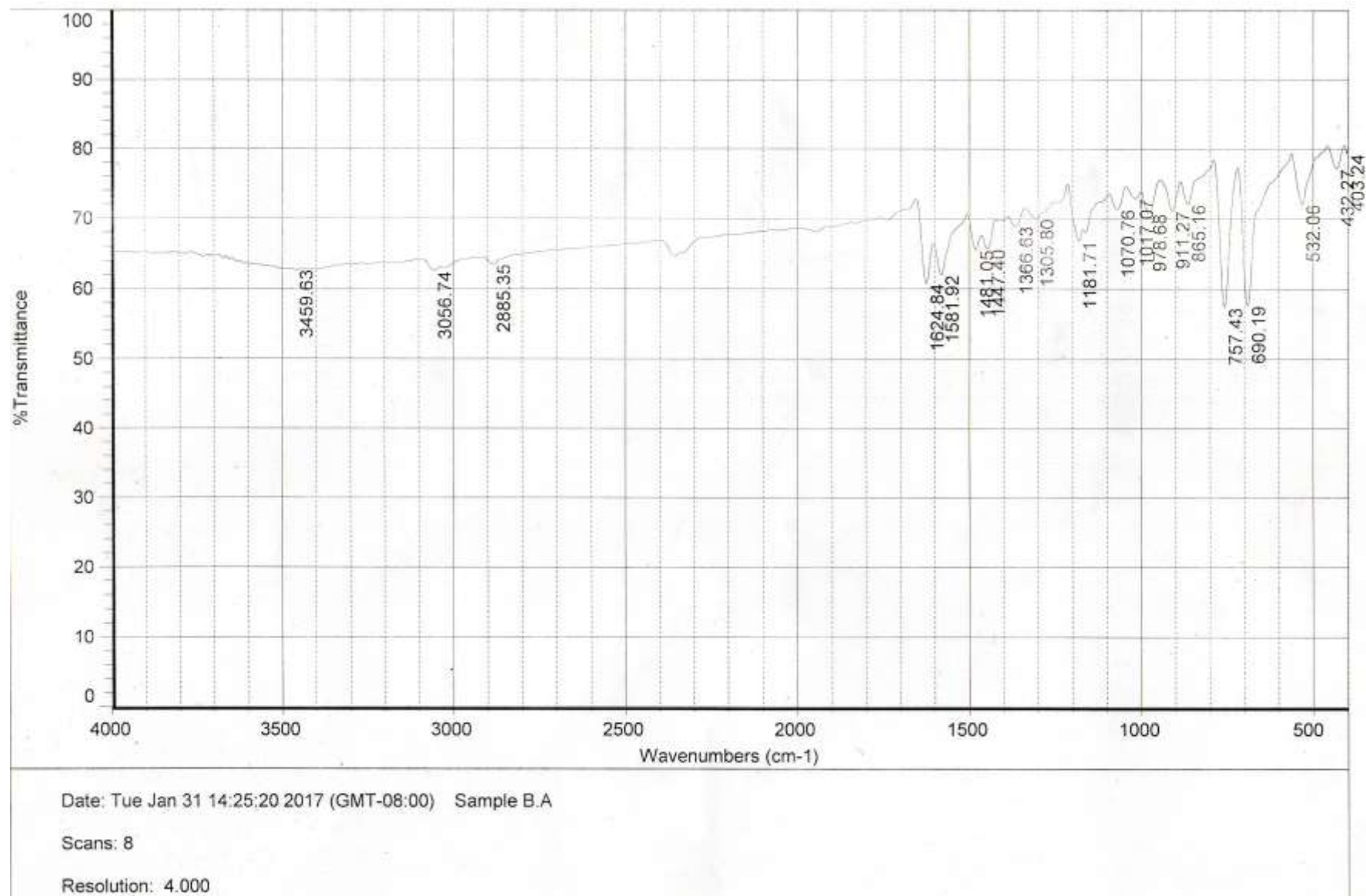
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