Abbreviations

4-AAP	*4-Amino Antipyrine*
APDC	**AmmoniumPyrrolidineDithioCarbamate**
Bipy	*2,2'-Bipyridine*
5-Br-PADAP	*2-(5-bromo-2-pyridylazo)-5-diethylamino Hydrochloride*
CDTA	*1,2-CyclohexaneDiamineTetraacetic Acid*
CL	*Chemiluminescence*
CPE	*Cloud Point Extraction*
CSV	*Cathodic Stripping Voltammetry*
DDTC	*Diethyldithiocarbamate*
DP	*Differential Pulse*
DPC	*1,5-Diphenylcarbazide*
DPH	*Dopamine hydrochloride*
EDXRFS / WDXRFS	*Energy Dispersive X-Ray Fluorescence Spectrometry/Wavelength Dispersive X-Ray Fluorescence Spectrometry*
ET	*Electronic Tongue*
ETAAS	*Electro thermal Atomic Absorption Spectrometry*
FIA	*Flow Injection Analysis*
GF-AAS	*Graphite Furnas Atomic Absorption Spectrometry*
HMDE (DME)	*Hanging Drop Mercury Electrode Poloragraphy*
Htfa	*1,1,1-trifluaroacerylacetate*
8-HQ	*8-Hydroxyquinoline*

IC	***Ion Chromatography***
ICP	***Inductively Coupled Plasma***
ICP-AES	***Inductively Coupled Plasma -Atomic Emission Spectrometry***
IC-TLS	***Ion Chromatography - Thermal Lens Spectrometry***
ICP-OES	***Inductively Coupled Plasma–Optical Emission Spectrometry***
LLE	***Liquid Liquid Extraction***
MAS (UV-VIS)	***Molecular Absorption Spectrometry***
MBTH	***3-Methyl-2-benzothiazolinone hydrazine Hydrochloride***
MIBK	***Methyl isobutyl ketone***
MS	***Mass Spectrometry***
NEDA	***N-(1-naphthyl)ethylenediamine dihydrochloride***
PAR	***4-(2-pyridylazo) resorcinol***
RNAA	***Radio analytical Neutron Activation Analysis***
RP-HPLC	***Reverse phase- High Performance Liquid Chromatography***
RSD	***Relative Standard Deviation***
SPE	***Solid Point Extraction***
SPME	***Solid Point Micro Extraction***
SH	***Thioglycolic acids***
TTHA	***triethylenetetranitrilohexaacetic acid***
VB	***Variamine blue***
UV-LED	***Ultra Violet - Light Emitting Diode***
XPS	***X-Ray Photoelectron Spectroscopy***

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دراسة طيفية لتقدير الكروم والفناديوم وتطبيقاته

Introduction:-

For many years, the analysis of inorganic components resulted only in the total concentration of the studied element. Nowadays, the instrumentation allows us to determine the concentration of trace elements, but the obtained information is not worthy, because the investigation does not reveal the particular form and oxidation state of the element of our interest. Because of the difference of the toxicity of different redox states of some elements, there is a need to develop analytical methods to determine the element species separately with sufficient precision and sensitivity. It justifies the improvement of the method applied till this time, which provides a more efficient separation and a pre-concentration of the different species.

Till now, there are many methods have been developed in order to separate and determine the different metal species, but at the present there are only few analytical techniques with sufficient sensitivity and selectivity, which are available for the direct determination and speciation of metals. Spectrophotometer is one of the most common methods of analytical measurement of trace amount of metals [(1)].

1-1. Chromium

Chromium was discovered by Vauquelin in 1797, which is also known as the mineral crocoite's ($PbCrO_4$) [2,3]. Chromium and its compounds have been very important in many industries. Chromium occurs naturally and most abundantly as the mineral chromites. This ore, $FeCr_2O_4$ is a spinel and is the only commercial source of chromium [2].

1-1-1. Physical and Chemical Properties of Chromium:-

Chromium is a white, hard, lustrous and brittle metal that is extremely resistant to ordinary corrosive agents [4]. Chromium is a metal with atomic number 24, atomic mass 51.996, melting point (°c) about 1860, boiling point (°c) about 2670 and specific gravity 7.2 [2].

Chromium can exist in several chemical forms, which have oxidation states ranging from 0 to VI. However, only trivalent and hexavalent chromium are stable enough to occur in the environment [5,6]. Fig (1-1) shows the standard reduction potentials of the different oxidation states of chromium.

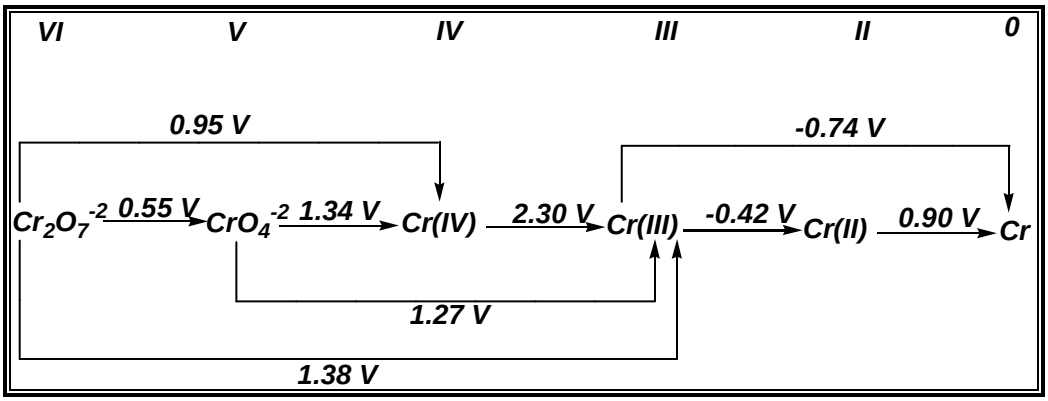

Figure (1-1): Standard reduction potential of chromium

1-1-2. Availability and the major uses of Chromium:-

Chromium is found in many minerals. It is the only commercial source of Cr [5]. Chromium is a naturally occurring element found in rocks, animals, plants, soil and in volcanic dust and gases [7]. Chromium is found to play a pivotal role in many industries.

Chromium is used in ferrous and nonferrous alloys in refractoriness, and chemicals, and it enhances the alloys hardened ability, creep, impact strength, and resistance to corrosion oxidation and wear ferrous alloys mainly stainless steels [8].

1-1-3. Chromium Biochemistry:-

Chromium is known to be essential trace elements but it is found to be toxic at high levels [9].

1-1-3-1. Essentiality of Chromium

a. Function

Chromium is an essential nutrient required for normal glucose and lipid metabolism as it enhances the effect of insulin [10].

Insulin is secreted by the pancreas in response to the increased blood glucose levels. Insulin binds to receptors on cell surfaces, which cause the uptake of glucose by the cells. Thus insulin provides the cells with glucose and also prevents blood glucose levels from becoming elevated [11].

Insulin also plays a role in the metabolism of fat and protein. Thus chromium plays an important role in the body as it behaves as a cofactor by enhancing the response of the insulin receptor to insulin [12].

b. Sources

Chromium is found in most fresh foods and drinking water. Sources rich in chromium include bread, cereals, spices, fresh vegetables, meats, fish, brewer's yeast and beer, etc [13].

c. Deficiency [13,14]

Chromium deficiency has been associated with impaired glucose tolerance, fasting hyperglycemia, glucosuria, elevated percent body fat, decreased lean body mass, maturity-onset diabetes, cardiovascular disease and impaired fertility. Thus, it can be seen that it is an essential nutrient. There is no recommended dietary allowance for chromium; however, a safe and an adequate daily intake of 50-200 μg/day has been set.

1-1-3-2. Chromium as insulin enhancing agent.

Chromium is an essential trace mineral that participates actively in the carbohydrate metabolism [15], Mainly co-acting with insulin, improving the glucose tolerance. However, due to its action in stimulating the insulin sensitivity, chromium may also influence the protein metabolism, causing higher stimulation in the amino acids uptake and hence increasing the synthesis of proteins [16].

The chromium action does not seem to be limited to the coadjuvant participation with insulin. Although no chromium-dependent enzyme has been identified, this mineral seems to inhibit the hydroxymethyl glutaryl-CoA reductase hepatic enzyme, reducing the cholesterol plasmatic concentration. [17]

From several in vivo and vitro studies [18], it was initially thought that chromium potentate the action of insulin as part of an organic complex, glucose tolerance factor (GTF). Emerging evidence has shown that the

biologically active chromium is chromium – oligopeptide complexes as biomimetic chromium supplements [19].

The chromium complex of picolinic acid and the most popularly used dietary supplements have been shown to modulate intracellular path ways of glucose metabolism and improve comerbidities associated with insulin resistance in several animal and human studies [20].

Four $Cr.^{3+}$atoms bind to the apochromodulin making it active under the form of chromodulin that, in turn, binds to the active site in the insulin receptor, fulfilling its activation and amplifying the insulin signal figure (1-2) [21].

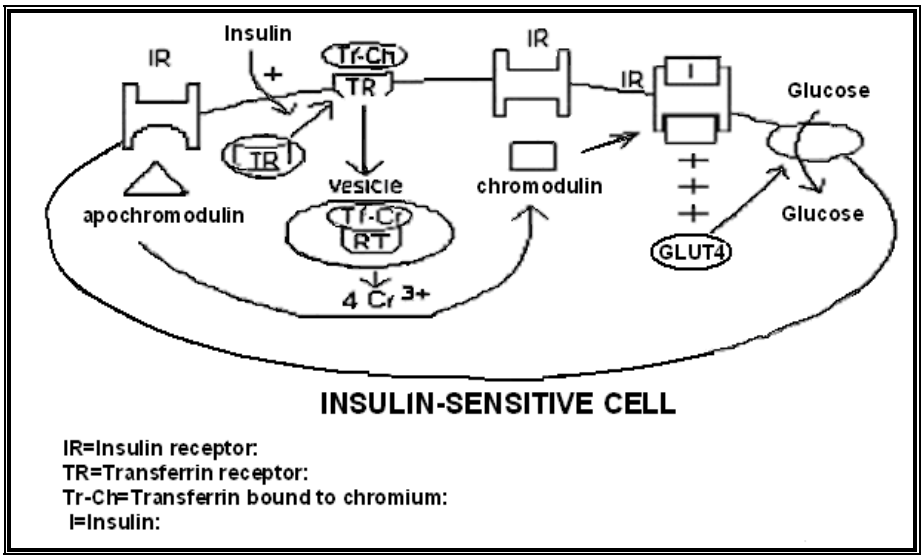

Figure (1-2): Mechanism proposed for the chromium participation in the insulin action

1-2. Vanadium

Vanadium is a member of group VB of the periodic table. It was named after the Norse goddess Vanadis, the goddess of beauty and fertility. Andres Manuel Del Rio was the first chemist to provide the idea of this new element in 1801. But it was discovered by Nils Sefstrom, a Swedish chemist in 1830 [22]. Vanadium and its compounds have been very important in many industrial and environmental processes [23].

1-2-1. Physical and Chemical Properties of Vanadium:-

Vanadium is a metal with a high purity form. It is soft and ductile, but it can be hardened and embroiled by oxygen, nitrogen, carbon, and hydrogen [24]. Vanadium is a metal with atomic number 23, atomic mass 50.9415, melting point (°c) about 1910, and boiling point (°c) about 3407.

In nature, vanadium occurs in two different oxidation forms, V (V) and V (IV). Both species can exist in the environment but V (V) is the most stable and also the most toxic species. Other oxidation states such as V (II) and V (III) are not stable and will be oxidized to V (IV) and V (V) by atmospheric oxygen [25,26].

1-2-2. Availability and the major uses of Vanadium:-

Vanadium is a naturally occurring element found in rocks, some iron ores, and crude petroleum deposit [27].

Vanadium is used widely in industrial processes including the production of special steels, temperature resistant alloys, in glass industry, in the manufacture of pigment and points. For lining are welding electrodes and catalysts. Its use with non-ferrous metals is of a particular importance in the atomic energy industry [28].

1-2-3. Vanadium Biochemistry:-

Vanadium is known to be essential trace elements but it is found to be toxic at high levels [29].

1-2-3-1. Essentiality of Vanadium

a. Function

Vanadium is essentially required as a beneficial element that helps in carbohydrate metabolism, prevention of some heart diseases [30].

Vanadium is an essential micronutrient needed for cellular metabolism, and it may play a role in reducing cholesterol. Vanadium has been found to stimulate insulin action. Vanadium is thought to activate insulin receptors making the cells more receptive to insulin and through this, stimulates insulin activity. Vanadium improves insulin sensitivity. It is also useful as a supplement for Type II diabetics, resulting in modest reductions of blood sugar and hepatic (liver) insulin resistance [31].

b. Sources

Vanadium is found in very small amounts in a wide variety of foods, including many cereals, fishes, fresh fruits and vegetables contain this element more than 40 mg per gram of food. Foods rich in vanadium include mushrooms, shellfish, dill seed, parsley, black pepper, etc [32].

C. Deficiency [33]

Vanadium is an ultra-trace mineral found in the human diet and human body. It is essential for some animals. Deficiency symptoms in these animals include growth retardation, bone deformities, and infertility; however, vanadium has not proven to be an essential mineral for humans [33].

1-2-3-2. Vanadium as insulin enhancing agent [34]

Vanadium compounds mimic actions of insulin through alternative signaling pathways which involve the inhibition of phosphotyrosine phosphates and the interplay between two non-insulin receptor tyrosine kinesis [35,36].

The insulin-like potential of vanadium has been demonstrated in vitro, and in vivo in rodents (where the oxidation states IV and V were found to be equipotent)[37], and more recently in human diabetic subjects [38].The clinical studies performed so far have used the simple naturally occurring inorganic vanadium salts (metavanadate (V) or vanadyl sulphate (VS, IV)) [39].

Vanadium compounds have been synthesized [40]. Among which organic vanadium (IV) complexes (vanadyl cation coordinated to an organic ligand) merit further attention.

1-3. Toxicity of Chromium and Vanadium [41-43]

Chromium and Vanadium enter the body through inhalation, ingestion or by breathing the contaminated work place air or skin contact during work, or by living near uncontrolled hazardous waste site containing chromium and vanadium or industries that use these metals.

Exposure to high levels of these metals can cause harmful health effects. The major effects from breathing high level of chromium and vanadium can cause irritation to nose. Including runny nose, nose bleeds, and ulcers and holes in the nasal septum.

Ingesting large amounts of these metals can cause stomach upsets and ulcers, convulsions, kidney and liver damage, and even death. Skin contact with certain compounds can cause skin ulcers. Some people are extremely sensitive to chromium and vanadium.

Allergic reaction consisting of severe redness and swelling of the skin have been noted. Several studies have shown that chromium and vanadium compounds can increase the risk of lung cancer. Animal studies have also shown an increased risk of cancer.

1-4. Chromium and Vanadium Speciation Analysis: - (A literature review)

Chromium and Vanadium are introduced into the environment by effluents in several industries. It is important to control these elements since they are both toxic and carcinogenic. As this toxicity depends on oxidation state, it is especially interesting to determine the most abundant species.

In this overview [44,45], we describe the requirements for chromium and vanadium determination and speciation and review the analytical methods that have been used in these studies. Focusing in particular on developments, we examine the features of detection techniques, pre-treatments and applications of the various methods [46].

Chromium and Vanadium speciation analysis is shown to predominantly involve two important issues: separation of the species such that they are preconcentrated and detection of the species.

1-4-1. Quantitative Separation of Chromium and Vanadium.

Various methods exist for the separation of chromium and vanadium species. Some methods involve preconcentration or derivitisation of one or both species. Certain methods involve the determination of one species and the calculation of the other species as the difference between the total chromium and vanadium concentration and that of the measured species while in other methods both species are determined simultaneously [47].

a. Extraction:

Extraction is primarily used to separate analyte from a matrix thus eliminating or reducing interferences from other components. Secondly, it is used to concentrate the analyte up to a detectable concentration level. The process must not only be done in such a way as to prevent loss or contamination but also to prevent changes in the determination of the metal. There are some publication researches in this field.

Table (1-1): Comparative data from some recent studies on chromium and vanadium determination by extraction technique.

Ion determine	*Technique*	*Method*	*D.L*	*Ref.*
Cr^{VI}, Cr^{III} in water samples.	CPE	By CPE with diethyldithiocarbamate (DDTC) as the chelating agent and Triton X-114 as the extracting. Baseline separation of the DDTC chelates of Cr(III) and Cr(VI) was realized on a RP-C18 column with the use of a mixture of methanol–water–acetonitrile buffered with NaAc–HAc solution (pH 3.6) as the mobile phase at a flow rate of 1.0 ml min^{-1}.	3.4, 5.2 µg/l respectively	48
Cr^{III} in water samples.	SPME	By (SPME) coupled with (GC)-(FPD) was developed Aqueous Cr (III) was first converted to the volatile chromium trifluoroacetylacetonate ($Cr(tfa)_3$) by derivatization with 1,1,1-trifluoroacetylacetone (Htfa), and using a polyimide-coated silica fiber.	2 ng ml^{-1}	49
Cr^{VI}, Cr^{III} in mineral waters and Salinas samples	SPE	Cr (VI) species were separated From Cr (III) by (SPE) with APDC. The APDC complexes were formed in the sample solution under proper conditions, adsorbed on Diaion HP-2MG resin and the resin was separated from the sample. After elution with concentrated nitric acid Cr (VI) was determined by GF-AAS.	0.03,0.3 µg/l respectively	50
Cr^{VI} in waters samples	LLE	Diperoxo chromium oxide is produced by reaction of hydrogen peroxide on Cr (VI). Diperoxo chromium creates a complex with ethyl acetate, while Cr(III) remains in an unchanged form in the aqueous phase. By this means Cr(VI)	50 ng dm^{-3}	51

		can be extracted into ethyl acetate from the aqueous phase. The optimal conditions of Cr(III)–Cr(VI) separation, as well as the chromium content of the ethyl acetate phase were determined with GFAAS.		
Cr^{VI}, Cr^{III} in natural water, soil and sediment samples	**SPE**	**Cr (VI) has been separated from Cr(III) and preconcentrated as Cr(III) diphenyl carbazone complex by using Ambers orb 563 resin and determined by spectrophotometer method at 540 nm. Effect of analytical parameters such as sulfuric acid concentration**	–	**52**
Cr^{VI}, Cr^{III} in soils samples	**SPE**	**By (GFAAS), using extraction with EDTA followed by strong anionic (SPE). The step gradient elution technique with 0.1 and 0.5 M NaCl as eluent in sequence was sufficient to separate Cr (III) and Cr (VI) with recoveries of 99.7 and 93.4%, respectively.**	–	**53**
V^{IV} in petroleum crude's and natural water, samples	**SPE**	**A micro determination method for vanadium by SPE spectrophotometers has been developed. 5-Bromosalicyl-hydroxamic acid was used as chromogenic reagent to form a 1:2 violet complex which is easily sorbed and concentrated on a dextran-type anion-exchange resin. The resin-phase absorbance's at 560 and 850 nm were measured directly**	–	**54**
V^{IV}, V^{V} in biological samples	**SPE**	**Separation based on Controlling the pH of media both V^{IV} and V^{V} cations transform to oxo-acid anion along with pH changes in the solution. The author and coworker have already developed an HPLC separation method utilizing this separation concept.**	–	**55**

b. Ion-Exchange:

Ion-exchange resins have several applications in analytical chemistry and useful for removal of in interfering ions, particularly where these ions have a charge opposite that of the analyte. There are some publication researches in this field.

Table (1-2): Comparative data from some recent studies on chromium and vanadium determination by ion-exchange technique.

Ion determine	*Technique*	*Method*	*D.L.*	*Ref.*
Cr^{VI} in Industrial Hygiene Samples	**anion exchange**	**Using Ultrasonic Extraction and FIA in alkaline solutions with $(NH_4)_2SO_4$–NH_3 The Cr(VI) in the sample solution was then separated as an anion from Cr(III) and other cations by elution from the anion-exchange resin with $(NH_4)_2SO_4$ in NH_3 (pH 8) buffer solution. The eluate was then acidified with hydrochloric acid and complexes with DPC reagent prior to FIA.**	**0.11 ng**	**56**
V^{IV}, V^{V} in synthetic and minerals processing samples.	**cation exchange**	**The method is based on chromatographic separation of V^{IV}, V^{V} in acidic medium followed by the determination with ICP-OES. Vanadium species exist in acidic solution (pH < 3) as VO^{2+}, $V^{IV}$and VO_2^{+} for V^{V}. The two vanadium species were chromatogram - phically separated using a cation exchange column, Dionex Ion Pack CG10.**	**40,30 µg/l respectively**	**57**
V^{IV}, V^{V} in spiked water and industrial samples	**anion exchange**	**Using a hyphenated techniques approach with IC-ICP-OES, V(VI)&V(V) species were completed with EDTA using a DionexAG5 anion exchange guard column and using a modified buffer carbonate & bicarbonate.**	**0.02,0.05 mg/L respectively**	**58**

C. Chromatography:

Chromatography is generally faster than other separation procedures and it allows for the direct determination of the analysis of species thus decreasing the risk of contamination by a lengthy sample pre-treatment. There are some publication researches in this field.

Table (1-3): Comparative data from some recent studies on chromium and vanadium determination by chromatography technique.

Ion determine	*Technique*	*Method*	*D.L*	*Ref.*
Cr^{VI}, species in water	HPLC-ICP-MS	By coupling of anion-exchange LC and (ICP-MS). Optimizations of the chromatographic conditions led to baseline separation of the seven species in 14 min using gradient elution with NH NO, pH 8.7 as mobile phase.	130 ng/ml	59
Cr^{VI}, in fresh water,	HPLC-MS	By coupling an anion-exchange column to an (ICP) Optimization of chromatographic conditions led to baseline separation of signals from the five species in approximately 9 min using gradient elution	5.5 mg/ml	60
Cr^{VI}in Alloys	RP-HPLC	An RP-HPLC method with UV–VIS spectrophotometric using a C-bonded 18 silica column, (PAR) chelates determined at 480 nm. Tetrabutyl ammonium bromide (TBAB) was used as the ion-pair reagent.	4.2 ng/ml	61
Cr^{VI}, Cr^{III} in spiked tap-water	RP-HPLC	Using ion-pairing reagent, pH and polarity of the mobile phase have been optimized for two different ion-pairing reagents, tetrabutylamm-oniumphosphate (TBA) and tetraethyl ammonium nitrate (TEA). Best chromato. Conditions have been obtained with a polymer-based RP-column (Hamilton PRP1) and mobile phases containing either TBA in methanol-water TEA in water at a pH= 3-4.	24, 40 µg/L respectively	62
$Cr^{VI}$is a primary drinking water	IC	This method specifies the use of a high-capacity Ion Pac AS7 anion-exchange column and UV–Vis detection after post column reaction with DPC detection at 530 nm	0.02 µg/L	63
Cr^{VI}, Cr^{III} in real samples	IC	By ion interaction chroma. with UV detection was investigated. The separation of Cr(III) and Cr(VI) was based on anionic interactions. Since the Cr(III) did not exist in an anionic form like the Cr(VI) ($Cr_2O_7^{2-}$) presented at the optimum condition, Cr(III) was	0.02, 0.3 µg/L respectively	64

		chelated with EDTA before injecting into a C_{18} column which had been dynamically coated with octylammonium		
Cr^{VI}in waste water	**IC**	**Using dialysis technique for (IC) has been developed to remove water-soluble anionic dyes and particulate colorants and other substances to facilitate Cr(VI) quantification and the method is discussed. The dialysis was optimized with Cr(VI) standard solutions for quantification. DPC as chelating agent.**	**5 µg/L**	**65**
Cr^{VI}in rain distilled water	**IC**	**Using an ion chromatography system with UV detector, without any sample preconcentration method.**	**0.2,0.1 µg/L**	**66**
Cr^{VI}, Cr^{III} in urine samples	**liquid or gas chroma.**	**Using SFE and chroma. The chromium was quantified from diabetic and normal subjects were applied. GC–flame ionization date and HPLC–UV detection**	**0.02,0.18 µg/mL respectively**	**67**
V^{IV}, V^{V} in steel	**RP-HPLC**	**The (RP-HPLC) behavior of the binary chelates of V(V) and V(IV) with 4-(2-pyridylazo) resorcinol (PAR) and ternary chelates of vanadium with PAR and auxiliary legends: hydrogen peroxide, hydroxylamine, tartrate and citrate were studied using a C_{18} column. The complex double-peak chromatograms of V(IV)/V(V) -PAR systems with hydrogen peroxide was found exclusively in V(V)-H_2O_2-PAR complex**	**-**	**68**
V^{V} in rice and flour sample	**RP-HPLC**	**By RP-HPLC with CALKS (Chromazol KS)and PAR chelating on AYMG-ODS column was developed**	**3.5ng/ml**	**69**
V^{V}, in fertilizer samples	**RP-HPLC**	**Ternary complex formed with (PAR) and hydrogen peroxide using ion-interaction RP-HPLC on a C_{18} column has been 18 investigated. The optimal mobile phase was a methanol – water solution containing tetrabutylammo-nium bromide, acetic acid and citrate buffer at pH 7, with absorbance detection at 540 nm.**	**0.09 ng/ml**	**70**
V^{IV},V^{V} spiked water and industrial samples	**IC-ICP-OES**	**Using anion chroma. With a Dionex AG5 anion exchange guard column,& inductively coupled plasma optical emission spectrometry is described. were complexes with EDTA**	**0.02,0.05 µg/mL respectively**	**71**

V^{IV}, V^{V} species in sediment, mussel and fish muscle tissue samples	**LC**	**Using EDTA complexes was developed using RP-HPLC with ICP-MS detection. A C-8 reversed-phase column a solution containing ammonium acetate, tetrabutylam-monium hydroxide, ammonium di-phosphate at pH 6 was used as the mobile phase in order to avoid the use of organic solvents that reduce the sensitivity of the determination**	–	**72**
V^{IV}, V^{V} petroleum oils and mineral ore samples	**LC**	**Based on precolumn derivatization of V(V) with 2-acetylpyridine-4-phenyl-3-thiosemicarbazone (APPT). The complex is extracted in chloroform together with palladium(II), tin(II) and iron(III) and eluted and separated completely from Kromasil 100 C_{18}, column with methanol:water:aceto-nitrile. UV detection was at 260 nm.**	**8 ng/ml**	**73**

1-4-2. Detection Methods:

Usually the most sensitive method of detection is employed in chromium and vanadium determination analysis as these metals occur at trace levels. However, the detection system is limited by the requirements as well as the expense of the machinery. Detection systems used are usually determined by whatever system is available to researchers.

a. Atomic Absorption Spectroscopy:

Atomic absorption spectroscopy (AAS) is one of the most extensively used spectroscopic methods for the determination of chromium. A major advantage of AAS is the minimal interferences that occur from other elements in the sample as the hallow cathode lamp used is metal specific. AAS has also found a wide application due to its simplicity and relatively low cost. There are some publication researches in this field.

Table (1-4): Comparative data from some recent studies on chromium and vanadium determination by AAS technique.

Ion determine	*Technique*	*Method*	*D.L*	*Ref.*
Cr^{VI} in table salt	AAS	SFE procedure on Amberlite XAD-1180 resin AAS. The analyte ions were quantitatively taken at $_{P}H$ 9 by using ammonia/ammonium acetate buffer without any chelating agent.	0.27 μgml^{-1}	74
Cr^{VI} drinking water	GF-AAS	In acidic medium and in the presence of chloride ions 2-[2-(4-methoxy-phenylamino)-vinyl]-1,3,3-trimethyl-3H -indolium chloride forms complex with Cr(VI).	0.15 μgml^{-1}	75
Cr^{VI} ions urine, soil ,sediment, natural water	FAAS	Using erbium hydroxide on NaOH medium. The co precipitant could be easily dissolved with nitric acid. The presence of up to 15 g/l of erbium ions did not interfere with the AAS determination of analyte ions.	0.87 µg/l	76
Cr^{VI}, Cr^{III} in potable water	ET-AAS	The studies have been carried out using ET-AAS. The method developed preconcentration of Cr(VI) using oxalate form of Dowex-1 The resin was found to adsorb Cr(VI) selectively in presence of Cr(III).	0.027 ng/ml	77
Cr^{III}, in Water Samples	FAAS	By (FAAS) after preconcentrating on a column containing *carlsbergensis* immobilized on Amberlite XAD-4 has been developed.	7.4 $ngml^{-1}$	78
Cr^{VI} Tannery effluents	FAAS	By (FAAS) in conjunction with coprecipitative preconcentration of its ethyl xanthate complex on to naphthalene. The solid mixture consisting of the Cr(VI) complex together with naphthalene is dissolved in (DMF)	0.5 µg/l	79
Cr,V	AAS	By AAS using Graphite furnaces coated with boron	0.5 μgml^{-1}	80
V^{IV}, V^{V} in Urine	ETAAS	Using BaF_2 and Triton X-100 as matrix modifiers with preconcentration of the sample directly into the graphite tube	0.11,0.37 μgml^{-1} respectively	81

V^{IV} in river water sample	**AAS**	**Based on sorption onto chelating resins seem convenient, rapid and capable to achieve a high concentration factor. Amberlite IRA-904 resin functionalized with porphyrin ligands modified with tetrakis (*p*-carboxyphenyl) porphyrin (TCPP) as a complexing agent was used to pre-concentrate vanadium species to check the possibility**	–	**82**
V^{IV} in natural water	**GFAAS**	**By GFAAS after preconcentration on silica-gel modified with 3-aminopropy ltriethoxysilane**	**0.006 µg/l**	**83**
V^{IV}, V^{V} from water	**GFAAS**	**Use of a new type of 8-hydroxyquinoline-5-sulphonic acid cellulose (sulphoxine cellulose) by Mannish reaction from amino ethyl cellulose or via chlorodeoxy and ethylenediamine cellulose is also described**	**0.244 µg/l**	**84**
V^{IV}, V^{V} in fuel oil	**ETAAS with Zeeman effect back ground correction**	**Based on the preparation of a micro emulsion followed by direct injection into the graphite tube. The pyrolysis and atomization temperatures, 1500 and 2700 °C.**	–	**85**

b. Inductively Coupled Plasma – Atomic Emission Spectroscopy & Mass-spectrometry:

The analytical method for the determination of chromium and vanadium at highly sensitive is (ICP-AES/MS).

Inductively coupled plasma – atomic emission spectroscopy (ICP-AES) is a multi-element technique, which has minor matrix and memory effects. It cannot perform elemental determination without the prior separation of the species.

Inductively coupled plasma - mass spectrometry (ICP-AES-MS) is another multi-element technique, which is rapidly becoming the detector of choice due to its sensitivity. This technique has the advantage of very low detection limits. It cannot distinguish between species, so previous

separation of chromium and vanadium is needed. ICP-AES-MS is a very accurate and precise tool.

There are some publication researches in this field.

Table (1-5): Comparative data from some recent studies on chromium and vanadium determination by ICP-AES-MS technique.

Ion determine	*Method*	*D.L*	*Ref.*
Cr^{VI}, Cr^{III} in water samples	Using solvent extraction with tributylphosphate (TBP) and back-extraction is described. The method utilizes 10 ml of TBP and 500 ml of sample solution at pH 1. Chromium(VI) is back-extracted from the organic phase by solution containing ammonium acetate and ammonium carbonate	1.0 ,0.9 μgml^{-1} respectively	86
Cr^{VI}, Cr^{III} in sea water	Preconcentration and determination were carried out by using (ICP-AES) with dual mini-columns containing a chelating resin	0.04,0.09 μgml^{-1}	87
Cr^{III}	Using 1-phenyl-3-methyl-4-benzoyl pyrazol-5-one and reduction of Cr (VI) CPE Triton X-100	0.81 μgml^{-1}	88
Vanadium in urine	Using ICP-MS complicated by ClO^{+} ions from chlorine matrices. Cryogenic desolvation reduces the amount of chloride reaching the plasma by condensing it as hydrogen chloride and reduces the amount of oxide formation by removing water vapor.	-	89
vanadyl porphyrins extracted from (mussel & tissues)	Using of ICP-AES coupled to (UV/VIS) spectrometry as detection techniques to determine the extracted Vanadium-containing compounds.	50 ng	90
Vanadium sea water	Using 8-HQ, which forms neutral complexes with these metals, followed by adsorption on C18 chemically bonded silica gel.	-	91

C. Electrometric methods (polarography)

Electroanalytical methods are based upon electrolytic oxidation or reduction of an analyte for a sufficient period to assure its quantitative conversion to a new oxidation state.

A polargraphic method used to determine the trace amount of chromium and vanadium. There are some publication researches in this field

Table (1-6): Comparative data from some recent studies on chromium and vanadium determination by this technique.

Ion determine	*Method*	*D.L.*	*Ref.*
Cr^{VI}, Cr^{III} in natural waters	**The method is based on the preconcentration of the Cr(III)-TTHA complex by adsorption at the HMDE at the potential of –1.0 V vs. Ag/AgCl. The adsorbed complex is then reduced producing a response with a peak potential of –1.29 V and the peak height of the Cr(III) reduction is measured. The catalytic action of the nitrate ions on the Cr(III)-TTHA reduction has been elucidated using cyclic voltammetry.**	**15 ng L^{-1}**	**92**
V^{V} in material water sample	**A new catalytic adsorptive system of Vanadium–CAA–bromate by means of DP paleography and adsorptive stripping voltammetry. The new procedure was examined and successfully utilized for the CAdSV determination of a low vanadium concentration**	**2.8×10^{-9}M**	**93**
V^{IV},V^{V}	**The electronic tongue (ET) multisensor system has been employed for the detection of metal-oxygen cluster anions (polyoxometalates) containing vanadium (IV/V) atoms at different oxidation states.**	–	**94**
V^{V} real samples	**Using 2, 5-dichloro-1, 4-dihydroxy-3, 6-benzoquinone (chloranilic acid) as complex forming reagent. The complex is stable in acetate buffer (pH 4.6) solution and adsorbed at the electrode surface in a potential range between –150 mV and –400 mV.**	–	**95**

1-4-3. Miscellaneous methods for the determination of vanadium and chromium:

Other methods which have been suggested for determination of chromium and vanadium, but are not frequently used include: x-ray, thermal lens spectrometry, radio analytical neutron activation analysis, act. There are some publication researches in this field

Table (1-7): Comparative data from some recent studies on chromium and vanadium determination by this technique.

Ion determine	*Technique*	*Reagent*	*D.L.*	*Ref.*
Cr(III) in steel	microwave radiation	4-(2- Thiazolylazo)-Resorcinol (TAR)	17 ng mL^{-1}	96
Cr(VI) Cr(III) in liquid samples	EDXRF	ammoniumpyrrolidinedithiocarbamat (APDC)	_	97
Cr(III) in Sea water	CSV	_	160 µg/l	98
Cr(III) in Water	EDXRF/WD XRF	_	0.10/0.8 µg/l	99
Cr(VI) in Natural waters	MAS	1,5-Diphenyl carbazide	50µg/l	100
Cr(VI) in Urine	MAS	1-(2-Pyridyl-azo)2-naphthol	_	101
Cr(III) and Cr(VI) in the wastewater	ICP OES	a tetraazamacrocyclic compound (TAMC)	300,45.5 pg mL^{-1}	102
Cr(VI) and Cr(III)	IC–TLS	_	10,0.1 mg	103
chromate ions in water	UV LED	_	0.1 ng	104
V^{4+} and V^{5+}in alloys	XPS	_	_	105
vanadium in sports dietary supplements	RNAA	N-benzoyl-N-phenylhydroxyl amine (BPHA)	_	106
V, Ni, Fe petroleum	EDXRF	_	_	107

1-5.Flow Injection Analysis (FIA):

Flow-injection analysis (FIA) is defined as an automated or semi-automated analytical process consisting of a sequential insertion of discrete sample solution into an unsegmented continuously flowing liquid steam with subsequent detection of the analyte. It is a relatively new analytical process [(108)], which shows a considerable potential for high-speed precise.

Flow-injection analysis is based on the injection of a liquid sample into a moving non segmented continuous carries stream of a suitable liquid. The injected sample forms a zone, which is then transported toward a detector that continuously records the absorbance [(109)]. FIA is based on the technology of flow (FIA); the quick chemistry offers high sample throughput coupled with simple and rapid method change over to maximize productivity in determining ionic species in a diversity of sample matrices from sub-ppb to percent concentrations. The simplicity and ruggedness of FIA are combined with the outstanding accuracy, precision and minimum detection limits. Automated flow injection system has been applied to on-line process analysis in industrial and environmental situation with a great deal of success.

FIA is also ideally suited to monitoring solution phase chemiluminescences reactions due to the capability to mix-sample and reagent in close proximity to a detector [(110)], using minimum amounts of sample and reactants, with excellent reproducibility.

There are some publication researches in this field.

Table (1-8): Determination of chromium and vanadium by FIA technique coupling with other method.

Ion determine	*Method*	*D.L*	*Ref.*
Cr^{VI}, real sample	Critically the flow through sorbet extraction optosensing concept at octadecyl chemically-modified silica gel sorbents, currently used as a packing material of commercial available flow-through cells for the single or multiparametric determination of either non-polar active constituents in pharmaceutical formulations	–	111
Cr^{III} in dietary supplement	Using EDTA and an FI system with a column packed with amberlite IR-120(H)	18 µg	112
Cr^{VI}, Cr^{III} in electro-plating wastewater Samples.	The method is based on separation and preconcentration of Cr(III) on a micro column of immobilized 8-HQ on surfactant-coated alumina. The adsorbed analyte is then eluted with ethanolic solution of hydrochloric acid and is transported to a FIA for quantify-cation.	0.16 ng/mL	113
Cr^{VI}, Cr^{III} in urine and alloys	The new semiautomated unit for determination of all common ionic chromium species Cr(III),Cr(VI) as chromate and Cr(VI) as dichromate through the conversion of all these valency forms of chromium ions into chromium peroxide.	6.53, 8, 7.12 ng/200µl respectively	114
V^{IV}, V^{V} in water samples	The method is based on the catalytic effect of V(V) on the bromate oxidation of N,N-bis(2-hydroxyl-3-sulfopropyl)-tolidine.1,2-Dihydroxybenzene-3,5-disulfonate was used as an activator in the V (V)-catalyzed reaction and significantly enhanced the sensitivity of the method.	0.008,0.2 ng/mL respectively	115
V^{IV}, V^{V} in natural waters	This was achieved by using acetyl acetone and the 8-quinolinol immobilized on partially fluorinated silicon alkoxide glass columns (MAF-AA and MAF-8HQ).	–	116

1-6. Chemiluminescence:

A chemiluminescence [117] method means emission of light through a chemical reaction at the room temperature. This product accepts the energy needed to transfer to the excited state and emitted light when returned to ground state. There are some publication researches in this field.

Table (1-9): A chemiluminescence determination of chromium and vanadium coupled with FIA technique.

Ion determine	*Analysis technique*	*Method*	*D.L.*	*Ref.*
Cr^{III} in real water sample	FIA-CL	This method is based on the fact that both Co (II) and Cr (III) catalyze the luminal–H_2O_2 CL reaction, and that their catalytic activities are significantly different on the same reaction condition.	-	118
Cr^{VI}, Cr^{III}	FIA-CE-CL	Based on luminal oxidation by hydrogen peroxide in basic aqueous solution catalyzed by Cr(III) ion followed by capillary electrophoresis separation. Based on in-capillary reduction, Cr^{VI} can be reduced by acidic sodium hydrogen sulfite to form Cr^{III} while the sample is running through the capillary.	6×10^{-13}, 8×10^{-12} mol. l^{-1} respectively	119
V^{IV} in aqueous sample	FIA-CL	The oxovanadium(IV) ion was extracted into chloroform as its acethylacetone complex from an aqueous solution (pH 5.4) followed by membrane phase seperation in a flow system. In a flow cell of a detector, the extact was mixed with the reversed micellar solution of cetyltrimethyl ammonium chloride in chloroform-water (buffered with 0.8 M sodium carbonate) containing luminol.	1.0 ng cm^{-3}	120
V^{IV} , V^{V},V^{III}	FIA-CL	Study the CL reaction of V(IV) in the form of $VOSO_4.5H_2O$ and V(V) in the form of V_2O_5 and V(III) in the form of V_2O_3 using the system [LU-KOH-V^{n+}].	6, 3, 4 ng/10µl respectively	121

1-7. Spectrophotometric method:

Spectrophotometric methods of analysis have experienced a high evolution in the last 25 years [122] and widely used as a tool for quantitative analysis, characterization, and quality control in agricultural, pharmaceutical, and biomedical fields [123].

One of the most common methods of analytical measurement of trace amount of metals is by spectrophotometric means. Spectrophotometric techniques utilize the property of selective absorption of radiant energy by chemical substances. Photometric methods whether UV, visible, or IR, are characterized by their sensitivity and selectivity [(124)].

The accuracy and precision of spectrophotometric method depend on three major factors: instrumental limitations, chemical variables, and operator skill. Instrumental limitations are often determined by the quality of the instrument's optical, mechanical, and electronic systems. These may widely vary depending on the cost of the instrument. Chemical variables are determined by purity of standards, reagent and chromophore stability, reaction rates, reaction stoichiometry, pH, and temperature control. These factors are usually determined by the methodology chosen for the analysis [(125)].

The ultraviolet region of the spectrum is generally considered to range from about 200 to about 400 nm and the visible region from about 400 to 800 nm. The corresponding energies for these regions are about 150 to 72 and 72 to 36 kcal mole $^{-1}$, respectively. Energy of this magnitude often corresponds to the energy difference between electronic level states of many molecules.

Molecules with the ability to exhibit electronic transitions are said to possess chromophores (from the Greek words *chroma*, meaning color, and *phoros*, meaning producer). Chromophores are often associated with certain molecular groups. These molecular groups may contain a double bond (such as ethylenes, acetylenes, carbonyls and azo compounds). Non bonding electrons in addition to a double bond may be present (such as carbonyls, nitro groups and azo compounds).

Transition metals commonly exhibit absorption bands in the UV/VIS region of the spectrum. These often result form the energy differences in

the various *d*-electron states arising from electron interactions of coordinated donor atoms. Analogous behavior can be seen, although to a lesser degree, with many metals from the lanthanide series, resulting from differences in their *f*-electron states.

Transition metals having unfilled *d*-orbital usually exhibit absorption bands in the UV/VIS region. Samples that absorb significantly in the visible region are always colored because color results when a band of frequencies is absorbed from a visible light. The actual wavelength of *d*-*d*-transitions depends on the metal involved (the number of *d*-electrons initially present), the number of coordinating groups, the strength (basicity) of the donor atoms, and the geometry of the coordinating groups [(126)].

UV/VIS absorption spectra are often very useful in qualitative identification of molecular species. This often is accomplished by comparing the spectrum of an unknown species with a spectrum of a suspected substance from a library of spectra.

UV/VIS absorption spectral data are widely used for determining stochiometry of complex ions and sometimes the determination of the equilibrium constant. Many procedures have been developed for this purpose. Some of these are methods of continuous variations, mole ratio method and slope ratio methods [(127)].

The greatest use of UV/VIS absorption spectroscopy lies in its application to quantitative measurements. The reasons for this is the ease with which most spectrophotometric measurements can be made, their sensitivity and precision, and the relatively low cost of instrument purchase and operation. A variety of techniques have been developed for the different types of samples. Direct determinations are made when the analyte molecule contains a chromophore, thus allowing the direct measurement of its absorbance. Standards must be used to determine the

absorptivity so that concentration can be calculated by Eq. (1-1) or by establishing a calibration plot from which the concentration can be determined by graphic interpretation or by regression analysis. Indirect determinations are commonly used when the analyses are made to quantitatively react with a molecule containing a chromophore and correlating the diminution of absorbance with the concentration of the analyte or by reacting with a reagent, which produces a chromophoric group [128].

$$A=abc \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1\text{-}1)$$

where: a is the proportionality constant known as the absorptivity.

b and c are the sample thickness and concentration, respectively.

Many spectrophotometric methods for the determination of some elements are based on the complex formation. The sensitivity and selectivity of the spectrophotometric determination of some elements are increased and the matrix effects suppressed or diminished in the presence of appropriate organic analytical reagents (OARs) [129]. Some of the proposed organic reagents for the spectrophotometric determination of chromium and vanadium as shawn in table (1-10) and (1-11).

Table (1-10): Some organic reagents used for the spectrophotometric determination of chromium.

Reagent	*Absorbance λmax*	*Molar Abs. ($l.mol^{-1} cm^{-1}$)*	*Ref.*
2-(5-bromo-2-pyridlozo)5-diethyl amino phenol	580	2.62×10^{4}	130
4-methoxy-n-tolybenzohydroxamic acids	370	1.2×10^{3}	131
Diantipyrinyl-1-phenyl propane	450	3.7×10^{4}	132
Penta methylene bis (triphenyl phosphonium) cation	365	1.38×10^{3}	133

***Table (1-11)*: Some reagents used for the spectrophotometric determination of vanadium.**

Reagent	*Absorbance λmax*	*Molar Abs. ($l.mol^{-1}$ cm^{-1})*	*Ref.*
N-Benzoyl-N-phenylhydroxyl amine	530	4650	134
Ferron + tribenzylamine	430	18200	135
Benzohydroxamic acid	450	3650	136
N-P-Methoxyphenyl-2-furylacrol ohydroxamic acid + 3-(O-carboxyphenyl)-1-phenyltriazin e-N-Oxide	450	14000	137
P-Sulphobenzeneazo-4(2,3-dihydroxy pyridine)	520	5045	138
KIO_4+PBHA+CV	535	7200	139

There are some publication researches as shown in table (1-12).

Table (1-12) Spectrophotometric methods for determination of chromium and vanadium.

Ion determine	*Method*	*Abs. λmax*	*D.L*	*Ref.*
Cr(VI) in alloy steels	Using variamine blue as a chromogenic reagent. The proposed method is based on the reaction of chromium(VI) with potassium iodide in acid medium to liberate iodine, which oxidizes variamine blue to form a violet colored species	556nm	0.02 µg mL^{-1}	140
Cr (III) in alloys	Using N-methyl aniline carbodithioate complex into molten naphthalene. Maximum extraction was obtained in the pH range of 2.0 – 3.5. Naphthalene containing the metal complex was dissolved in DMF.	340nm	2.6-31.2 µg /10 ml	141
Cr^{VI}, Cr^{III} in industrial waste water	The method is based upon the extraction of the complex ion-associate formed between the chloro chromate (CrO_3Cl^-) anion and the ion-pair reagent ($TPAs^+Cl^-$) or (TPP^+Br^-) at pH ≤ 0 in chloroforms	355nm	-	142
Cr(III) ion in the real samples	Using α-Benzoine oxime (α-BO) in the presence of non-ionic surfactant Triton X-100 has been performed	295nm	0.1-2.0 µg ml^{-1}	143
Cr (III) ion in real samples.	Based on the formation of chromium (III)/azide a complex was established by investigating a new band in the ultraviolet region. The best experimental conditions for the analytical determination of this metallic ion	493 nm 287 nm	0.702-2.81 mg L^{-1}	144

V(V) in steel	**Using variamine blue (VB) as a chromogenic reagent. The method is based on the oxidation of variamine blue to form a violet colored species on reaction with vanadium(V),**	**570nm**	**0.1-2.0 µg ml^{-1}**	**145**
V real alloy samples	**A partial least-squares multivariate calibration method as their complexes with 8-hydroxyquinoline (oxine) has been proposed.**	**550nm**	**288 µmol L^{-1}**	**146**
V species in V-MCM-41 molecular	**Direct spectroscopic evidence for vanadium species in V-MCM-41 molecular sieve characterized by UV resonance Raman spectroscopy**	**-**	**0.1-2.0 µg ml^{-1}**	**147**
V(V) in environmental, biological sample	**Based on the reaction of 3-methyl-2-benzothiazolinone hydrazine hydrochloride (MBTH) with *N*-(1-naphthyl) ethylenediamine dihydrochloride (NEDA) in the presence of vanadium to give blue colored derivative or on oxidation of dopamine hydrochloride (DPH) by vanadium in acidic medium and coupling with MBTH to yield pink color derivative.**	**595nm 526nm**	**0.05-6.0 µgml^{-1}**	**148**
V(V) in biological samples	**Based on either the oxidation of (4-AAP) by vanadium in acidic medium (pH 3) and coupling with (NEDA) to give violet color derivative or on the oxidation of (DPH) by vanadium in acidic medium and coupling with 4-AAP to yield red color derivative.**	**565 nm 494 nm**	**0.025-4.5 µg ml^{-1}**	**149**
V (V) in carbonaceous shale's (stone coal ores).	**Based on the reaction of V(V) with the chromophore reagent (5-Br-PADAP) in the presence of hydrogen peroxide. In a 0.072 mol l^{-1} sulfuric acid medium, 5-Br-PADAP reacts with V(V) to form a red-violet complex**	**596 nm**	**-**	**150**
V (IV) in real seawater	**Using a column filled with palmitoyl quinolin-8-ol bonded to amberlite XAD 2 resins. Both V species were retained on the resin and eluted together from the resin column using a suitable stripping agent, and finally determined with PAR reagent, and a selectivity that was not accessible in adsorption/elution stage could be achieved in subsequent photometric determination by use of CDTA as masking agent for V(IV).**	**542 nm**	**1.6 µg l^{-1}**	**151**

1.8- Aim of the work:-

According to our knowledge of what was been mentioned before regarding the studies, applications and techniques used to assess and separate chromium and vanadium ions following spectral methods, the idea of the present work was been suggested to include the separation and determination of chromium and vanadium ions spectrophotometricaly by the complex formation technique using different ligands, i.e. [Cr (VI, III)-DPC, Cr (VI)-bipy, VO-SH, V (V)-8-HQ]. This is to be accomplished by the determination of optimum conditions for the complex formation by studying the effect of reagent concentration, pH solution, time, light and temperature.