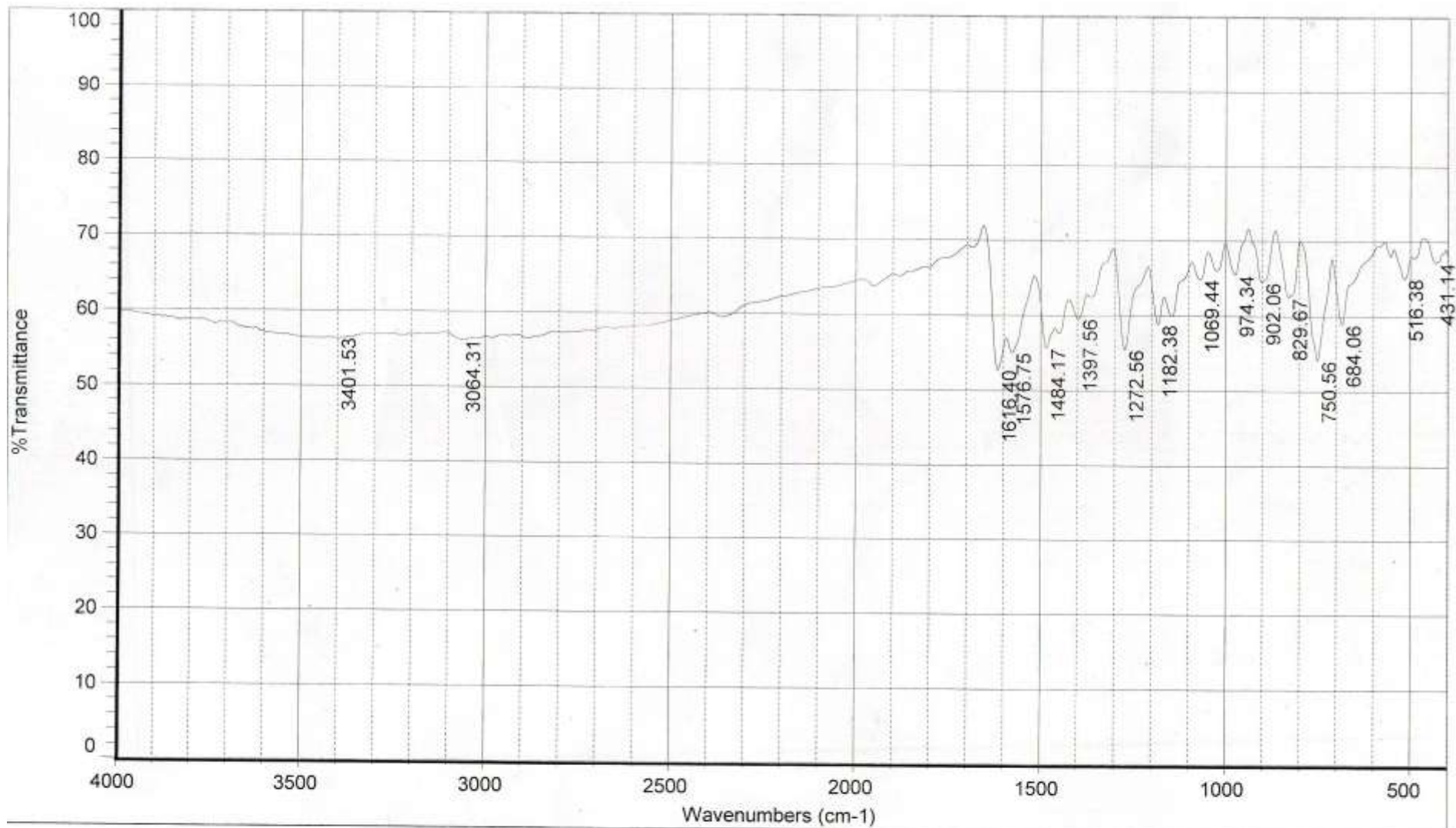
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Appendices