Different metal salts in different oxidation states are to be used. The calibration curves for all complexes are also to be prepared. The work also aims to study the effect of selected interfering positive and negative ions of the separation and determination process. This effect is to be explained thermodynamically by determining E_{cell}, k_{eq}. and ΔG values. Then the ion-exchange technique is to be followed to separate the interfering ions form chromium and vanadium ions.

Finally, the results should be utilized to determine the two elements in biological samples (blood and urine for chromium, and plants and foods for vanadium).

Experimental part

2-1. Instruments and Equipments:-

The instruments used in this work were:

1- Double-beam UV–Visible spectrophotometer model (UV-1650 PC) Shimadzu/ (Japan) interfaced with computer via a shemadzu UV-probe data system program.

2- pH meter Orion expandable ion analyzer model (EA 940) equipped with a glass combination electrode.

2-2. Chemicals:-

The following chemicals molecular weight and purity were used in this study:

Table (2-1): chemicals purity and molecular weight which inter in this study.

chemicals	% purity	M.wt (g/l)	Supplied from
Potassium dichromate	-	294.2	BDH
Chromium nitrate	-	400	Riedel-de-Haen
1,5-Diphenylcarbazide	-	242.28	Fluka A.G
2,2'-Bipyridine	99	156.19	Fluke A.G
Vanadyl sulfate	-	253	BDH
Vanadium pentoxide	-	181.88	BDH
Thioglycolic acid	98	92.12	Fluke A.G
8-Hydroxylquinoline	-	145.16	BDH
Sodium hydroxide	-	40	BDH
Acetic acid	96	60	Fluke A.G
Acetone	99	58	BDH
Chloroform	98	153.8	BDH
Ethyl acetate	98	72	BDH
Phosphoric acid	98	98	BDH
Sulphuric acid	98	98.08	BDH
Hydrochloric acid	37	36.46	BDH
Nitric acid	98	63.01	BDH
Hydrogen peroxide	99	34	Solvay

2-2-1. Solutions used for the Determination of Chromium:

Potassium dichromate $K_2Cr_2O_7$, 100 ppm was prepared by dissolving 0.02827g in 100ml of distilled water; other standard solutions were prepared by a subsequent dilution of stock solution.

Chromium nitrate $Cr(NO_3)_3.9H_2O$, 100 ppm was prepared by dissolving 0.07692g in 100ml of distilled water, other standard solutions were prepared by a subsequent dilution of stock solution

1,5-Diphenylcarbazide, 2.58×10^{-2}M was prepared by dissolving 0.125g of the reagent in 100ml of acetone, the solution was kept in an amber-glass bottle

2,2'-Bipyridine, 1mM was prepared by dissolving 0.015612g of reagent in to 100ml of distilled water.

Phosphoric acid H_3PO_4, 1:1 (V/V) was prepared by diluting 50ml of phosphoric acid (15.717M) in 50ml of distilled water in 100ml volumetric flask.

2-2-2. Solution used for the Determination of Vanadium:

Vanadyl sulfate $VOSO_4.5H_2O$, was prepared 100ppm (VO^{+2}) was prepared by dissolving 0.04966g in 100ml of distilled water, other standard solutions were prepared by subsequent dilution of stock solution.

Vanadium pentoxide V_2O_5, 100ppm (VO_2^+) was prepared by dissolving 0.017843g in 100ml of distilled water, other standard solutions were prepared by subsequent dilution of stock solution.

Thioglycolic acid $HS\text{-}CH_2COOH$, 3mM was prepared by diluting 5ml stock solution of commercial reagent grade to 50ml.

8-Hydroxylquinoline 8-HQ, 1mM was prepared by dissolving 0.01452g in 100ml of chloroform.

2-2-3. Preparation of Acids and Bases Solution:-

Sodium hydroxide NaOH, stock solution of 1M was prepared by dissolving 4g in 100 ml of distilled water.

Sulphuric acid H_2SO_4, stock solution of 1M was prepared by dilute 27.864 ml from commercial grade reagent at (17.944 M) sulphuric acid to 500 ml of distilled water.

Hydrochloric acid HCl, stock solution of 1M was prepared by dilute 8.548 ml from commercial gaud reagent (11.63 M) hydrochloric acid to 100ml of solution with distilled water.

Nitric acid HNO_3, stock solution of solution of 1M was prepared by dilute 4.593ml of commercial grade reagent (21.774M) nitric acid to 100ml with distilled water.

Acetic acid CH_3COOH, stock solution of 1M was prepared by dilute 28.74ml of commercial grade reagent (17.396M) acetic acid to 500ml with distilled water.

Phosphoric acid H_3PO_4, stock solution of 1M was prepared by diluting 31.813ml of commercial grade reagent (15.717M) phosphoric acid to 500ml of solution with distilled water.

Sodium acetate CH_3COONa, stock solution of 1M was prepared by dissolving 8.2 g in 100 ml distilled water.

Hydrogen peroxide H_2O_2, stock solution of 2M was prepared by diluting 60.7ml of commercial grade reagent (16.47M) Hydrogen peroxide to 500ml of solution with distilled water.

Hydrogen peroxide was calibrated with potassium permanganate as standard solution at (0.0966 M) in present of H_2SO_4 at 1:8 (V/V), the reaction included:-

$$2MnO_4^- + 5H_2O_2 + 6H^+ \rightleftharpoons 2Mn^{2+} + 5O_2 + 8H_2O$$

2-3. Interferences solutions:-

100 ppm of interferences ions was prepared in 100 ml volumetric flask as shown in table (2-2).

Table (2-2): Weights and molecular weight of chemicals which inter the preparation of interference ions.

Substance	*Chemical formula*	*Interference ion*	*Weight (g)*	M.wt (g/l)	*Supplied company*
Cobalt nitrate	$Co(NO_3)_2.6H_2O$	Co^{++}	0.04937	290.03	BDH
Cadmium nitrate	$Cd(NO_3)_2.3H_2O$	Cd^{++}	0.02744	308.41	BDH
Copper nitrate	$Cu(NO_3)_2.3H_2O$	Cu^{++}	0.03842	241.55	Hopkin & willoms
Magnesium sulfate	$MgSO_4.7H_2O$	Mg^{++}	0.01013	246.38	Fluka A.G
Manganese sulfate	$Mn(NO_3)_2.4H_2O$	Mn^{++}	0.0457	250.94	Fluka A.G
Ferric nitrate	$Fe(NO_3)_3.9H_2O$	Fe^{+++}	0.07231	403.85	Fluka A.G
Zinc chloride	$ZnCl_2$	Zn^{++}	0.02084	136.28	BDH
Nickel nitrate	$Ni(NO_3)_2.6H_2O$	Ni^{++}	0.0495	290.71	BDH
Chromium nitrate	$Cr(NO_3)_3.9H_2O$	Cr^{+++}	0.07693	400	Riedel-de-Hean
Lithium bromide	LiBr	Br^{-}	0.01084	86.843	Fluka A.G
Sodium iodate	$NaIO_3$	IO_3^{-}	0.011314	197.89	BDH
Sodium thiosulphate	$Na_2S_2O_3.5H_2O$	$S_2O_3^{=}$	0.02214	247.98	BDH
Sodium oxalate	$Na_2C_2O_4$	$C_2O_4^{=}$	0.01523	134	BDH
Ammonium iodide	NH_4I	I^{-}	0.01142	144.91	Fluka A.G

2-4. Separation of Columns:-

2-4-1. Strong Cation Exchange Amberlite Resin IR-120 (Na^+).

2-4-2. Strong Anion Exchange Amberlite Resin IR-400 (Cl^-).

2-5. Preparation of complexes:-

2-5-1. Chromium – (1,5-Diphenyl carbazide) complex. [114]

The spectrophotometer method uses the selective reaction Cr (VI) with 1,5-diphenylcarbazide in basic media to yield a red-violet diphenyl carbazone complex the spectrum of complex has shown an absorbance at 542 nm wave length.

A concentration range of (0.5-9) ppm of Cr (VI) has been prepared by diluting a standard solution of 25ppm concentration at (pH=8-8.5) using 1ml of 1M NaOH, in volumetric flask 50ml, 1ml of diphenylcarbazide was added with stirring to the chromium solutions followed by 2.5ml H_3PO_4 (1:1) and then diluted to the mark by distilled water.

A sample from the flask transferred to a spectrophotometer cell and the absorbance was measured at 542 nm.

2-5-2. Chromium - (2,2′-Bipyridine) complex. [152]

The spectrophotometer method uses the selective reaction Cr (VI) with 2,2'-Bipyridine in acidic media to yield a light blue complex the spectrum of complex has shown an absorbance at 308 nm wave length.

A concentration range of (0.5-9) ppm of Cr (VI) was prepared in 25ml volumetric flask. An aliquot of this solution was transferred to a 125ml separators funnel and acidified with 1ml of 1M sulfuric acid. Sufficient distilled water was added to bring the total volume to 20ml and then about 20ml of ethyl acetate was added.

The funnel and its contents were cooled at 10°C for 1/2 hour. After cooling, add 1ml of a 3% solution of hydrogen peroxide was added and also cooled at 10°C and immediately extracted for 30 seconds by vigorously shaking the separatory funnel. After the layers being

separated, the aqueous layer was discarded. The ethyl a acetate layer was added to 10 ml of 0.6 mM aqueous solution of 2,2'-bipyridine which was also cooled at 10°C and immediately extracted for 30 seconds by a vigorous shaking. After the layers were separated, the aqueous layer was discarded and the ethyl acetate layer was transferred to a 25ml volumetric flask, and then diluted to the mark with an additional ethyl acetate.

A sample from the flask transferred to a spectrophotometer cell and the absorbance was measured at 308 nm.

2-5-3. Vanadium – Thioglycolic acid (SH) complex. [153]

The spectrophotometer method uses the selective reaction V (IV) with Thioglycolic acid to yield a very light blue complex the spectrum of complex has shown an absorbance at 225 nm wave length.

A concentration range of (0.5-9) ppm of V (IV) was prepared per 50 ml of volumetric flask, 5ml of 30 mM thioglycolic acid and 1ml of 0.15M sodium acetate were added and the solution was kept at (pH=5.0-5.5), the solution was diluted to the mark by distilled water and the solution was shacked, A sample from the flask transferred to a spectrophotometer cell and the absorbance was measured at 225 nm.

2-5-4. Vanadium – 8-Hydroxyquinoline (8-HQ) complex. [154]

The spectrophotometer method uses the selective reaction V (V) with 8-Hydroxyquinoline in acidic media to yield a brawn complex the spectrum of complex has shown an absorbance at 550 nm wave length.

A concentration range of (0.5-9) ppm of V (V) was prepared in 50 ml volumetric flask, 1ml of 1M H_2SO_4 was added; the solution was kept at (pH=3.5-4.5) and the solution was transferred to 100 ml separators funnel. Then 5 ml of 1mM 8-HQ was added and immediately extracted

for 30 seconds by a vigorous shaking. After the layer was separated, the aqueous layer was discarded and transferred to 50 ml of volumetric flask and then diluted to the mark by distilled water.

A sample from the flask transferred to a spectrophotometer cell and the absorbance was measured at 550 nm.

2-6. Treatments of samples:-

- **Urine samples**

The urine samples were treatment with 2ml of perchloric acid 60 % [117] for the purpose of the protein sedimentation.

- **Blood samples**

The blood samples were treatment with 5ml of H_2O_2 and conc. HNO_3, the solution was heating until the excess acid was expelled. After drying 5ml HCl and 5ml HNO_3 was added at (1:1) ratio concentration, followed by the addition of 20ml D.W, and then the solution was filtered.

- **Plants and foods samples**

The plants and foods samples was treatment by dissolving 0.5g for each sample (mushroom, cereal and strawberry) in 50ml of mixture HCl:HNO_3 at 1:1 concentration with heating to ensure a complete conversion into ions dissolved in solution for easy measuring, then the solution was filtered and was diluted to 250 ml volumetric flask by distilled water.

Contents

Supervisor Certification

We certify that this thesis was prepared under our supervision at the Department of Chemistry, College of Science, AL- Nahrain University as partial requirements for the **Degree of Master of Science in Chemistry.**

Signature:
Supervisor: Prof. Dr. Ayad H. Jassim
Date:

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Supervisor: Dr. Bushra B. Kasim
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In View of the available recommendations, I forward this thesis for debate by the Examining Committee.

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Examining Committee's Certification

We, the Examining Committee, certify that we have read this thesis and examined the student (Aseel Salah Mansoor) in its contents, and that in our opinion it is adequate with ( ) standing as a thesis for the Degree of **Master of Science, in Chemistry.**

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Chapter One

Introduction

Chapter Two

Experimental Part

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List of figures

List of tables

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Spectrophotometric Study for the determination of Chromium, Vanadium and its application

A Thesis submitted to the College of Science Al-Nahrain University in partial fulfillment of the requirements for the Degree of Master of Science in Chemistry

By
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B.Sc. in Chemistry (Al-Nahrain University 2005)

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Summary

This thesis falls into three main chapters. **Chapter I** deals with a general survey of literature which discusses an introduction for chromium and vanadium (discovery, valances, uses, availability and toxic effects); also it includes the different techniques used for there determination. Focus was made on the determination of chromium and vanadium ions using spectrophotometric method in various different biological, industrial, drinking and sewage water samples. Chapter I also describes the aim of the research work conducted.

Chapter II describes the preparation of chemicals and sample pretreatment. It also includes all the equipments used.

Chapter III is divided into four parts (A, B, C and D)

Part A: describes an integrated spectral study of complexes [(Cr (VI, III)-DPC), (Cr(VI)-bipy), (VO-SH), (V(V)-8-HQ)], it includes a study of the optimum conditions for the complex formation including the (determination of ligand concentration, effect of pH, determination of buffer concentration), also it includes a study of all the physical variables affecting the complex formation (time, temperature, light effect), and study of the nature of complexes following the ***continuous variation*** method.

Part B: This part includes the preparation of calibration curves of the complexes and treatment data resulted by modern statistical analytical

methods which involve different equation formulae for calculating linear regression equation, relative error, correlation coefficient, slop, intercept, and the theoretical limit of detection was also calculated.

Part C: This part comprises two paragraphs: the first one includes a study of the effect of selected interfering positive and negative ions on the separation and determination processes. This effect is to explain thermodynamically by determining $E_{1/2}$, K_{eq}. and ΔG values. The second paragraph includes a study of separating the interfering ions from chromium and vanadium ions using ***ion exchange*** columns.

Part D: Describes the application of the method to determine chromium in the biological samples (blood and urine) and determine vanadium in plants and foods (mushrooms, strawberry and cereals) using the optimum conditions for determination.

الخلاصة

تضمنت الرسالة ثلاثة فصول رئيسة :-

تناول الفصل الأول مسحا"عاما" للأدبيات وشملت مقدمة عن الكروم والفناديوم (اكتشافة، تكافؤاتة، وجوده والتاثيرات السمية) كما تضمن تقدير ايوني الكروم والفناديوم بمختلف التقنيات وتم التركيز على تقدير ايوني الكروم والفناديوم بالطريقة الطيفية في مختلف الانموذجات الأحيائية والصناعية ومياه الشرب كما تم تحديد الهدف من البحث.

اما الفصل الثاني فقد تضمن المواد الكيمياوية والأجهزة المستخدمة وطرق التحضير المختلفة لاجراء البحث.

وقد تضمن الفصل الثالث اربعة اجزاء اساسية، الجزء A: يتضمن هذا الجزء دراسة طيفية متكاملة لمعقدات الكروم والفناديوم [Cr(VI, III)-DPC, Cr(VI)-bipy, V(IV)-SH, V(V)-8-HQ] وتحديد λ_{max}، وتضمن ايضا" دراسة الظروف الفضلى لتكوين المعقد من حيث(مفاضلة تراكيز الكاشف الانتقائي وتاثير pH المحلول على تكوين المعقد ومفاضلة تراكيز البفر)، وكذالك دراسة كافة المتغيرات الفيزيائية وتاثيرها على ثبوتية المعقد (الزمن ، الحرارة ، الضوء) ودراسة طبيعة المعقد بطريقة التغاير المستمر.

الجزء B: تضمن هذا الجزء تحضير منحنيات المعايرة للمعقدات المحضرة واجراء المعالجات الاحصائية الحديثة للبيانات التحليلية الناتجة، فقد تم استخدام معادلات مختلفه لاحتساب الخط المستقيم ونسبة الخطأ ومعامل الارتباط كذلك الميل ونقطة التقاطع كما تم احتساب حد الكشف الناتج من القياسات العملية والمحسوبة باسلوب احصائي على وفق المعادلات الاحصائية (حد الكشف النظري).

الجزء C: تضمن هذا الجزء فقرتين، اذ اشتملت الفقره الاولى دراسة تاثير تداخل الأيونات الموجبة والسالبة في الكروم السداسي والفناديوم الرباعي وقد تم تفسير ميكانيكية التفاعلات هذه من ناحية الداينمية الحرارية من خلال حسابات $K_{eq.}$, ΔG, $E_{1/2}$ للتفاعلات قيد الدراسة من خلال $E_{1/2}$ للتفاعلات وقد أمكن ربط الكثير من النتائج العملية بالتفسير النظري المعتمد على قيم $E_{1/2}$ للمعادلات المستنبطة خلال هذا البحث، اما الفقرة الثانيه فتشمل دراسة امكانية ازالة هذه المتداخلات الأيونية باستخدام اعمدة التبادل الايوني

الجزء D: تضمن هذا الجزء تطبيق الطريقة المستخدمة لتقدير الكروم في الانموذجات الحيه (الدم ،الادرار) وتقدير الفناديوم في النباتات والاطعمه (الفطر، السيريلاك، والفراولة) واستخدام أفضل الظروف لاجراء التقدير.

الاهداء

إلى من أحب الخير لأبناءه ... وأنار درينا بالأدب والمعرفة

...

إلى من رحل بعيدا" عنا لكنه مازال حاضرا" بالقلب والعقل...

إلى من لم يكل أو يبخل لنا بأي نصيحة ومساعدة.

إلى من دفع دمه في سبيل العلم لإنارة درب المستقبل...

إلى الروح الطاهره للأستاذ الشهيد...

الدكتور أياد حمزه جاسم

بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيم

الْحَمْدُ لِلَّهِ الَّذِي هَدَانَا لِهَذَا وَمَا كُنَّا

لِنَهْتَدِيَ لَوْلا أَنْ هَدَانَا اللَّهُ

صدق الله العظيم

سورة الأعراف الآية(٤٣)

جمهورية العراق
وزارة التعليم العالي والبحث العلمي
جامعة النهرين/كلية العلوم
قسم الكيمياء

دراسة طيفية لتقدير الكروم والفناديوم وتطبيقاته

رسالة
مقدمة إلى كلية العلوم- جامعة النهرين
وهي جزء من متطلبات نيل درجة الماجستير في الكيمياء

من قبل
أسيل صلاح منصور

بكالوريوس كيمياء ٢٠٠٥ (جامعة النهرين)

١٢٤٩ هـ
جماد الثاني

٢٠٠٨ م
تموز

3-A. Spectrophotometric study of chromium and vanadium complexes of various valences:-

3-A-1. Study of [Cr (VI)-1,5-Diphenylcarbazide (DPC)] Complex.

This study includes the scanning of the spectrum of the reagent (DPC) in the ultraviolet-visible region, by taking certain volumes of DPC (25.8 mM) in a measuring cell versus a solvent (acetone) in reference cell. Figure (3-1) shows that the maximum absorption of DPC was at (λ_{max} =250nm). Scanning the spectrum of the complex produced by the reaction of dichromate ion with DPC reagent in the range of (200-800) nm versus the solvent (acetone) in the reference cell and also scanning of the spectrum of Cr (VI) ion alone were performed.

Figure (3-1) shows a comparison of the absorption spectra of the complex formed, ion and reagent. It can be noticed that the DPC reagent at (25.8mM) has the ability to form a complex with Cr (VI) at (6 ppm) with the highest absorbance at (λ_{max}=542nm). This absorption wavelength was different from that of Cr (VI) ion (λ_{max} =350nm) and that of reagent (λ_{max} =250nm).

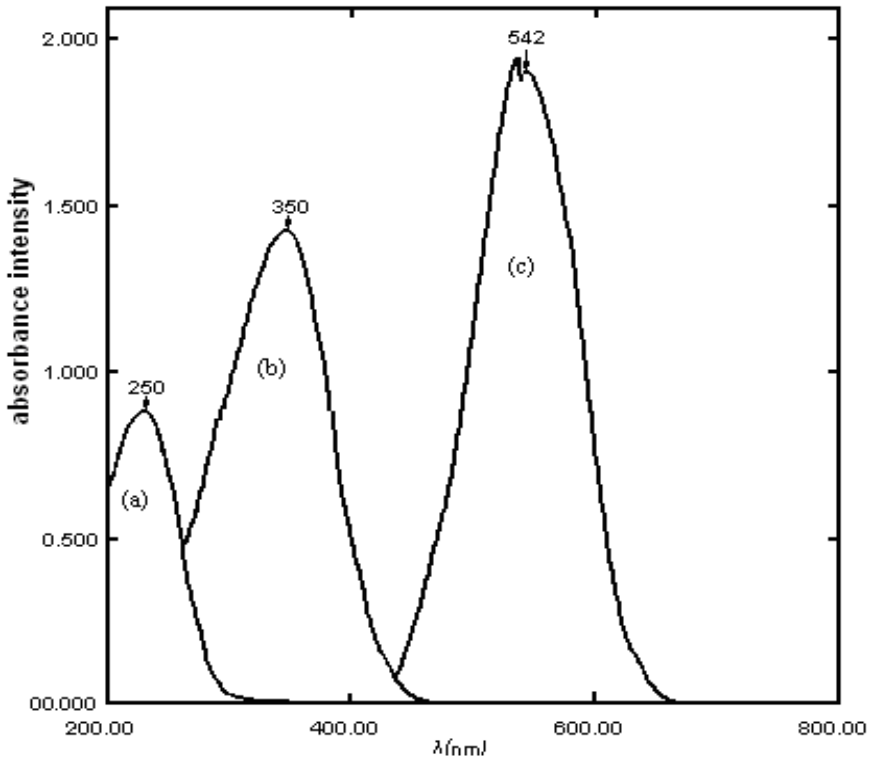


Figure (3-1): Comparison of the absorption spectra of (a)reagent at (DPC=25.8 mM)(b) metal ion at (Cr(VI)=6ppm) and (c) complex at (Cr(VI) =6ppm, pH=8-8.5, λ_{max} =542nm, DPC=25.8mM).

The position and shape of the resulting complex peak allowed the possibility of employing this reaction to estimate the chromium ions without overlapping with the ion and reagent peaks.

3-A-1-1. Studying the optimum conditions for complex formation:-

- ***Effect of the reagent (1,5-diphenylcarbazide) concentration on the complex formation:-***

A set of variable concentrations of DPC has been prepared to determine the optimum concentration to the highest absorption intensity. Figure (3-2) shows that the optimum concentration of DPC was (25.8 mM), which gave a regular increase to the signal which is appropriate for analytical purposes.

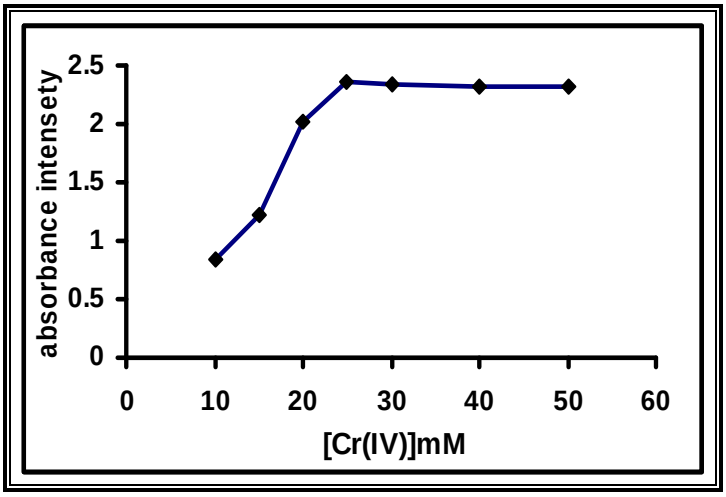


Figure (3-2): Effect of reagent concentration on the absorbance Intensity of the complex [Cr(VI)-DPC] at (Cr(VI)=6ppm, pH=8-8.5, λ_{max} =542nm, DPC=25.8mM)

❖ ***Effect of pH of the solution on the complex formation:-***

This effect has been studied by using a fixed concentration of both Cr (VI) ion at (6ppm) and DPC solution at (25.8mM), where a series of solutions have been prepared; in the first series, the complex formation was studied at different type of solutions [1M H_2SO_4, 1M H_3PO_4, 1M CH_3COOH, (0.2M CH_3COOH + 0.2M CH_3COONa), 1M CH_3COONa, 1M NaOH], where 1 ml of each solution was taken. The second series of solutions include the reagent only, the absorbance was measured first, and then the pH was measured for the standard solutions. The results show that the maximum absorbance of the complex (Cr(VI)-DPC) was at (pH=8-8.5) in the presence of NaOH.

❖ ***Effect of (NaOH) concentration on the complex formation:-***

A set of solutions of variable concentrations has been prepared to determine the optimum concentration which shows the highest absorption intensity. Figure (3-3) shows that the optimum concentration of complex at the constant reagent and ion concentration when added 1ml of 1M NaOH solution, which gave a regular shape and a suitable height of the signal. The high concentrations of NaOH gave a deviation and steep

decline of the absorption intensity, because the Cr (VI) ion was precipitated.

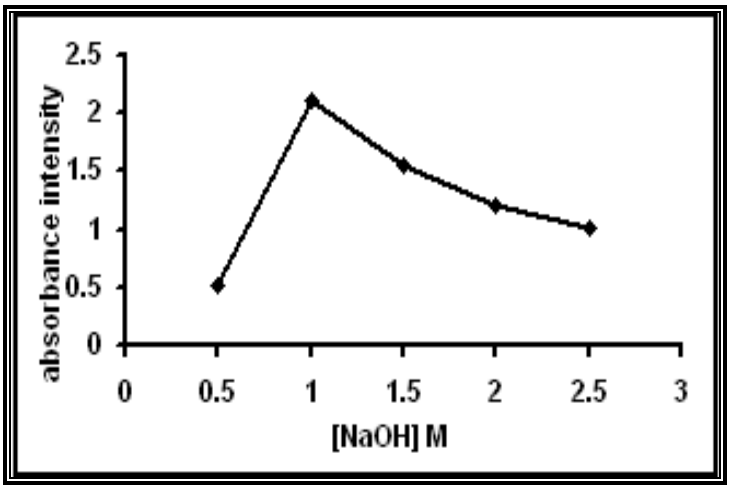


Figure (3-3): Effect of NaOH concentration on the absorbance intensity of the complex [Cr(VI)-DPC] at (Cr(VI)=6ppm, pH=8-8.5, λ_{max} =542nm, DPC=25.8mM)

3-A-1-2. Studying the effect of the physical variable on complex formation:-

❖ ***Time Effect:-***

The absorbance was measured at different periods of time in the absence of light. It can be noticed from figure (3-4) that the complex was fixed for long periods of time up to several hours through the constant absorbance of the complex. The complex solution should be kept for 15 minutes for the completion of interaction.

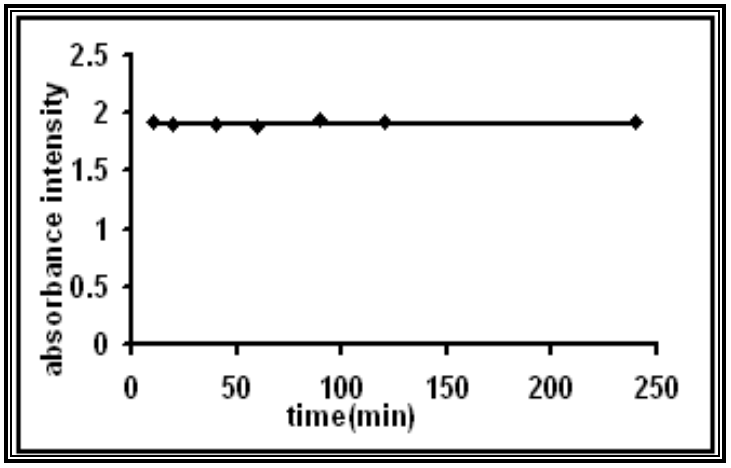


Figure (3-4): Effect of time on the absorbance intensity of the complex [Cr(VI)-DPC] at (Cr(VI)=6ppm, pH=8-8.5, λ_{max} =542nm, DPC=25.8mM)

❖ ***Light Effect:-***

The absorbance was measured at different periods of time in the presence of daylight and radiation light can be noticed from figure (3-5).

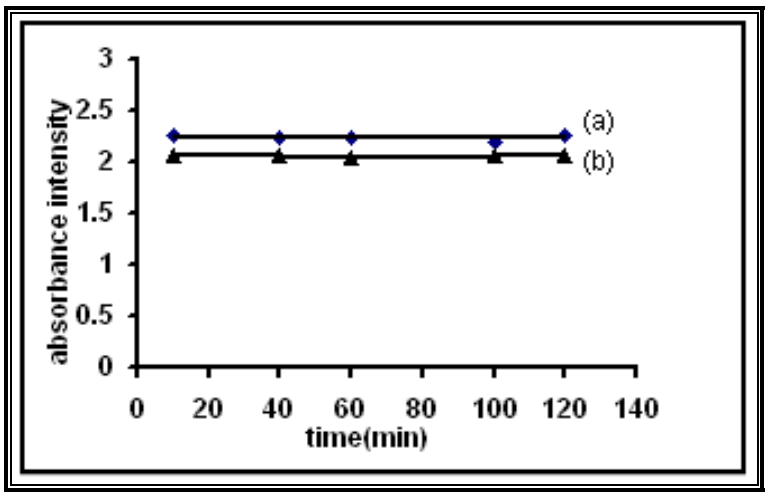


Figure (3-5): Effect of light on the absorbance intensity of complex [Cr(VI)-DPC] at (Cr(VI)=6ppm, pH=8-8.5, λ_{max} =542nm, DPC=25.8mM)(a) daylight effect (b)radiation light effect,

The results show the absence of any influence of daylight and radiation light on the complex stability for a period of time ranging from several minute to several hours.

❖ ***Temperature Effect:-***

Figure (3-6) shows the influence of temperature on the complex absorption. The results show that the analysis within the room temperature (20-70)°C was appropriate where the complex was stable. At high temperatures, a sharp decline of the complex absorption was observed which means that the complex disintegrated at temperatures higher than 70°C and the pink color of the complex disappeared.

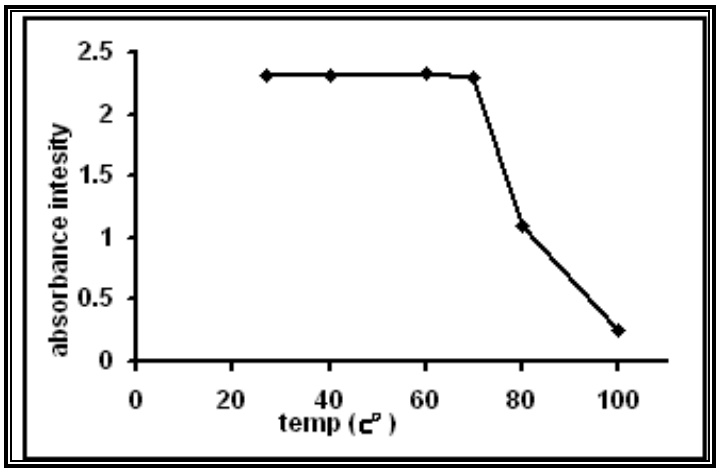


Figure (3-6): Effect of temperatures on the absorption intensity of the complex [Cr(VI)-DPC] at (Cr(VI)=6ppm,pH=8-8.5, λ_{max}=542nm,DPC=25.8mM)

3-A-1-3. Studying the Nature of [Cr (VI)-diphenylcarbazide] Complex:-

Appling the optimum conditions, which were obtained previously, the Cr to DPC ratio in the complex was obtained following continuous variation method, where a series of solutions was prepared in which the formal concentration of the Cr(VI) ion and DPC were held constant (0.5M) while varying volume ratios. The final volume was 10 ml for each solution. Figure (3-7) shows the plot of the absorbance versus mole fraction of the reactants. The ration appeared to be 1:2 at pH=8-8.5 and λ_{max}=542 nm.

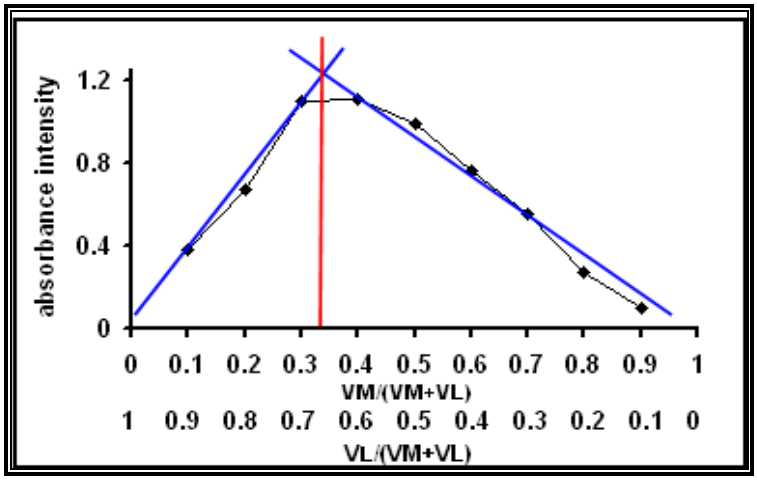
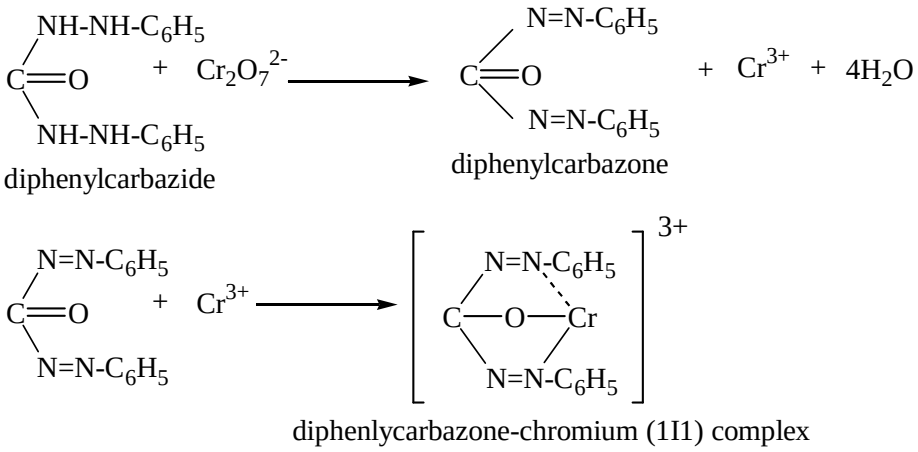


Figure (3-7): Continuous variation plot for the complex [Cr (VI)-DPC] at (Cr(VI)=0.5M, DPC=0.5M)

The general mechanism was illustrated for oxidation of diphenylcarbazide with Cr (VI) was shown in the following equation [6]:-



diphenlycarbazone-chromium (1I1) complex

Figure (3-8) shows the suggested structure of the [Chromium-1,5-diphenylcarbazone] complex.

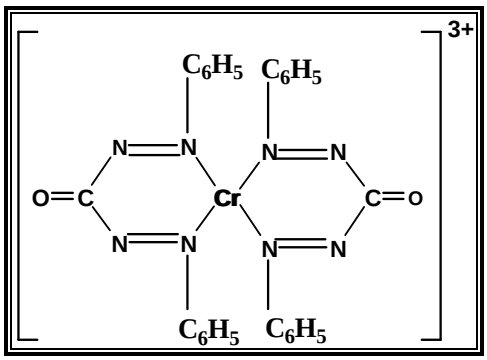


Figure (3-8): The suggested structure of the [Chromium-1,5-diphenyl carbazone] complex

3-A-1-4. [Cr-diphenylcarbazide] Complex formation using Chromium nitrate (Cr $(NO_3)_3.9H_2O$):-

The [Cr(VI)-DPC] complex was formed starting with chromium (III) ions after oxidization to Cr (VI) in adding an excess sodium hydroxide (NaOH) followed by a few ml of 6% hydrogen peroxide (H_2O_2) [155].

Figure (3-9) shows a comparison of the absorption spectra of the complex formed starting with potassium dichromate $Cr_2O_7^{=}$ and the absorption spectra of the complex formed starting with Cr (III). It has

been found that the absorption intensity of the complex was less than that obtained with $Cr_2O_7^{=}$ ion.

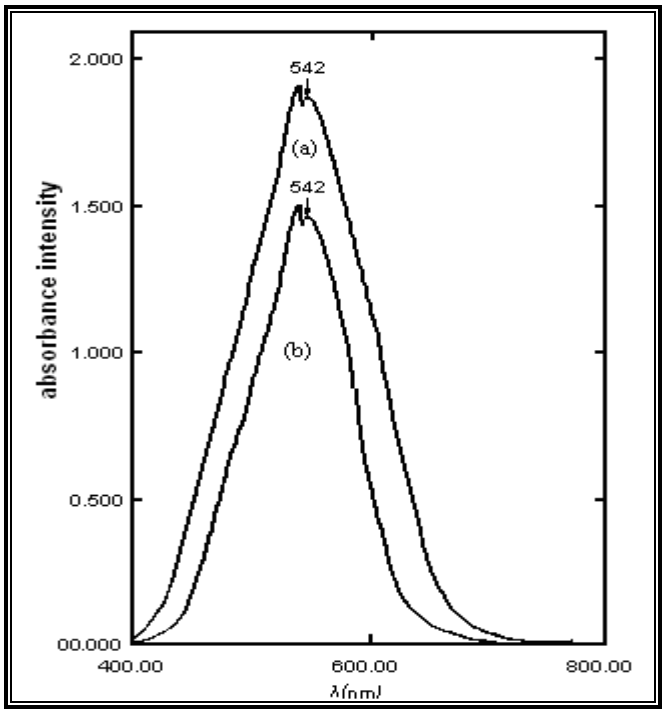


Figure (3-9): Comparison of the absorption spectra of complex (a) starting with Cr(VI) at (Cr(VI)=8ppm, pH=8-8.5, λ_{max}=542nm, DPC=25.8mM) (b)starting with Cr(III) at (Cr(III)=8ppm, pH=8-8.5, λ_{max}=542nm, DPC=25.8mM)

3-A-2.Study of [Cr(VI)-2,2'-bipyridine (bipy)] Complex.

This study includes scanning the spectrum of the complex, which was produced by the reaction of dichromate ion with bipyridine reagent in the range of (200-800) nm versus distilled water in reference cell. Scanning the spectrum of the reagent (bipy) and also scanning the spectrum of Cr (VI) ion alone were performed.

Figure (3-10) shows a comparison of the absorption spectra of the complex formed, ion and reagent. It can be noticed that the (bipy) reagent at (0.6mM) has the ability to form a complex with Cr (VI) at (8ppm) with highest absorption at (λ_{max} =308nm). This absorption wavelength was different from that of Cr (VI) ion (λ_{max} =350nm) and that of reagent (λ_{max} =225nm).

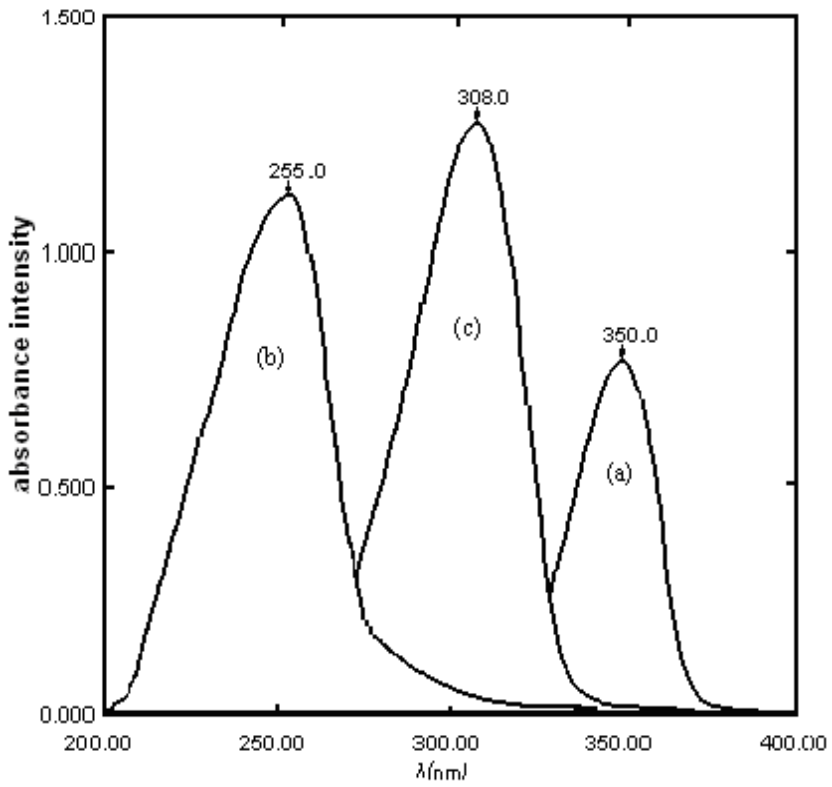


Figure (3-10): Comparison of the absorption spectra of (a) metal ion at (Cr(VI)=8ppm) (b) reagent at (bipy=0.6mM) and (c) complex at (Cr(VI)=8ppm, pH=4-4.5, λ_{max}=308nm, bipy=0.6mM).

The position and shape of the resulting complex peak allowed the possibility of employing this reaction to estimate the chromium ions without overlapping with the ion and reagent peaks.

3-A-2-1. Studying the optimum conditions for complex formation:-

- ***Effect of reagent (2,2'-bipyridine) concentration on the complex formation:-***

A set of variable concentrations of (bipy) has been prepared to determine the optimum concentration of it which gives the highest absorption intensity. Figure (3-11) shows that the optimum concentration of (bipy) was (0.6mM), which gave a regular increase to the peak which is appropriate for analytical purposes, but at higher than 0.6mM the absorbance intensity decrease, because the Cr(VI) ion was precipitated or the complex was disintegrated.

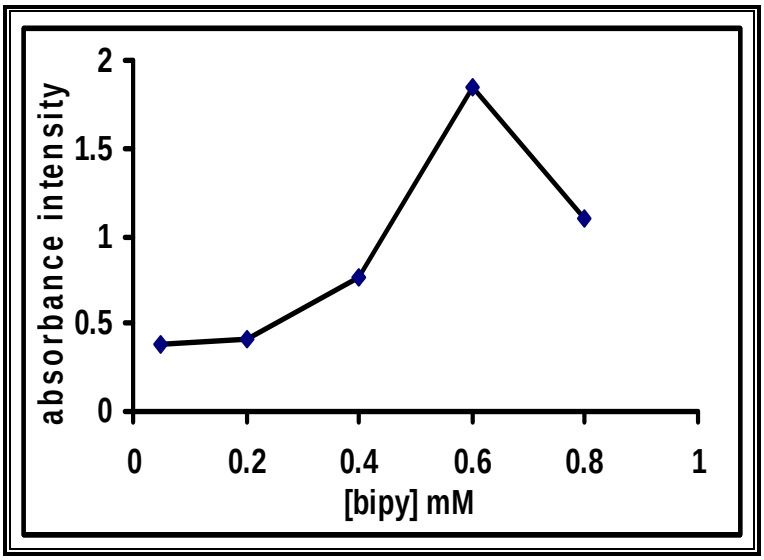


Figure (3-11): Effect of reagent concentration on the absorbance Intensity of the complex [Cr(VI)-bipy] at (Cr(VI)=8ppm, pH=4-4.5, λ_{max}=308nm, bipy=0.6mM).

❖ ***Effect of pH of the solution on the complex formation:-***

This effect has been studied by using a fixed concentration of both Cr (VI) ion and (bipy) solution, where a series of solutions have been prepared. In the first series, the complex formation was studied at different types of solutions [1M HCl, 1M H_2SO_4, 1M H_3PO_4, 1M CH_3COOH, (0.2M CH_3COOH + 0.2M CH_3COONa)] where 1 ml of each solution was taken. The second series of solutions included the reagent only, the absorbance was measured first, and then the pH was measured for the standard solutions. Figure (3-12) shows that the maximum absorbance of the complex (Cr-bipy) was at (pH=4-4.5) in the presence of H_2SO_4, but in higher alkaline media gave a deviation and steep decline of the absorbance intensity, because the Cr (VI) ion was precipitated.

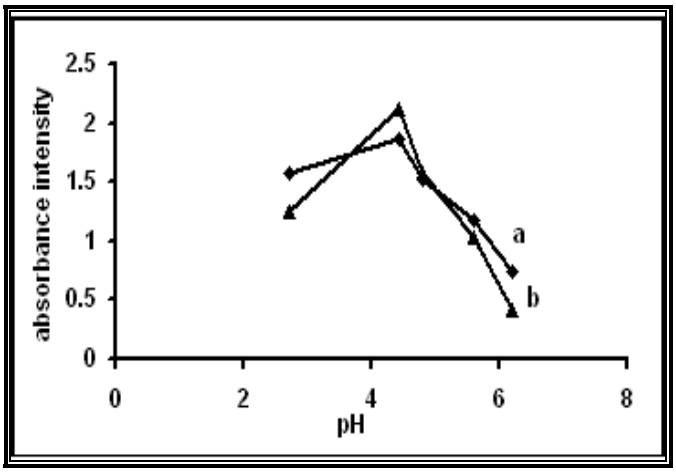


Figure (3-12): Effect of pH solution on the absorbance intensity of the complex [Cr(VI)-bipy](a) existence both Cr(VI) ion and reagent solution with H_2SO_4 at (λ_{max} =308 nm) (b) existence reagent only at (λ_{max} =350nm).

❖ *Effect of (H_2SO_4) concentration on the complex formation:-*

A set of solutions of variable concentrations has been prepared to determine the optimum concentration which shows the highest absorption intensity.

Figure (3-13) shows that the optimum concentration of the complex at constant reagent and ion concentrations when added 1ml of 1M H_2SO_4 solution, which gave a regular shape and suitable height of the signal, the high concentrations of H_2SO_4 gave the deviation and steep decline of the absorbance intensity, because the Cr (VI) was disintegrated.