IR spectrum of BA

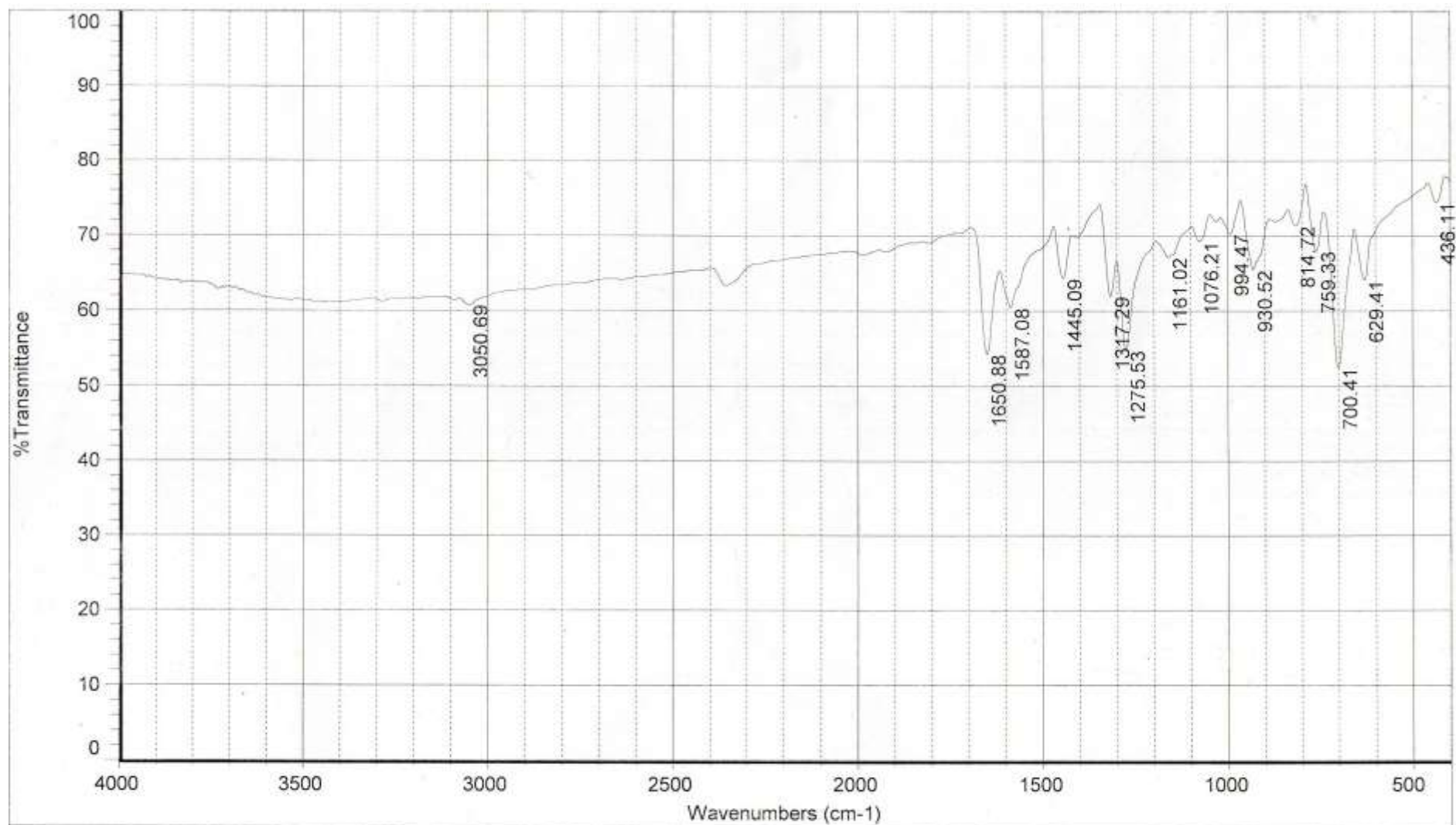


Date: Tue Jan 31 13:35:02 2017 (GMT-08:00) Sample S.A

Scans: 8

Resolution: 4.000

IR spectrum of SA



Date: Tue Jan 31 14:01:09 2017 (GMT-08:00) Sample B.ph.A

Scans: 8

Resolution: 4.000

IR spectrum of BPhA



IR spectrophotometer



UV/ VIS spectrophotometer



Melting point