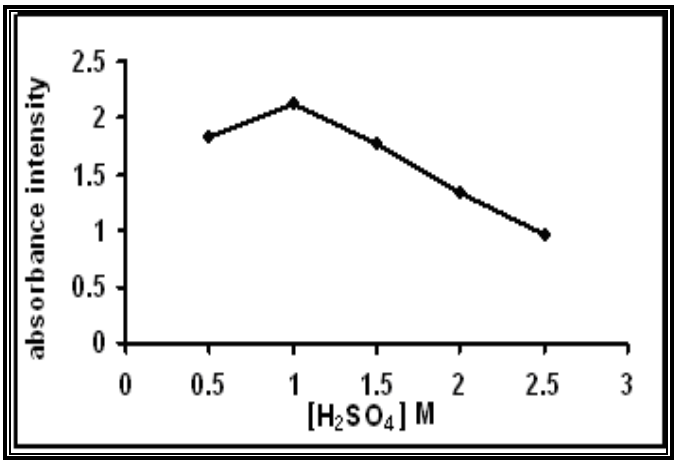


Figure (3-13): Effect of H_2SO_4 concentration on the absorbance intensity of the complex [Cr (VI)-bipy] at (Cr(VI)=8ppm, pH=4-4.5, λ_{max}=308nm, bipy=0.6mM).

3-A-2-2. Studying the effect of the physical variable on complex formation:-

❖ ***Time Effect:-***

The absorbance was measured at different periods of time in the absence of light. It can be noticed from figure (3-14) that the complex was fixed for long periods of time up to several hours through the constant absorbance of the complex. The complex solution should be kept for 15 minutes for the completion of interaction.

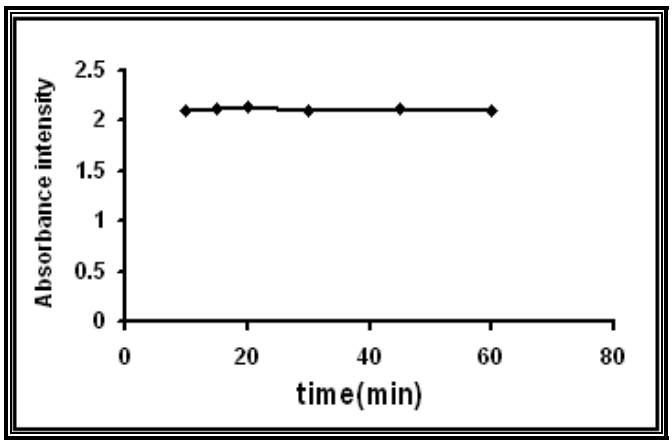


Figure (3-14): Effect of time on the absorbance intensity of the complex [Cr(VI)-bipy] at (Cr(VI)=8ppm, pH=4-4.5, λ_{max}=308nm, bipy=0.6mM).

❖ ***Light Effect:-***

The absorbance was measured at different periods of time in the presence of daylight and radiation light. This can be noticed from figure (3-15).The results show the absence of any influence of daylight and radiation light on the complex stability for a period of time ranging from several minutes to several hours.

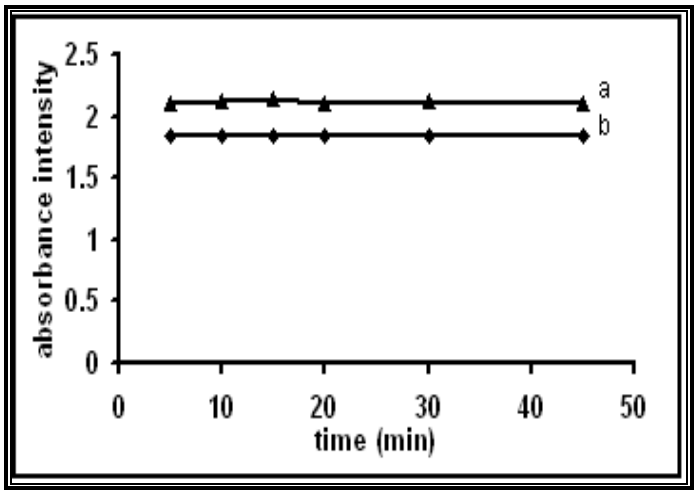


Figure (3-15): Effect of light on the absorbance intensity of the complex [Cr(VI)-bipy] at ((Cr(VI)=8ppm, pH=4-4.5, λ_{max} =308nm, bipy=0.6mM) (a)daylight effect (b)radiation light effect.

❖ ***Temperatures Effect:-***

Figure (3-16) shows the influence of temperature on the complex absorption. The results show that the analysis at (10-15) °C was appropriate where the complex was stable. But at higher than (15) °C the absorbance intensity increase, because the complex was disintegrated.

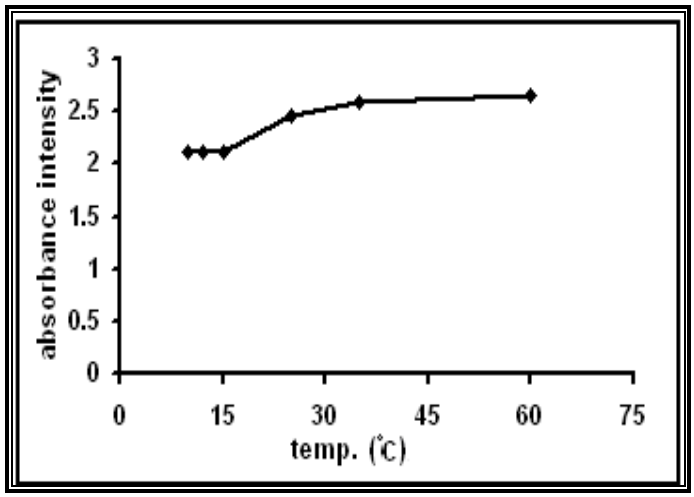


Figure (3-16): Effect of temperatures on the absorbance intensity of the complex [Cr(VI)-bipy] at (Cr(VI)=8ppm, pH=4-4.5, λ_{max}=308nm, bipy=0.6mM).

3-A-1-3.Studying the Nature of [Cr (VI)-bipyridine] Complex:-

Appling the optimum conditions, which were obtained previously, the Cr to (bipy) ratio in the complex was obtained following the continuous variation method, where a series of solutions was prepared in which the formal concentration of the Cr(VI) ion and (bipy) were held constant (0.5M) during the varying volume ratios. The final volume was 10 ml for each solution. Figure (3-16) shows the plot of the absorbance versus mole fraction of the reactants, the ration appeared to be 1:2 at pH=4-4.5 and λ_{max}=308 nm.

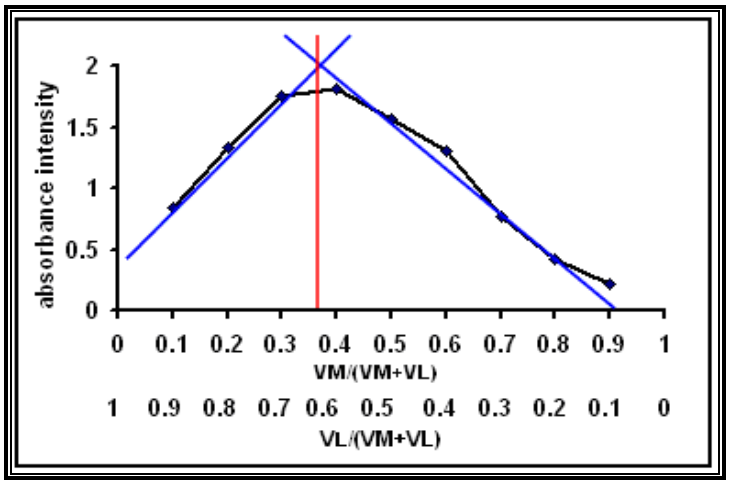


Figure (3-17): Continuous variation plot for the [Cr(VI)-bipy] at (Cr(VI)=0.5M, bipy=0.5M)

Figure (3-18) shows the suggested structure of the (Chromium-2,2'-bipyridine) complex.

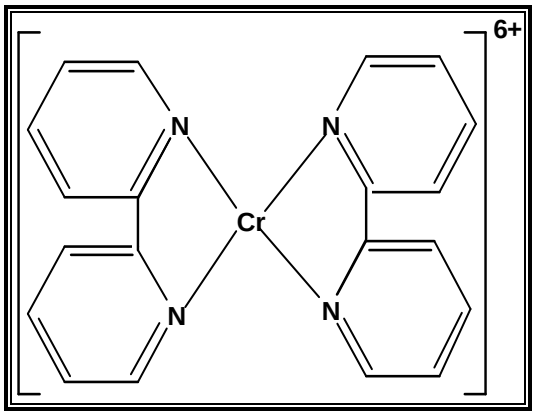


Figure (3-18): The suggested structure of the [Chromium-2,2'-bipyridine] complex

3-A-3. Study of [Vanadium (IV)-Thioglycolic acid (SH)] Complex.

This study includes scanning the spectrum of the complex in the ultraviolet-visible region, which was produced by the reaction of vanadyl sulphate with (SH) reagent in the range of (200-800) nm versus distilled water in reference cell. Scanning the spectrum of the reagent and also scanning the spectrum of V (IV) ion alone were performed. Figure (3-19) shows a comparison of the absorption spectra of the complex formed, ion and reagent. It can be noticed that the SH reagent at (3mM) has the ability to form a complex with V (IV) at (8ppm) with the highest absorbance at (λ_{max} =225nm). This absorption wavelength was different from that of V(VI) ion (λ_{max} =214nm) and that of reagent (λ_{max} =246nm).The position and shape of the resulting complex peak allowed the possibility of employing this reaction to estimate the vanadium element without overlapping with the ion and reagent peaks.

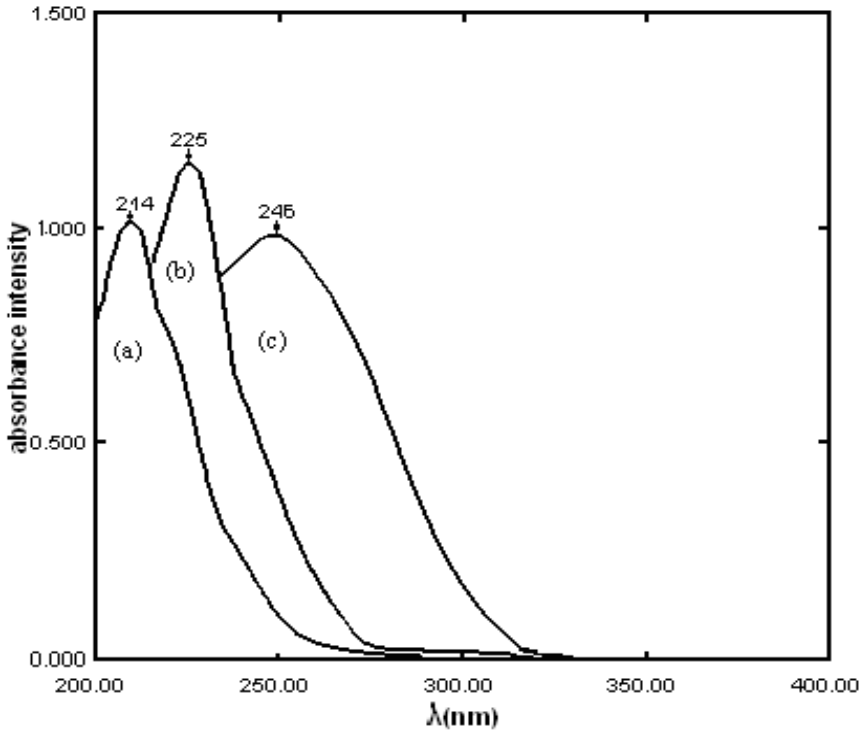


Figure (3-19): Comparison of the absorption spectra of (a) metal ion at (V(IV)=8ppm) (b) complex at (V(IV)=8ppm, pH=5-5.5, λ_{max}=225nm, SH=3mM)and (c) reagent at (SH=3mM).

3-A-3-1. Studying the optimum conditions for complex formation:-

❖ ***Effect of reagent (Thioglycolic acid) concentration on the complex formation:-***

A set of variable concentrations of (SH) has been prepared to determine the optimum concentration of it give the highest absorption intensity. Figure (3-20) shows the variation of absorbance intensity versus the SH concentration. It was found that 3mM was the optimum concentration.

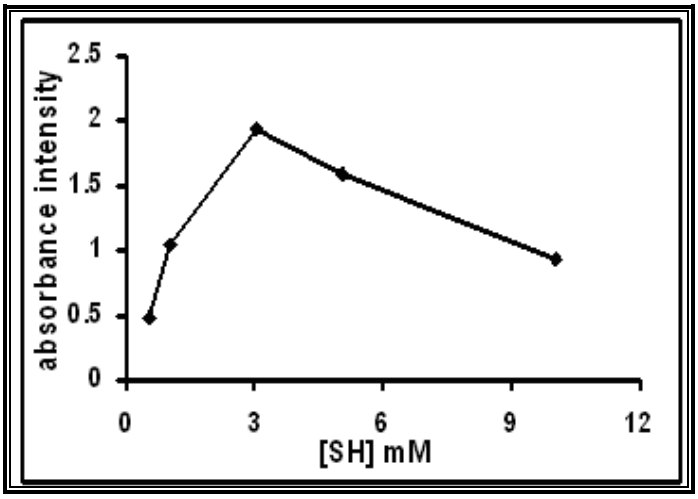


Figure (3-20): Effect of reagent concentration on the absorbance intensity of the complex [VO-SH] at (V(IV)=8ppm, pH=5-5.5, λ_{max}=225nm, SH=3mM)

❖ ***Effect of pH of the solution on the complex formation:-***

This effect has been studied by using a fixed concentration of both V (IV) ion and (SH) solution, where a series of solutions has been prepared. In the first series the complex formation was studied at different types of solutions [1M CH_3COOH, 1M CH_3COONa, (0.2M CH_3COOH + 0.2M CH_3COONa), 1M H_3PO_4, 1M H_2SO_4, 1M NaOH] where 1 ml of each solution was taken. The second series of solutions included the reagent only, the absorbance was measured first, and then the pH was measured for the standard solutions. Figure (3-21) shows that the maximum

absorbance of the complex (VO-SH) was at (pH=5-5.5) in the presence of CH_3COONa. But in higher alkaline media gave a deviation and steep decline of the absorbance intensity, because the V(IV) ion was precipitated or the complex was disintegrated.

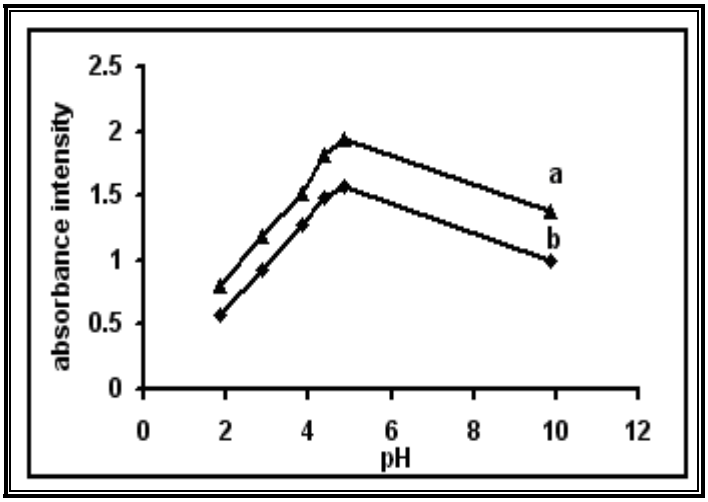


Figure (3-21): Effect of pH solution on the absorbance intensity of the complex [VO-SH] (a) existence both V (IV) ion and reagent solution with CH_3COONa at λ_{max}=225 nm (b) existence reagent only λ_{max}=246 nm.

- ***Effect of (CH_3COONa) concentration on the complex formation:-***

A set of solutions of variable concentrations has been prepared to determine the optimum concentration which shows the highest absorption intensity.

Figure (3-22) shows that the optimum concentration of the complex at a constant reagent and the ion concentration when added 1ml of (0.15M) CH_3COONa, which gave a regular shape and a suitable height of the signal. The high concentrations of CH_3COONa gave deviation and steep decline of the absorbance intensity, because the complex was disintegrated or the complex was precipitated.

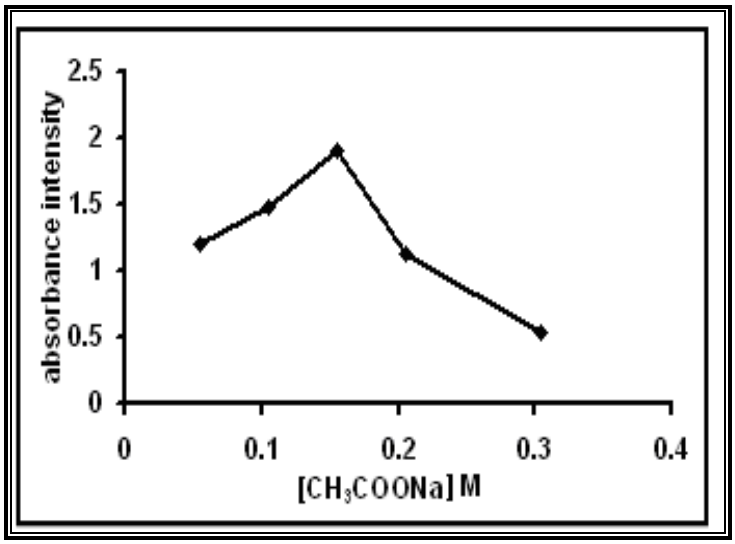


Figure (3-22): Effect of CH_3COONa concentration on the absorbance intensity of the complex [VO-SH] at (V (IV)=8ppm, pH=5-5.5, λ_{max}=225nm, SH=3mM)

3-A-3-2. Studying the effect of the physical variable on complex formation:-

❖ ***Time Effect:-***

The absorbance was measured at different periods of time in the absence of light. It can be noticed from figure (3-23) that the complex was fixed for long periods of time up to several hours through constant absorbance of the complex. The complex solution should be kept for 15 minutes for the completion of interaction.

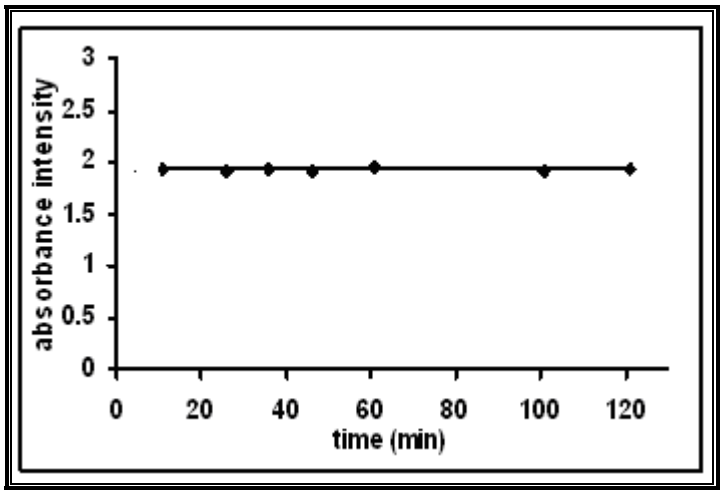


Figure (3-23): Effect of time on the absorbance intensity of the complex [VO-SH] at (V(IV)=8ppm, pH=5-5.5, λ_{max}=225nm, SH=3mM)

❖ ***Light Effect:-***

The absorbance was measured at different periods of time in the presence of daylight and radiation light can be noticed from fig (3-24). The results show the absence of any influence of daylight and radiation light on the complex stability for periods of time ranging from several minutes to several hours.

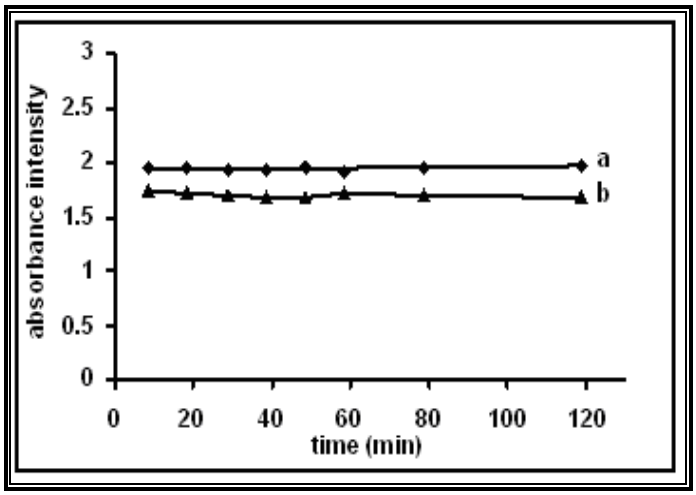


Figure (3-24): Effect of light on the absorbance intensity of the complex [VO-SH] at (V(IV)=8ppm, pH=5-5.5, λ_{max}=225nm, SH=3mM) (a)daylight effect (b)radiation light effect.

❖ ***Temperature Effect:-***

Figure (3-25) shows the influence of temperature on the complex absorption.

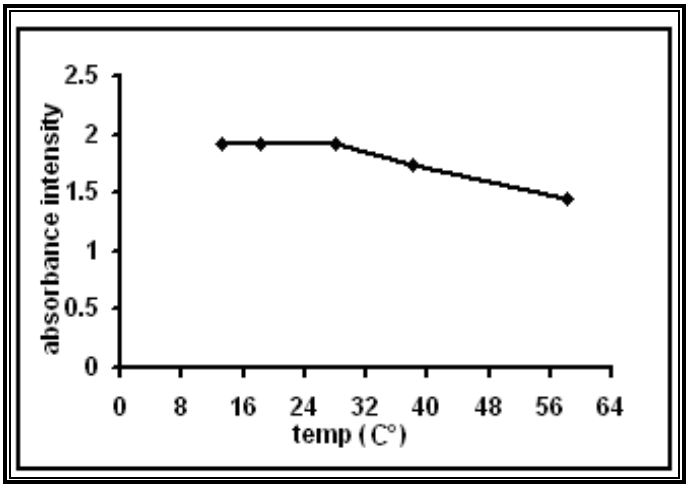


Figure (3-25): Effect of temperatures on the absorbance intensity of the complex [VO-SH] at (V(IV)=8ppm, pH=5-5.5, λ_{max}=225nm, SH=3mM)

The results show that the analysis within the room temperature (20-30)°C was appropriate where the complex was stable, but at higher than (30) °C the absorbance intensity decrease, because that the complex was disintegrated.

3-A-3-3. Studying the Nature of [VO-Thioglycolic acid] Complex:-

Appling the optimum conditions, which were obtained previously, the V to (SH) ratio in the complex was obtained following the continuous variation method, where a series of solutions was prepared in which the formal concentrations of the V(IV) ion and (SH) were held constant (0.5M) during the varying volume ratios. The final volume was 10 ml for each solution. Figure (3-26) shows the plot of the absorbance versus mole fraction of the reactants, the ration appeared to be 3:2 at pH=5-5.5 and λ_{max}=225 nm.

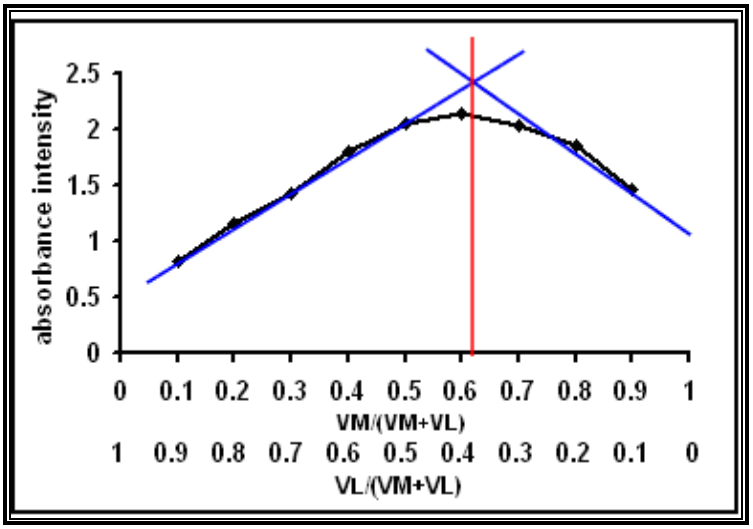


Figure (3-26): Continuous variation method for the complex [VO-SH] at (V (IV)=0.5M, SH=0.5M)

Figure (3-27) shows the suggested structure of complex (VO-thioglycolic acid).

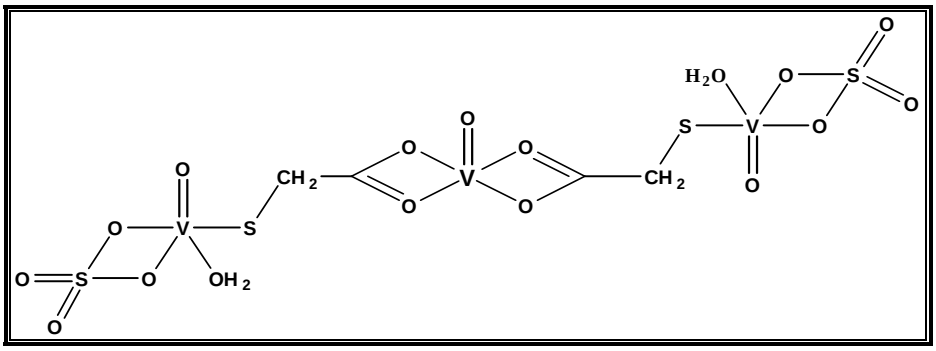


Figure (3-27): The suggested structure of the complex (VO-thioglycolic acid)

3-A-4. Study of [Vanadium (V)-8-Hydroxyquinoline (8-HQ)] Complexes.

This study includes scanning the spectrum of the complex in the ultraviolet-visible region, which was produced by the reaction of vanadium pentoxide (VO_2^+) with (8-HQ) reagent in the range of (200-800) nm versus chloroform in reference cell. Scanning the spectrum of the reagent (8-HQ) and also scanning the spectrum of V (V) ion alone were performed.

Figure (3-28) shows a comparison of the absorption spectra of the complex formed, ion and reagent. It can be noticed that the (8-HQ) reagent at (1mM) has the ability to form a complex with V (V) at (8ppm) with the highest absorbance at (λ_{max} =550nm). This absorption wavelength was different from that of V (V) ion (λ_{max} =210nm) and that of reagent (λ_{max} =300nm).The position and shape of the resulting complex peak allowed the possibility of employing this reaction to estimate the vanadium element without overlapping with the ion and reagent peaks.

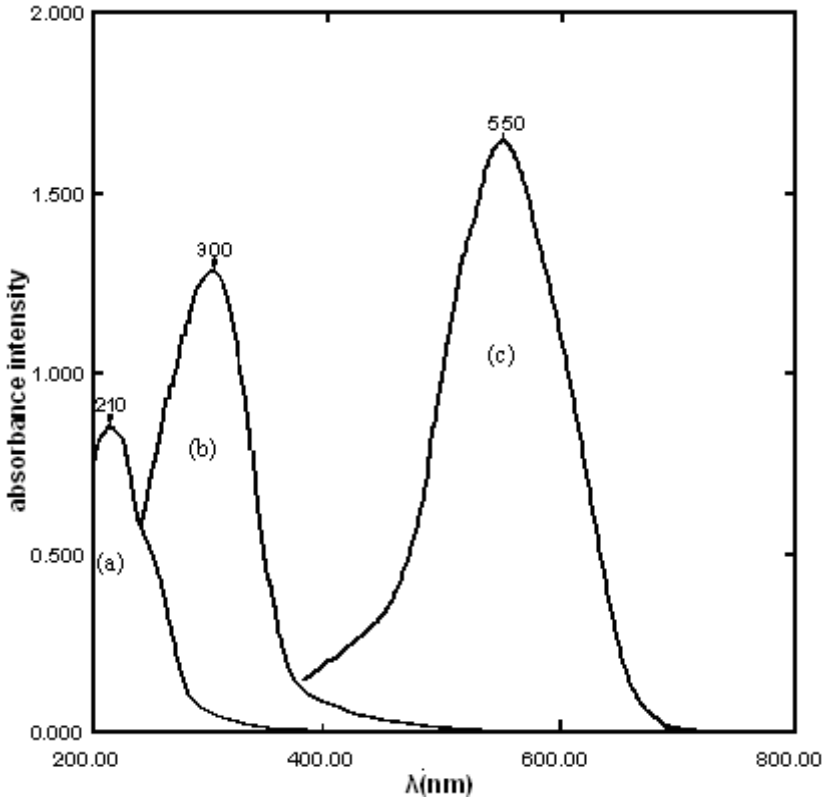


Figure (3-28): Comparison of the absorption spectra of (a) metal ion at (V(V)=8ppm) (b) reagent at (8-HQ=1mM) and (c) complex at (V(V)=8ppm, pH=3.5-4.5, λ_{max}=550nm, 8-HQ=1mM).

3-A-4-1. Studying the optimum conditions for complex formation:-

- ***Effect of the reagent (8-hydroxyquinoline) concentration on the complex formation:-***

A set of variable concentrations of (8-HQ) has been prepared to determine the optimum concentration to give the highest absorption intensity. Figure (3-29) shows that the optimum concentration of (8-HQ) was (1mM), which gave a regular increase to the peak which is appropriate for analytical purposes, but at higher than 1mM the absorbance intensity decrease, because that the complex was disintegrated.

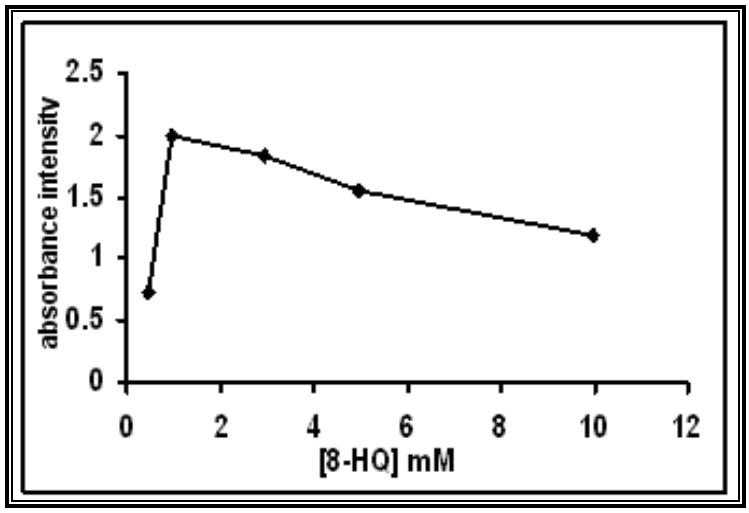


Figure (3-29): Effect of reagent concentration on the absorbance intensity of the complex [V(V)-8-HQ] at (V(V)=8ppm, pH=3.5-4.5, λ_{max}=550nm, 8-HQ=1mM).

❖ ***Effect of pH of the solution on the complex formation:-***

This effect has been studied by using a fixed concentration of both V(V) ion and (8-HQ) solution, where a series of solutions have been prepared; in the first series the complex formation was studied at different type of solutions [1M HCl, 1M H_3PO_4, 1M H_2SO_4, 1M CH_3COOH, (0.2M CH_3COOH + 0.2M CH_3COONa), 1M CH_3COONa] where 1 ml of each solution was taken. The second series of solutions included the reagent only, the absorbance was measured first, and then the pH was measured for the standard solutions. Figure (3-30) shows that the maximum absorbance of the complex (V(V)-8-HQ) was at (pH=3.5-4.5) in the presence of H_2SO_4. But in alkaline media gave a deviation and steep decline of the absorbance intensity, because the V(V) ion were precipitated or the complex was disintegrated.

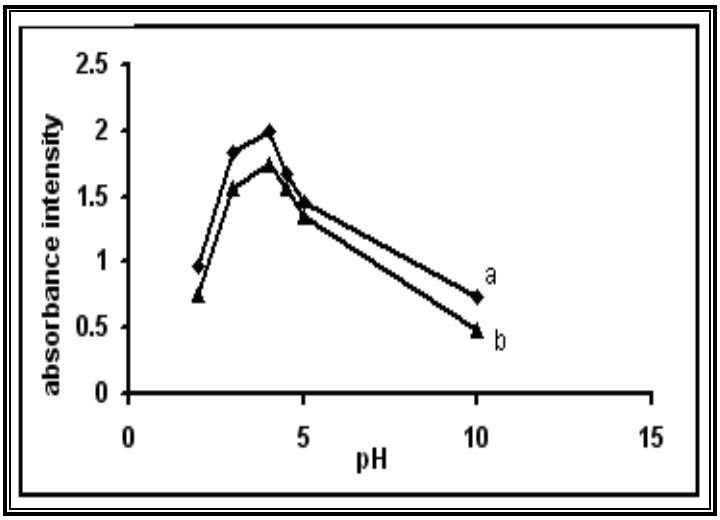


Figure (3-30): Effect of pH solution on the absorbance intensity of the complex [V(V)–8-HQ] (a)existence both V (V) ion and reagent solution with H_2SO_4 which prepare λ_{max}=550nm (b) existence reagent only λ_{max}=300 nm .

❖ ***Effect of (H_2SO_4) concentration on the complex formation:-***

A set of buffer solutions of variable concentrations has been prepared to determine the optimum concentration which showed the highest absorption intensity. Figure (3-31) shows that the optimum concentration of the complex at the constant reagent and ion concentration when added 1ml of (0.1M) H_2SO_4 solution, which gave a regular shape and a suitable height of the signal. The high concentrations of H_2SO_4 gave the deviation and steep decline of the absorption intensity, because the V (V) was disintegrated.

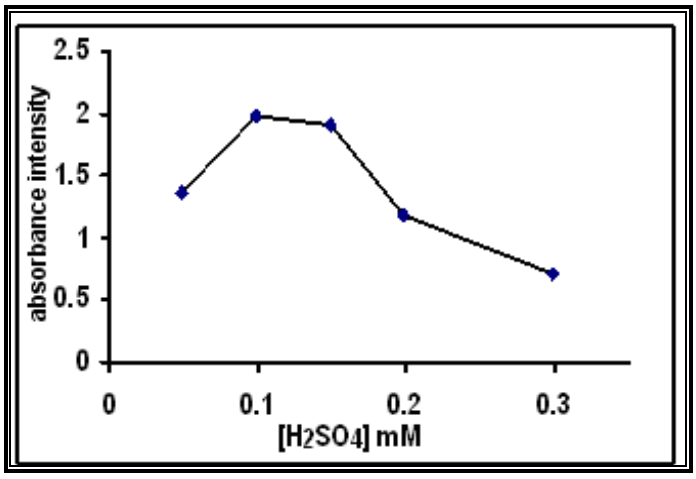


Figure (3-31): Effect of H_2SO_4 concentration on the absorbance intensity of the complex [V(V)- 8-HQ] at (V(V)=8ppm, pH=3.5-4.5, λ_{max}=550nm, 8-HQ=1mM).

3-A-4-2. Studying the effect of the physical variable on complex formation:-

❖ ***Time Effect:-***

The absorbance was measured at different periods of time in the absence of light. It can be noticed from figure (3-32) that the complex was fixed for long periods of time up to several hours through constant absorbance of the complex. The complex solution should be kept for 15 minutes for the completion of interaction.

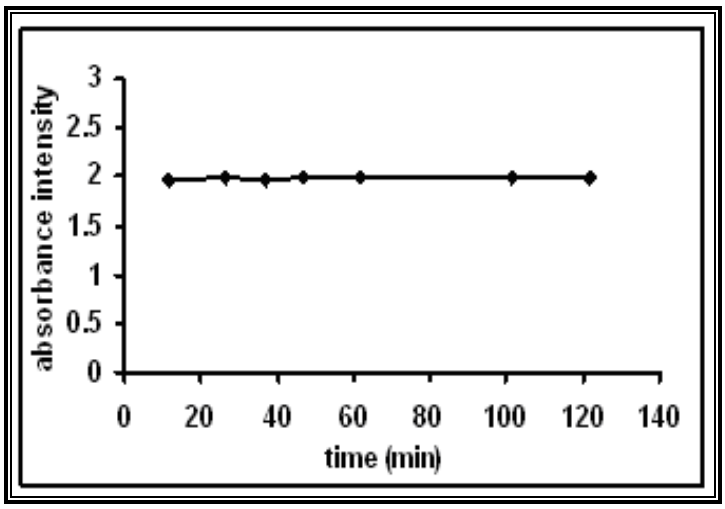


Figure (3-32): Effect of time on the absorbance intensity of the complex [V(V)-8-HQ] at (V(V)=8ppm, pH=3.5-4.5, λ_{max}=550nm, 8-HQ=1mM).

❖ ***Light Effect:-***

The absorbance was measured at different periods of time in the presence of daylight and radiation light. It can be noticed from figure (3-33). The results show the absence of any influence of daylight and radiation light on the complex stability for a period of time ranging from several minute to several hours.

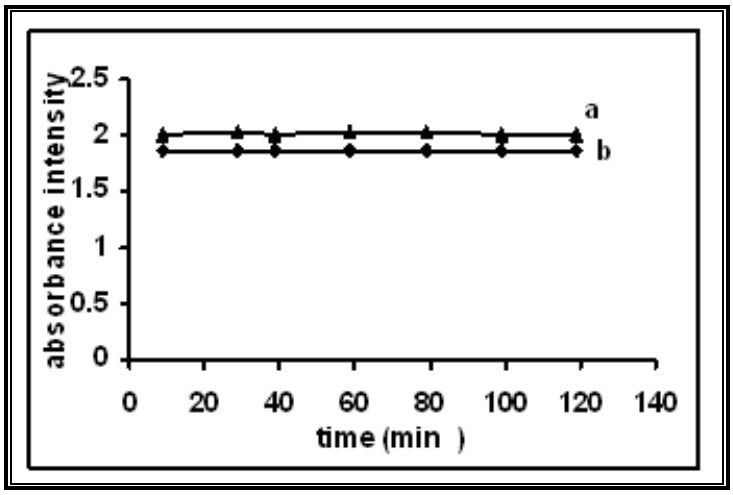


Figure (3-33): Effect of light on the absorbance intensity of the complex [V (V)-8-HQ] at (V(V)=8ppm, pH=3.5-4.5, λ_{max}=550nm, 8-HQ=1mM). (a)daylight effect (b)radiation light effect.

❖ ***Temperature Effect:-***

Figure (3-34) shows the influence of temperature on the complex absorption.The results show that the analysis within the room temperature (20-30)°C was appropriate where the complex was stable, but at higher than (30) °C the absorbance intensity decrease, because the V(V) was disintegrated.

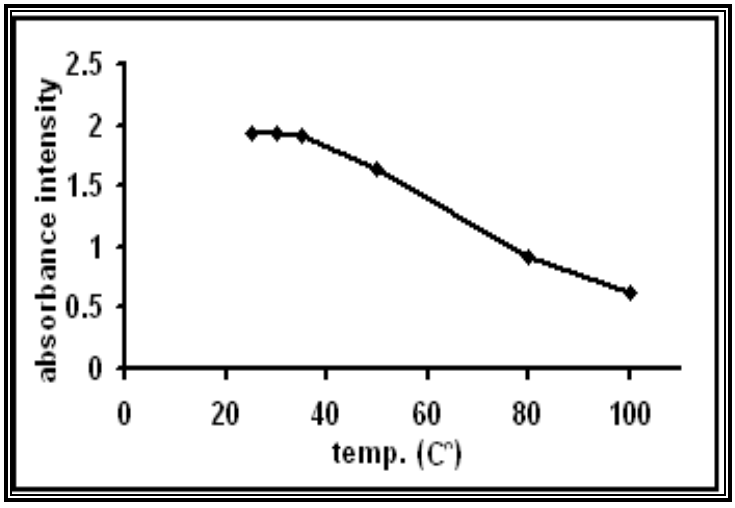


Figure (3-34): Effect of temperatures on the absorbance intensity of the complex [V(V)- 8-HQ] at (V(V)=8ppm, pH=3.5-4.5, λ_{max}=550nm, 8-HQ=1mM).

3-A-4-3. Studying the Nature of [V(V)-8-hydroxyquinoline] Complex:-

Appling the optimum conditions, which were obtained previously, the V(V) to (8-HQ) ratio in the complex was obtained following a continuous variation method, where a series of solutions was prepared in which the formal concentration of the V(V) ion and (8-HQ) were held constant (0.5mM) during the varying volume ratios. The final volume was 10 ml for each solution. Figure (3-35) shows the plot of the absorbance versus mole ratio of the reactants, the ration appeared to be 1:2 at pH=3.5-4.5 and λ_{max}=308 nm.

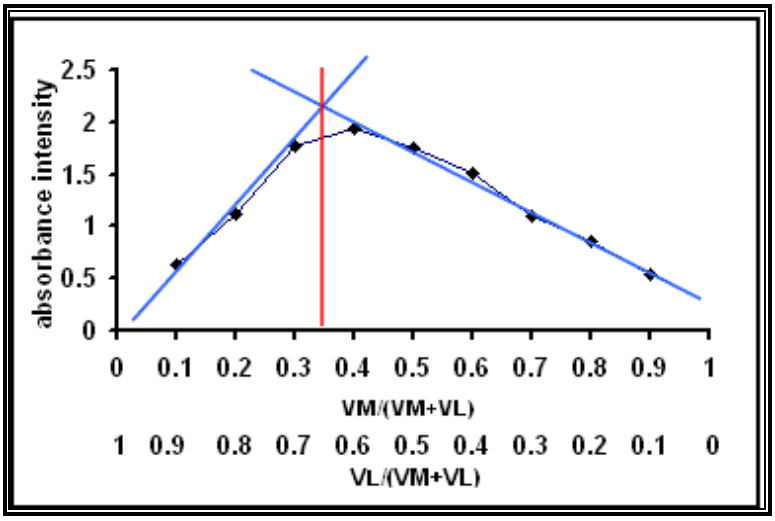


Figure (3-35): Continuous variation plot for the complex [V(V)- 8-HQ] at (V(V)=0.5M, 8-HQ=0.5M)

Figure (3-36) shows the suggested structure of the (Vanadium (V)/oxine) complex.

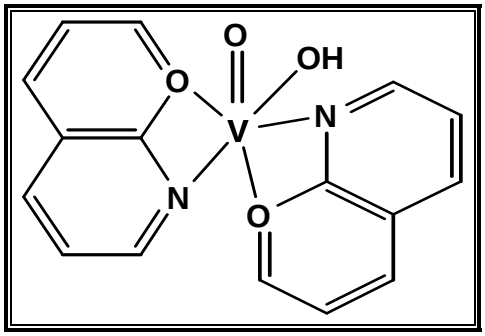


Figure (3-36): The suggested structure of the complex [Vanadium (V)-oxine]

3-B. Calibration curves for complexes formation:-

3-B-1. Calibration curve for Cr (VI) with the selective reagent 1, 5-diphenylcarbazide (DPC):-

A calibration curve was prepared from a series of standard solutions in the range (0.5-9) ppm, using the optimum conditions (pH=8-8.5, DPC=25.8mM, λ_{max} =542nm) for the reaction between dichromate ions, DPC reagent and measuring the absorbance as shown in the table (3-1). The absorbance measurements were made at 542 nm, the curve was described in figure (3-37) with the linear equation:

$$y=0.203 + 0.2883\ [Cr\ (VI)]\ \mu g.ml^{-1} \text{---------- (3-1)}$$

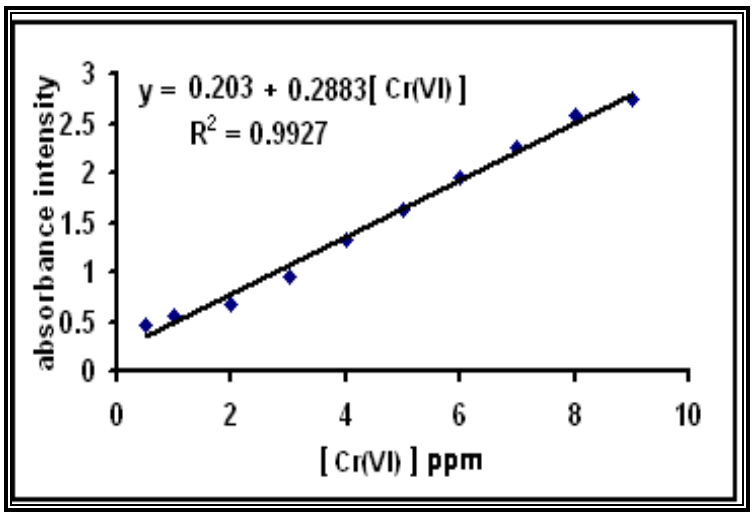


Figure (3-37): Product-moment relationship between the concentration of dichromate ion [$Cr_2O_7^{=}$] with DPC reagent and absorbance intensity within the range (0.5-9) ppm.

Table (3-1): Contrasting absorbance values against concentration of dichromate ions within the range (0.5-9) ppm.

[Cr(VI)] ppm (X_i)	Absorbance Intensity	Average $\bar{x}$	Standard deviation (σ_{n-1})	%R* %RSD
0.5	0.454, 0.455, 0.454	0.454	5.77×10^{-4}	0.127
1	0.548, 0.548, 0.548	0.548	5.77×10^{-4}	0.105
2	0.674, 0.674, 0.673	0.674	5.77×10^{-4}	0.086
3	0.965, 0.964, 0.964	0.964	5.77×10^{-4}	0.0599
4	1.325, 1.326, 1.326	1.326	5.77×10^{-4}	0.0435
5	1.625, 1.625, 1.625	1.625	0	0
6	1.958, 1.958, 1.958	1.958	0	0
7	2.261, 2.262, 2.262	2.262	5.77×10^{-4}	0.0255
8	2.585, 2.585, 2.585	2.585	0	0
9	2.753, 2.753, 2.753	2.753	0	0

$$\%R^{*} = Repeatability = \frac{\sigma_{n-1}}{\bar{x}} \times 100$$

Figure (3-37) shows the relationship between the absorbance intensity and Cr (VI) ion concentration. We took concentrations within the linear equation (taking the concentration that fall within the linear range of the curve) to get linearity (r^2%) approach to 1 and maximum slop value in the calibration curve. The curve gave a linear range (2-8) ppm as shown in figure (3-38). While the linear equation was:

$$y=0.0275+ 0.320\ [Cr(VI)]\ \mu g.ml^{-1} \text{---------- (3-2)}$$

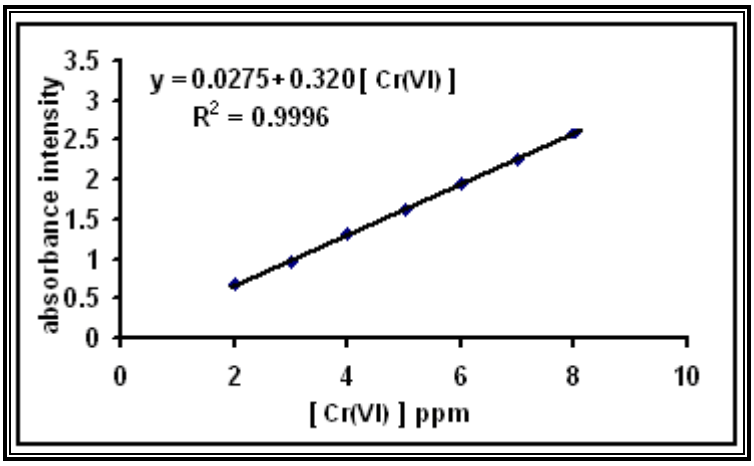


Figure (3-38): linear calibration curve for determination of Cr(VI) ion with DPC reagent within the range (2-8) ppm.

Table (3-2) shows that treatment data resulted from modern statistical treatment [156-158] and calculated the limit of the linear regression equation, correlation coefficient and the linearity at the limit of the confidence 95% for (n-2) of both the intercept and the slop as shown in table (3-3).

The final linear regression equation for the determination of Cr (VI) ion was:-

$$y=0.0275 \mp 0.0039 + 0.320 \mp 0.0073\ [Cr\ (VI)]\ \mu g.ml^{-1} \text{ ------ (3-3)}$$

Table (3-2): Effect of chromium ions concentration on the absorbance intensity of the complex [Cr(VI)-DPC] within the range (2-8) ppm.

[Cr (VI)] ppm (X_i)	Absorbance intensity	Average $\bar{x}$	Standard deviation (σ_{n-1})	%R %RSD	$\bar{x} \mp t\frac{\sigma_{n-1}}{\sqrt{n}}$ at limit of confidence 95% for (n-1)	$\hat{y}$
2	0.674, 0.674, 0.673	0.674	5.77×10^{-4}	0.086	$0.674 \mp 5.77\times10^{-4}$	0.67
3	0.965, 0.964, 0.964	0.964	5.77×10^{-4}	0.0599	$0.964 \mp 5.77\times10^{-4}$	0.99
4	1.325, 1.326, 1.326	1.326	5.77×10^{-4}	0.0435	$1.326 \mp 5.77\times10^{-4}$	1.31
5	1.625, 1.625, 1.625	1.625	0	0	$1.625 \mp 5.77\times10^{-4}$	1.630
6	1.958, 1.958, 1.958	1.958	0	0	1.958 ∓ 0	1.950
7	2.261, 2.262, 2.262	2.262	5.77×10^{-4}	0.0255	$2.262 \mp 5.77\times10^{-4}$	2.270
8	2.585, 2.585, 2.585	2.585	0	0	2.585 ∓ 0	2.590

$\hat{y}$: *calculated from linear regression equation*

Table (3-3): Outline for the results of the linear regression equation of the [Cr (VI) – DPC] complex.

Measured type	Linear range [Cr (VI)]	Slop (b) at limit of confidence 95% for (n-2) $b \mp S^*_b t$	Intersection (a) at limit of confidence 95% for (n-2) $a \mp S^*_a t$	t* at 95% for (n-2)	t calculate value $t=\frac{/r/\sqrt{n-2}}{\sqrt{1-r^2}}$	Correlation coefficient (r)	Linearity $r^2\%$
Absorbance Intensity for chromium ions	(2-8)	0.32 ∓ 0.0073	0.0275 ∓ 0.0039	2.57 << 70.64		0.9985	99.7

S^*_b:- Standard deviation of the slop
Sa:- Standard deviation of the intersection, t= table value

The essential hypothesis H◦ to explain the non-straight line relationship when t table larger than t calculated ($t_{tab}>t_{cal}$) [157], but the alternative hypothesis A reject essential hypothesis and explain the straight line relationship when t calculate larger than t table.

Therefore, t calculate value = 70.64, t table at 95% limit of confidence for (n-2) = 2.57 Its mean $t_{cal}> t_{tab}$. According to this, essential hypothesis ignore and accept alternative hypothesis.

3-B-2. Calibration curve for Cr (III) with 1,5-diphenylcarbazide (DPC):-

A calibration curve was prepared from a series of standard solutions, in the range (0.5-9) ppm, using the optimum conditions (pH=8-8.5, DPC=25.8mM, λ_{max} =542nm) for the reaction between chromium (III) ions with DPC reagent after oxidization Cr (III) to Cr (VI) in adding an excess of sodium hydroxide to Cr (III) salt followed by a few ml of 6% hydrogen peroxide. The excess of hydrogen peroxide can be removed by boiling the mixture for a few minutes [155].

The absorbance measurements were made at 542 nm, the curve gave a linear range (2-8) ppm, and calibration curve was described in figure (3-39) with the linear regression equation:-

$$y=0.0448 + 0.3098\ [Cr\ (III)]\ \mu g.ml^{-1} \text{---------- (3-4)}$$

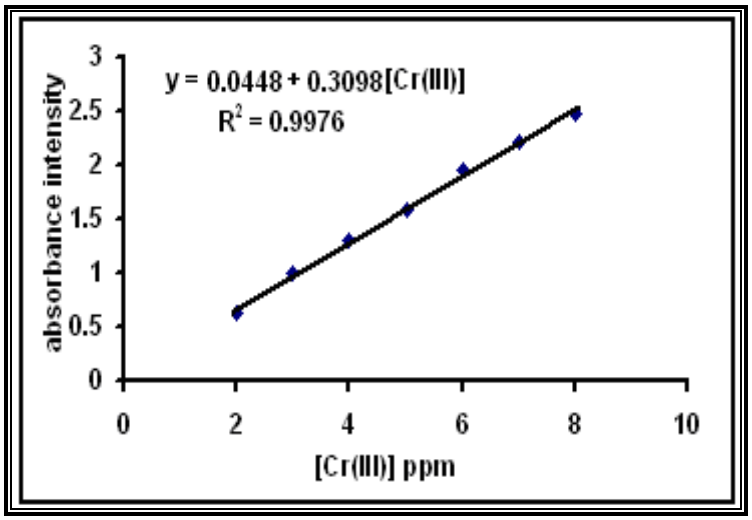


Figure (3-39): linear calibration curve for determination of Cr(III) ion with DPC reagent within the range (2-8) ppm.

Table (3-4) shows that the treatment data resulted from modern statistical treatment [156-158] and calculated the limits of the linear regression equation, correlation coefficient and the linearity at limit of the confidence 95% for (n-2) of both the intercept and the slop as shown in table (3-5), the final linear regression equation for the determination of Cr(III) ion was:-

$$y = 0.0448 \mp 0.0095 + 0.3098 \mp 0.018\ [Cr\ (III)]\ \mu g.ml^{-1} \text{ --------- (3-5)}$$

Table (3-4): Effect of Chromium (III) ions concentration on the absorbance intensity of the complex [Cr(III)-DPC] within the range (2-8) ppm.

Cr (III) ppm (X_i)	*Absorbance Intensity*	*Average* $\bar{x}$	*Standard deviation (σ_{n-1})*	*%R %RSD*	$\bar{x} + t\frac{\sigma_{n-1}}{\sqrt{n}}$ at limit of confidence 95%*for (n-1)*	$\hat{y}$
2	0.62, 0.61, 0.62	0.62	5.77×10^{-4}	0.9312	$0.62 \mp 5.34\times10^{-4}$	0.664
3	0.993, 0.993, 0.993	0.993	0	0	0.838 ∓ 0	0.974
4	1.31, 1.32, 1.31	1.31	0	0	1.147 ∓ 0	1.284
5	1.587, 1.587, 1.587	1.587	0	0	1.426 ∓ 0	1.594
6	1.95, 1.95, 1..95	1.95	5.77×10^{-4}	0.2961	$1.736 \mp 5.34\times10^{-4}$	1.904
7	2.22, 2.21, 2.21	2.21	5.77×10^{-4}	0.261	$1.996 \mp 5.34\times10^{-4}$	2.213
8	2.487, 2.487, 2.487	2.487	0	0	2.286 ∓ 0	2.523

Table (3-5): Outline for the results of the linear regression equation of the complex [Cr (III) – DPC]

Measured type	Linear range Cr (III)	Slop (b) at limit of confidence 95% for (n-2) b ∓S_bt	Intersection (a) at limit of confidence 95% for (n-2) a ∓ S_at	$t_{tab.}$ at 95% for (n-2)	t calculate value $t=\frac{/r/\sqrt{n-2}}{\sqrt{1-r^2}}$	Correlation coefficient (r)	Linearity r^2%
Absorbance Intensity for chromium (III) ions	(2-8)	0.3098∓0.018	0.0448∓0.0095	2.57 << 49.95		0.9989	99.8

The results in table (3-5) observe $t_{cal} > t_{tab}$ that means the relationship between Cr (III) ion concentration and absorbance intensity was linearity.

3-B-3.Calibration curve for Cr (VI) with the selective reagent 2,2'-bipyridine (bipy):-

Another calibration curve was prepared from a series of standard solutions in the range (0.5-9) ppm, using the optimum conditions (pH=4-4.5, bipy=0.6mM, λ_{max} =308nm) for the reaction between dichromate ions and (bipy) reagent; the curve gave a linear range (2-8) ppm. The absorbance measurements were made at 308 nm.

A linear calibration curve was obtained from (2-8) ppm, as shown in figure (3-40) with the linear regression equation:-

$$y=0.013 +0.284\ [Cr\ (VI)]\ \mu g.ml^{-1} \text{---------- (3-6)}$$

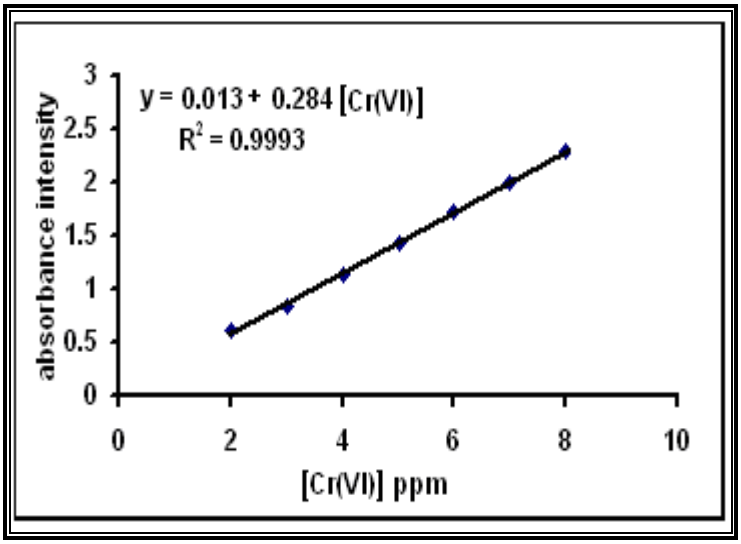


Figure (3-40): linear calibration curve for determination of Cr(VI) ion with 2,2'-bipyridine reagent within the range (2-8) ppm.

Table (3-6) shows that the treatment data resulted from modern statistical treatment [156-158] and calculated the limits of the linear equation, correlation coefficient and the linearity at limit of the confidence 95% for (n-2) of both the intercept and the slop as shown in table (3-7). The final linear regression equation for the determination of Cr (VI) ion with the bipyridine was:-

$$y = 0.013 \mp 0.049 + 0.284 \mp 0.0089\ [Cr\ (VI)]\ \mu g.ml^{-1} \text{--------} \quad (3\text{-}7)$$

Table (3-6): Effect of chromium (VI) ions concentration on the absorbance intensity of the complex [Cr (VI)-bipy] within the range (2-8) ppm.

[Cr (VI)] ppm (X_i)	Absorbance Intensity	Average $\bar{x}$	Standard deviation (σ_{n-1})	%R %RSD	$\bar{x} \mp t\frac{\sigma_{n-1}}{\sqrt{n}}$ at limit of confidence 95%for (n-1)	$\hat{y}$
2	0.603, 0.603, 0.603	0.603	0	0	0.603 ∓ 0	0.581
3	0.838, 0.838, 0.838	0.838	0	0	0.838 ∓ 0	0.861
4	1.148, 1.147, 1.147	1.147	5.77×10^{-4}	0.0503	1.147 ∓ 5.4×10^{-4}	1.149
5	1.426, 1.426, 1.426	1.426	0	0	1.426 ∓ 0	1.433
6	1.735, 1.736, 1.736	1.736	5.77×10^{-4}	0.0333	1.736 ∓ 5.4×10^{-4}	1.72
7	1.996, 1.995, 1.996	1.996	5.77×10^{-4}	0.029	1.996 ∓ 5.35×10^{-4}	2.001
8	2.286, 2.286, 2.287	2.287	5.77×10^{-4}	0.0253	2.286 ∓ 5.35×10^{-4}	2.285

Table (3-7): Outline for the results of the linear regression equation of the complex [Cr (VI) – bipy].

Measured type	Linear range [Cr(VI)]	Slop (b) at limit of confidence 95% for (n-2) b ∓S_bt	Intersection (a) at limit of confidence 95% for (n-2) a∓ S_at	$t_{tab.}$ at 95% for (n-2)	(t) calculate value $t = \frac{/r/\sqrt{n-2}}{\sqrt{1-r^2}}$	Correlation coefficient (r)	Linearity r^2%
Absorbance intensity for chromium (VI) ions	(2-8)	0.284∓0.0089	0.013∓0.049	2.57 << 49.95		0.9995	99.9

The results in table (3-7) observe $t_{cal} > t_{tab}$ that means the relationship between Cr (VI) ion concentration and absorbance intensity was linearity.

3-B-4. Calibration curve for V (IV) with thioglycolic acid (SH):-

A calibration curve was prepared from a series of standard solutions in the range (0.5-9) ppm, using the optimum conditions (pH=5-5.5, SH=3mM, λ_{max} =225nm) for the reaction between vanadyl sulphate (IV) and (SH) reagent, the curve gave a linear range (2-8) ppm. The absorbance measurements were made at 225 nm.

A linear curve was obtained as shown in figure (3-41) with the linear regression equation:-

$$y=0.026 + 0.3269\ [V\ (IV)]\ \mu g.ml^{-1} \text{-------- (3-8)}$$

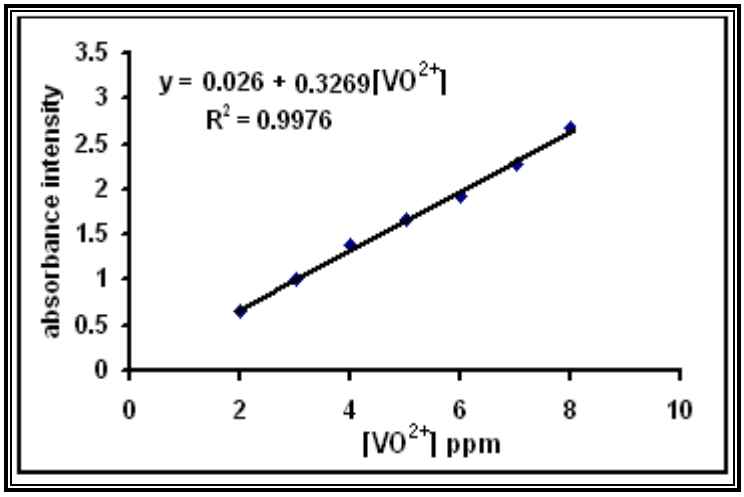


Figure (3-41): linear calibration curve for determination of V(IV) ion with thioglycolic acid reagent within the range (2-8) ppm.

Table (3-8) shows that the treatment data resulted from modern statistical treatment [156-158] and calculated the limits of the linear equation, correlation coefficient and the linearity at limit of the confidence 95% for (n-2) of both the intercept and the slop as shown in table (3-4). The final linear regression equation for the determination of VO^{2+} ion with SH reagent was:-

$$y=0.00257 \mp 0.010 + 0.327 \mp 0.0185\ [V(IV)]\ \mu g.ml^{-1} \text{ ---------- (3-9)}$$

Table (3-8): Effect of vanadium (IV) ions concentration on the absorbance intensity of the complex (VO-SH) within the range (2-8) ppm.

[V(IV)]ppm (X_i)	Absorbance Intensity	Average $\overline{x}$	Standard deviation (σ_{n-1})	%R %RSD	$\overline{x} \mp t\frac{\sigma_{n-1}}{\sqrt{n}}$ at limit of confidence 95% for (n-1)	$\hat{y}$
2	0.665, 0.664, 0.665	0.665	5.77×10^{-4}	0.09	$0.665 \mp 5.35\times10^{-4}$	0.68
3	1.002, 1.002, 1.002	1.002	0	0	1.002 ∓ 0	1.006
4	1.382, 1.381, 1.381	1.381	5.77×10^{-4}	0.042	$1.381 \mp 6.33\times10^{-4}$	1.333
5	1.677, 1.677, 1.678	1.677	5.77×10^{-4}	0.034	$1.677 \mp 6.32\times10^{-4}$	1.66
6	1.935, 1.936, 1.935	1.935	5.77×10^{-4}	0.0298	$1.935 \mp 6.32\times10^{-4}$	1.99
7	2.289, 2.289, 2.289	2.289	0	0	2.289 ∓ 0	2.314
8	2.672, 2.673, 2.672	2.673	5.78×10^{-4}	0.022	$2.673 \mp 6.32\times10^{-4}$	2.641

Table (3-9): Outline for the results of the linear regression equation of (VO-SH) complex.

Measured type	Linear range $[VO^{2+}]$	Slop (b) at limit of confidence 95% for (n-2) b ∓S_bt	Intersection (a) at limit of confidence 95% for (n-2) a ∓ S_at	$t_{tab.}$ at 95% for (n-2)	t calculate value $t=\frac{/r/\sqrt{n-2}}{\sqrt{1-r^2}}$	Correlation coefficient (r)	Linearity r^2%
Absorbance intensity for vanadium (IV) ions	(2-8)	0.327∓0.0185	0.0257∓0.0100	2.57 << 70.64		0.9989	99.8

The results in table (3-9) observe $t_{cal} > t_{tab}$ that means the relationship between V (IV) ion concentration and absorbance intensity was linearity.

3-B-5. Calibration curve for V(V) with 8-Hydroxyquinoline (8-HQ):-

A calibration curve was prepared from a series of standard solutions in the range (0.5-9) ppm, using the optimum conditions (pH=3.5-4.5, 8-HQ=1mM, λ_{max} =550nm) for the reaction between vanadium pentoxide (V) ions and (8-HQ) reagent; the curve gave a linear range (2-8) ppm. The measurements were made at 550 nm. The linear calibration curve was obtained as shown in figure (3-42) with the linear regression equation:-

$$y = -0.0884 + 0.2451\ [V\ (V)]\ \mu g.ml^{-1} \text{ ---------- (3-10)}$$

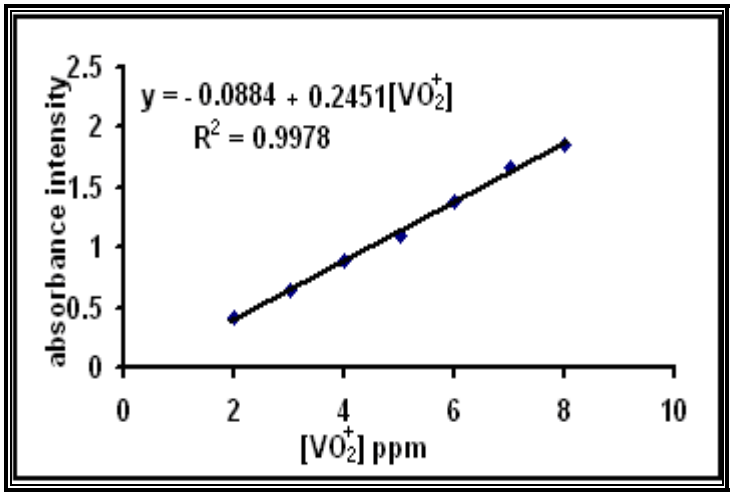


Figure (3-42): linear calibration curve for determination of V(V) ion with 8-HQ reagent within the range (2-8) ppm.

Table (3-10) shows that the treatment data resulted from modern statistical treatment [156-158] and calculated the limits of the linear equation, correlation coefficient and the linearity at limit of confidence 95% for (n-2) of both the intercept and the slop as shown in table (3-11). The final linear regression equation for the determination of VO_2^+ ion with 8-HQ reagent was:-

$$y = -0.0884 \mp 0.0072 + 0.2451 \mp 0.013\ [V(V)]\ \mu g.ml^{-1} \text{ --------- (3-11)}$$

Table (3-10): Effect of vanadium (V) ions concentration on the absorbance intensity of the complex [V(V)- 8-HQ] within the range (2-8) ppm.

[V(V)] ppm (X_i)	*Absorbance Intensity*	*Average* $\bar{x}$	*Standard deviation (σ_{n-1})*	*%R %RSD*	$\bar{x} \mp t\frac{\sigma_{n-1}}{\sqrt{n}}$ at limit of confidence 95%*for (n-1)*	$\hat{y}$
2	0.421, 0.422, 0.421	0.421	5.77×10^{-4}	0.137	$0.421 \mp 5.34\times10^{-4}$	0.402
3	0.641, 0.641, 0.641	0.641	0	0	0.641∓ 0	0.647
4	0.885, 0.885, 0.884	0.885	5.77×10^{-4}	0.065	$0.885 \mp 5.34\times10^{-4}$	0.892
5	1.107, 1.107, 1.107	1.107	5.77×10^{-4}	0.0522	$1.107 \mp 5.34\times10^{-4}$	1.137
6	1.375, 1.375, 1.375	1.375	0	0	1.375∓ 0	1.3822
7	1.673, 1.673, 1.673	1.673	0	0	1.673 ∓ 0	1.6273
8	1.858, 1.857, 1.857	1.857	5.78×10^{-4}	0.0311	$1.857 \mp 5.34\times10^{-4}$	1.872

Table (3-11): Outline for the results of the linear regression equation of the complex [V(V)-8-HQ]

Measured type	Linear range $[VO_2^+]$	Slop (b) at limit of confidence 95% for (n-2) $b \mp S_b t$	Intersection (a) at limit of confidence 95%for (n-2) $a \mp S_a t$	$t_{tab.}$ at 95% for (n-2)	t calculate value $t = \frac{/r/\sqrt{n-2}}{\sqrt{1-r^2}}$	Correlation coefficient (r)	Linearity $r^2\%$
Absorbance intensity for Vanadium (V) ions	(2-8)	0.2451∓0.013	0.0885∓0.072	2.57 << 49.95		0.9989	99.8

The results in table (3-11) observe $t_{cal} > t_{tab}$ that means the relationship between (V) ion concentration and absorbance intensity was linearity.

3-B-6. Detection Limit:-

Detection Limit (DL) is defined as the smallest material concentration to give signal equal to the blank signal expressed by intersection Y_B plus standard deviation for blank $3S_B$ [157]. The theoretical detection limit was estimated based on the linear regression equation for ion at limit of confidence 95% for (n-2) from degree of freedom and can estimating the practice detection limit as recorded in the devise the highest sensitivity of the lower concentration. Table (3-12) shows that the theoretical and practical detection limit was calculated at a percentage linearity of 99.5% within the range (2-8) ppm for each ion in complexes formation.

Table (3-12): The value of theoretical and practical detection limit.

Complexes	Theoretical Detection limit	Practical Detection limit
Cr(VI)-DPC	1.1ng/mL	7 ng/mL
Cr(VI)-Bipy	1.93 ng/mL	8 ng/mL
V(IV)-SH	1.39 ng/mL	10 ng/mL
V(V)-8HQ	3.3 ng/mL	10 ng/mL

3-C. Studying the effect of interferences:-

This study was conducted to interpret the effect of interferences of some positive and negative ions and to find the percentage effect of these ions on the absorption intensity, and also to demonstrate the effect of changing the metal's behavior and how some reactions were preferred thermodynamically (increasing the absorption intensity) and others were non- preferred (reducing the absorption intensity). The interpretation was explained on the basis of some thermodynamic quantities (ΔG, E°_{cell}, K_{eq}).

3-C-1. Studying the effect of metallic and non-metallic ions on the absorption intensity of chromium (VI) and vanadium (IV):-

The previous study (part A), was conducted to study the absorption of chromium (VI) and vanadium (IV) solutions, This method was highly sensitive and accurate, where it was possible to assess very low detection limits in estimating chromium and vanadium as ($Cr_2O_7^{=}$, VO^{2+}) respectively, but it is vulnerable to many interferences with positive or negative ions. Therefore, it is necessary to study the effect of interferences of these ions when estimating chromium and vanadium ions. These ions are characterized by various oxidation states, various colors and high stability. The existence of any competitive and influential ions may lead to increase or decrease the absorption intensity according to the nature of the reaction (properties of the interfering ion) as shown in table (3-13) and (3-14). According to the mechanism of the reaction there are some preferred reactions according to the thermodynamic view point, since E°_{cell} of the net reaction is positive, as will be explained later. The reaction is exothermic, represented by the negative value of ΔG, which means that the reaction is spontaneous.

The elected ions are:

Positive ions:

Cd(II), Cu(II), Co(II), Mg(II), Zn(II), Ni(II), V(IV), V(V) and Mn (II).

Negative ions:

I^-, Br^-, Cl^-, IO_3^-, NO_3^-, $S_2O_3^{=}$, $Cr_2O_7^{=}$and $C_2O_4^{=}$.

This procedure involve the use three volumetric flask 100 ml containing variable concentration of interfering ion (4,16) ppm and metals ions solution (chromium or vanadium) at 4 ppm concentration, the first volumetric containing metals ions only reference for comparison with the changing concentrations of interferences (in 2,3 volumetric flask).The percentage of the interferences effect was calculated after measuring the absorbance intensity of these solutions.

Table (3-13) shows the effect of V^{5+}, V^{4+}, Co^{2+} ions to increase the absorbance intensity of Cr(VI), which was explained by the following dynamic equations:-

$$Cr_2O_7^{=} + 14H^+ + 6e^- \rightleftharpoons 7H_2O + 2Cr^{3+} \quad \text{--------(1)} \quad E=1.33V$$

$$6\times[\, VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O\,] \quad \text{--------(2)} \quad E= +1.00V$$

$$Cr_2O_7^{=} + 14H^+ + 6e^- \rightleftharpoons 7H_2O + 2Cr^{3+} \quad \text{--------(1)} \quad E=1.33V$$

$$\mp 6VO_2^+ \mp 12H^+ \mp 6e^- \rightleftharpoons \mp 6VO^{2+} \mp 6H_2O \quad \text{--------(2)} \quad E= \mp 1.00V$$

$$Cr_2O_7^{=} + 6VO^{2+} + 2H^+ \rightleftharpoons 2Cr^{3+} + 6VO_2^+ + H_2O \quad \text{--------(3)} \quad E^\circ_{cell} = +0.33V$$

In equation (3), we notice that this reaction was preferred thermodynamically because the positive value of E°_{cell} and the negative value of ΔG equal to (-45.72Kcal). The reaction was exothermic which means it is spontaneous and the equilibrium constant ($K_{eq.}$) was calculated via applying the following equation:-

$$\text{Log } K = \frac{nFE_{cell}}{2.303\ RT}$$

$$K = 3.028\times10^{33}$$

Table (3-13):- The percentage of interferences effect of some positive and negative ions on the absorption intensity of dichromate ion [$Cr_2O_7^{=}$] under the same conditions for all measurements.

(A)

Positive ions ppm	Effect %								
	Co^{2+}	Cu^{2+}	Mg^{2+}	Ni^{2+}	Cd^{2+}	Mn^{2+}	Zn^{2+}	V^{4+}	V^{5+}
4	+8.26	+12.7	+8.85	-29.2	+15.7	-53.3	-13.22	+7.965	+12.41
16	+14.73	+21.81	+14.4	-35.39	+25.35	-21.3	-28.97	+42.63	+18.29

(B)

Negative ions ppm	Effect %						
	Cl^-	I^-	Br^-	$C_2O_4^{=}$	IO_3^-	$S_2O_3^{=}$	NO_3^-
4	+6.37	+19.44	+5.04	-10.47	-62.54	-38.7	-50.4
16	+15.46	+25.55	+10.21	-15.52	-66.47	-41.2	-85.3

The interference of iodide (I^-) with chromium ions also increased the absorbance intensity and this was explained by the following dynamic equations:-

$$Cr_2O_7^{=} + 14H^+ + 6e^- \rightleftharpoons 7H_2O + 2Cr^{3+} \quad \text{--------(1)} \quad E=1.33V$$
$$3\times[\, I_2 + 2e^- \rightleftharpoons 2I^- \,] \quad \text{--------(2)} \quad E= 0.535V$$

$$Cr_2O_7^{=} + 14H^+ + 6e^- \rightleftharpoons 7H_2O + 2Cr^{3+} \quad \text{--------(1)} \quad E=1.33V$$
$$\mp\, 3I_2 \mp 6e \rightleftharpoons \mp\, 6I^- \quad \text{--------(2)} \quad E= \mp\, 0.535V$$

$$Cr_2O_7^{=} + 6I^- + 14H^+ \rightleftharpoons 2Cr^{3+} + 3I_2 + 7H_2O \quad \text{--------(3)} \quad \mathring{E}_{cell}= +0.795V$$

In equation (3), the reaction was preferred thermodynamically because the value of E°_{cell} positive as the value of K_{eq}. is ($K=4.56\times10^{80}$), which means that the dichromate ions were able to oxidize (I^-) and liberates iodine (I_2). This reaction was spontaneous because of the negative value of the ΔG° (-110.13Kcal).

The other interferences could be explained in the same manner, since the values of potential cell index for Cu^{2+}, Cd^{2+}, Co^{2+}, and Mn^{2+} ions are: - 0.99, 1.73, 0.512, and -0.17 respectively.

Table (3-14):- The percentage of interferences effect of some positive and negative ions on the absorption intensity of vanadyl ion [VO^{2+}] under the same conditions for all measurements.

(A)

Positive ions ppm	***Effect %***						
	Co^{2+}	***Cu^{2+}***	***Mg^{2+}***	***Ni^{2+}***	***Cd^{2+}***	***Mn^{2+}***	***Zn^{2+}***
4	+7.92	+ 9.57	+5.29	+1.52	+17.3	-15.62	-16.53
16	+11.54	+19.65	+23.14	+8.3	+15.56	-23.32	-27.273

(B)

Negative ions ppm	***Effect %***							
	Cl^-	***I^-***	***Br^-***	***$Cr_2O_7^{=}$***	***$C_2O_4^{=}$***	***IO_3^-***	***$S_2O_3^{=}$***	***NO_3^-***
4	-11.5	+12.1	-12.31	-71.9	-22.3	-41.98	+44.8	+19.54
16	-43.7	+6.4	-25.62	-112	-2.48	-19.5	+47.19	+21.33

Table (3-14) the manganese ions (Mn^{2+}) decreased the absorbance intensity of V(IV)ion; and as shown in the following equations:-

$$5\times[VO^{2+} + 2H^{+} + e^{-} \rightleftharpoons V^{3+} + H_2O\ ] \quad \text{--------(1)} \quad E= 0.34V$$
$$MnO_4^{-} + 8H^{+} + 5e^{-} \rightleftharpoons Mn^{2+} + 4H_2O \quad \text{--------(2)} \quad E=+1.5V$$

$$5VO^{2+} + 10H^{+} + 5e^{-} \rightleftharpoons 5V^{3+} + 5H_2O \quad \text{--------(1)} \quad E= 0.34V$$
$$\mp MnO_4^{-} \mp 8H^{+} \mp 5e^{-} \rightleftharpoons \mp Mn^{2+} \mp 4H_2O \quad \text{--------(2)} \quad E= \mp 1.5V$$

$$Mn^{2+} + 5VO^{2+} + 2H^{+} \rightleftharpoons MnO_4^{-} + 5V^{3+} + H_2O \quad \text{-------(3)} \quad E^{\circ}_{cell}= -1.16V$$

The permanganate ion (MnO_4^{-}), Mn (VII) behaved as a strong oxidizing agent; (MnO_4^{-}) reduced the V (IV) to V (III) and gave a low response for the absorption intensity. This reaction was not-preferred thermodynamically because the positive value for ΔG° (+133.9 Kcal) and negative value of E°_{cell} (-1.16 V). The (VO^{2+}) may also be contributed to converting the Mn^{2+} to a lower oxidation state not only on Mn (VII). This resulted for the consumption of (VO^{2+}).

The interferences of Cd^{2+} ions with V (IV) increased the percentage effect; the ΔG (-34.17 Kcal) and E°_{cell} (+0.74 V); this means that the reaction was exothermic and spontaneous; thus, it was preferred thermodynamically according to the following equations: -

$$2\times[\ VO^{2+} + 2H^{+} + e^{-} \rightleftharpoons V^{3+} + H_2O\ ] \quad \text{--------(1)} \quad E= 0.34V$$
$$Cd^{2+} + 2e^{-} \rightleftharpoons Cd \quad \text{--------(2)} \quad E= -0.4V$$

$$2VO^{2+} + 4H^{+} + 2e^{-} \rightleftharpoons 2V^{3+} + 2H_2O \quad \text{--------(1)} \quad E= 0.34V$$
$$\mp Cd^{2+} \mp 2e^{-} \rightleftharpoons \mp Cd \quad \text{--------(2)} \quad E= \pm 0.4V$$

$$Cd + 2VO^{2+} + 4H^{+} \rightleftharpoons Cd^{2+} + 2V^{3+} + 2H_2O \quad \text{--------(3)} \quad E^{\circ}_{cell}= +0.74V$$

The interference of bromide (Br^-) ions with vanadium (IV) ions also decreased the absorbance intensity of V(IV) ions, this was explained by the following dynamic equations:-

$$2\times[VO^{2+} + 2H^+ + e^- \rightleftharpoons V^{3+} + H_2O] \quad \text{--------(1)} \quad E= 0.34V$$
$$Br_2 + 2e^- \rightleftharpoons 2Br^- \quad \text{--------(2)} \quad E= +1.07V$$
$$2VO^{2+} + 4H^+ + 2e^- \rightleftharpoons V^{3+} + H_2O \quad \text{--------(1)} \quad E= 0.34V$$
$$\mp Br_2 \mp 2e^- \rightleftharpoons \mp 2Br^- \quad \text{--------(2)} \quad E= \mp 1.07V$$
$$2Br^- + 2VO^{2+} + 4H^+ \rightleftharpoons Br_2 + 2V^{3+} + 2H_2O \quad \text{--------(3)} \quad E^\circ_{cell}= - 0.73V$$

What is noticed in equation (3) is that, the reaction was not-preferred thermodynamically because of the negative value of E°_{cell}, which means that the vanadium ions were able to oxidized Br^- and liberate Br_2. The reaction was non-spontaneous because of the positive value of the ΔG° (+33.71 Kcal).

The interference of magnesium (Mg^{2+}) ions with vanadyl ions increased the percentage effect, this was explained by the following dynamic equations:-

$$2\times[VO^{2+} + 2H^+ + e^- \rightleftharpoons V^{3+} + H_2O\ ] \quad \text{--------(1)} \quad E= 0.34V$$
$$Mg^{2+} + 2e^- \rightleftharpoons Mg \quad \text{--------(2)} \quad E= -2.34V$$
$$2VO^{2+} + 4H^+ + 2e^- \rightleftharpoons 2V^{3+} + 2H_2O \quad \text{--------(1)} \quad E= 0.34V$$
$$\mp Mg^{2+} \mp 2e^- \rightleftharpoons \mp Mg \quad \text{--------(2)} \quad E= \pm 2.34V$$
$$Mg + 2VO^{2+} + 4H^+ \rightleftharpoons Mg^{2+} + 2V^{3+} + 2H_2O \quad \text{--------(3)} \quad E^\circ_{cell}= +2.68V$$

What is noticed in equation (3), the reaction was preferred thermodynamically because of the positive value of E°_{cell}. The reaction is spontaneous because of the negative value of the ΔG° (-123.76 Kcal), but in the low concentration of interferences, the ions gave a high positive value; through the observation of the reaction equation of magnesium, the

ions may be remained in solution and than they increased the percentage effect.

3-C-2. Studying the possibility of removing the interferences ions:-

From the previous studies, we knew that the interfering ions were able to increase or decrease the absorption intensity of the metal ions. So these effects should be removed to obtain a result with a high accuracy for determination of chromium and vanadium ions. This is the aim of the work. The best method used to remove the interferences ions influence was ***ion exchange*** method.

3-C-2-1. Ion Exchange resin configuration

The resin was prepared by washing it with distilled water to remove the dust of the resin. The cation resin (Amberlit-IRA-120) was treated with 1M from hydrochloric acid, while anion resin (Amberlite-IRA-400) was treated with 1M from sodium hydroxide, then washed with distilled water for several times until giving a negative test for blue litmus paper for cation and vice versa for anion.

A glass wool was taken and placed within the column using a glass rod and then the resin was put above the wool, then an amount of distilled water was added to remove the bubbles in the column.

3-C-2-2. Using the cationic exchanger column

After observations, of the positive ions interferences for Cr (VI) and V (IV) ions are shown through table (3-13) and (3-14).

The cationic exchanger was used to remove some of the positive ions effect and to measure the percentage of interferences effect before and after the separation of Cr(VI) ions which are illustrated in table (3-15), and the column can be used with the same efficiency by allowing to pass

the hydrochloric acid into the column and then the distilled water was added for several times until giving a negative test for blue litmus paper.

Table (3-15): The percentage of interference effect using the cationic exchanger column for Cr(VI)ions.

The percentage of interference effect before and after separation of Cr(VI) ions			
Positive ions interferences	***Concentration of ions interferences with 4ppm of metals ions***	***Percentage of interferences effect***	
		Before separation	***After separation***
Cu^{2+}	***4ppm***	*+12.7*	*+3.45*
Mg^{2+}	***4ppm***	*+ 8.85*	*+2.26*
Ni^{2+}	***4ppm***	*- 29.2*	*-5.84*

According to the previous studies [159] it was found that vanadium V(IV) ion should an exceptional behavior, vanadyl ion carries a positive charge in the acidic media at (pH=1-6) of formula (VO^{2+}) and carries a negative charge in a strong alkaline media of formula $VO(OH)_3^-$ and $(VO_2)(OH)_5^-$ at (pH=8-12), thus vanadium has an ***Amphoteric*** behavior.

According to the above when removing the positive ions interferences from V(IV), the medium should be alkaline in order to ensure the existence of vanadium in the negative form [($VO(OH)_3^-$) and (($(VO_2)(OH)_5^-$)], but its difficult to remove these ions because vanadium precipitate in the high alkaline media. worked researcher [159] tried to dissolve this precipitate using (H_2SO_4); but another problem occurred, the V(IV) in acidic media carried a positive charge of formula (VO^{2+}); to overcome this problem we should change the ion exchanger from metallic to non-metallic, that is important because the aim of the experiment is to remove the positive ions interferences.

3-C-2-3. Using the anionic exchanger column

After observing the negative ions interference in table (3-13) and (3-14), the difficulty of removing the negative ions from the dichromate [$Cr_2O_7^{=}$] is noticed, thus, it should be converted from dichromate ions into chromate ions in basic media, then reduced chromate ion Cr (VI) to Cr (III) by ethanol with heating [(114)] and then the passing through the negative ion exchange column was allowed to take the interferences ions under study and to leave Cr (III) ions measured by spectrophotometry.

Table (3-15) shows the percentage of interference effect before and after the separation of Cr(VI) ions. We can deduce the possibility of using ion exchange column to remove the negative ions interference in appreciation and the column could be used with the same efficiency by allowing the sodium hydroxide to pass on column and then adding distilled water for several times until giving a negative test for blue litmus paper blue.

Table (3-16): The percentage of interference effect using the anionic exchanger column for Cr(VI) ions.

The percentage of interferences before and after separation for Cr(VI) ions			
Negative ions interferences	***Concentration of ions interferences with 4ppm of metals ions***	***Percentage of interferences effect***	
		Before separation	***After separation***
I^-	***4ppm***	*+19.44*	*+9.54*
$S_2O_3^{=}$	***4ppm***	*- 38.7*	*- 6.61*
NO_3^-	***4ppm***	*-50.4*	*-17.8*

To see ***Amphoteric*** behavior for vanadium [(159)], and to remove the negative ion interferences for V(IV), acidic media 1M H_2SO_4 was used at (pH=1-6) to ensure the vanadium ions as positive formula of (VO^{2+}). Than the negative ion exchange column was passed through to replace the

negative ions leaving vanadium ions measured by spectrophotometry which are illustrated in table (3-17)

Table (3-17): The percentage of interference effect using the anionic exchanger column for V(IV) ions .

The percentage of interferences before and after separation for V(IV) ions			
Negative ions interferences	***Concentration of ions interferences with 4ppm of metals ions***	***Percentage of interferences effect***	
		Before separation	***After separation***
I^-	***4ppm***	*+12.1*	*+5.81*
$S_2O_3^=$	***4ppm***	*+44.8*	*+14.5*
NO_3^-	***4ppm***	*+19.54*	*+ 8.33*

3-D. Applications:-

Chromium and Vanadium are essential trace minerals in the human body, they participate actively in carbohydrate metabolism, mainly co-acting with insulin, chromium and vanadium was determined in this work. Chromium was determined in biological samples (blood and urine); and also vanadium was determined in some plants and foods samples (cereal, mushroom and strawberry).

3-D-1. Determination of chromium (VI) ion in the biological samples:-

3-D-1-1. Determination of chromium (VI) ion in the urine sample

Chromium ion was determined in urine sample after treatment (2-6) The absorption was measured for the urine sample after treatment and after adding (0, Z, 2Z, 3Z) $mg.ml^{-1}$ of Cr (VI) to (5ml) of urine sample in (25ml) volumetric flask.

Figure (3-43) and (3-44) showed the relationship between chromium (VI) ions added to the urine samples against the absorbance, the intercept point (C) represented the amount of chromium ion.

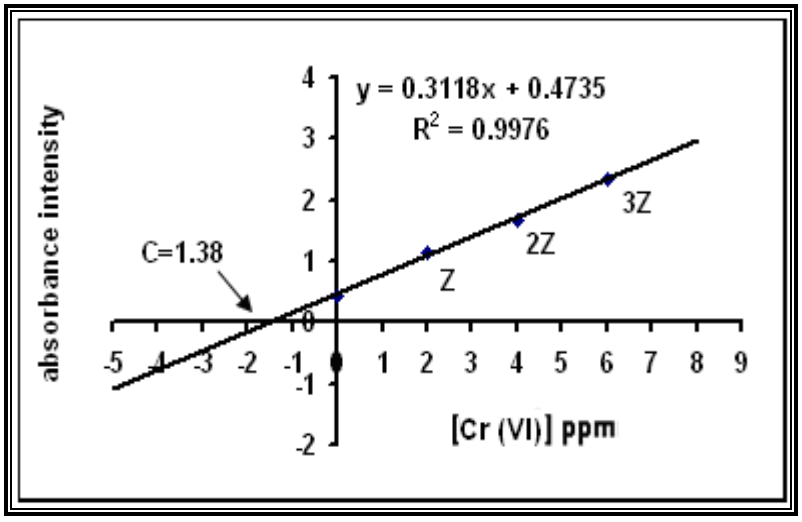


Figure (3-43): Standard addition curve for the determination of Chromium in urine sample (1) through the relationship between the amount of chromium added and the amount of absorbance intensity.

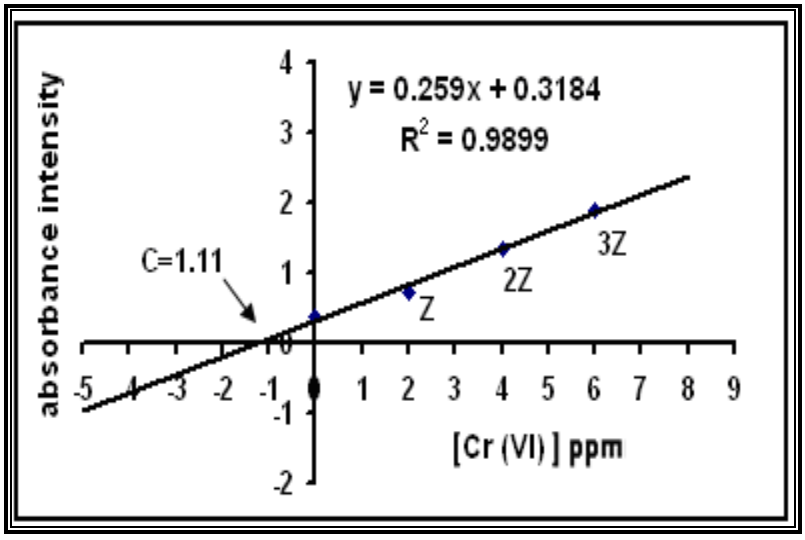


Figure (3-44): Standard addition curve for the determination of chromium in urine sample (2) through the relationship between the amount of chromium added and the amount of absorbance intensity.

Recovery for total amount of chromium and recovery for the amount of chromium in urine only (from calibration curve) was calculated and the quantity of Cr found in urine sample using spectrophotometric method (2-5-1) as shown in table (3-18).

Table (3-18): ***Spectrophotometric determination of Cr (VI) ion in urine samples.***

The presence of Cr in different urine samples	***The quantity of Cr found in urine sample only (practical) mg.ml^{-1}*** v	***The amount of standard chromium added to the urine sample (theoretical) mg.ml^{-1}*** y	***The quantity of Cr found (practical) [in urine sample + quantity of Cr added (theoretical)]*** x_1	***The quantity of total Cr (urine sample + the amount of Cr added) (theoretical)*** x_2	***Recovery for the total amount of chromium*** $\frac{x_1}{x_2} \times 100$	***The quantity of Cr found in urine sample mg.ml^{-1}*** $(x_1 - y)$	***Recovery for the Cr found in urine sample*** $\frac{v}{x_1 - y} \times 100$
(1) exhibition	*0.874*	***Z:*** *1.748* ***2Z:*** *3.496* ***3Z:*** *5.244*	***Z:*** *2.621* ***2Z:*** *4.367* ***3Z:*** *6.111*	*2.622* *4.37* *6.118*	*99.96* *100.93* *99.885*	*0.873* *0.871* *0.867*	*100.11* *100.34* *100.81*
(2) non-exhibition	0.685	***Z:*** *1.37* ***2Z:*** *2.74* ***3Z:*** *4.11*	***Z:*** *2.052* ***2Z:*** *3.418* ***3Z:*** *4.792*	*2.055* *3.425* *4.795*	*99.85* *99.796* *99.94*	*0.682* *0.682* *0.682*	*100.44* *101.03* *100.44*

3-D-1-2.Determination of chromium (VI) ions in blood sample: -

Chromium ion was determined in the exhibition and non-exhibition blood samples after treatment (2-6).The absorption was measured for blood sample after treatment and adding of (0, Z, 2Z, 3Z) $mg.ml^{-1}$ of chromium (VI) ion to 5ml of blood samples in 25ml volumetric flask.

Figure (3-45) and (3-46) show the relationship between chromium (VI) ions added to the blood samples against the absorbance. The intercept point (C) represented the amount of chromium ion.

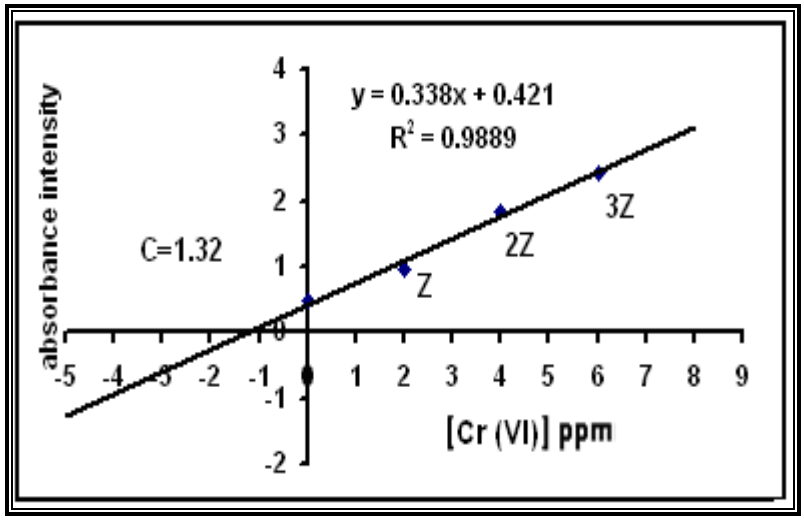


Figure (3-45): Standard addition curve for the determination of chromium in <u>blood sample (1)</u> exhibition through the relationship between the amount of chromium added and the amount of absorbance intensity.

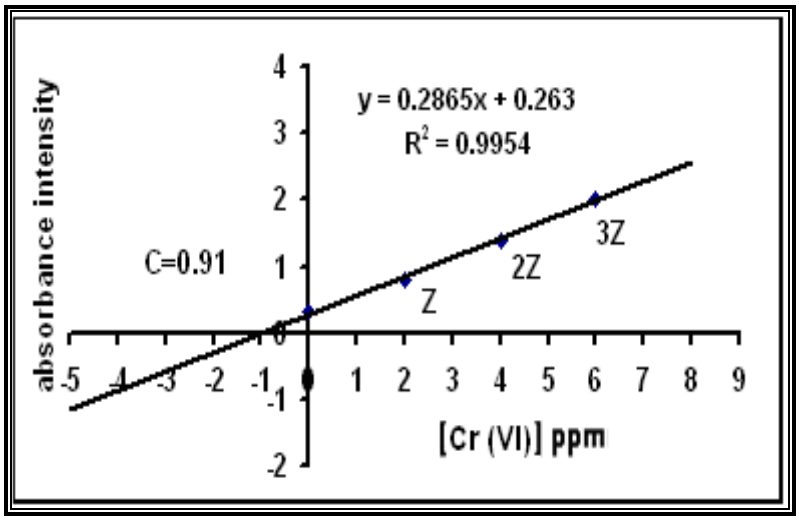


Figure (3-46): Standard addition curve for the determination of chromium in blood sample (2) non-exhibition through the relationship between the amount of chromium added and the amount of absorbance intensity.

Recovery for total amount of chromium and recovery for the amount of chromium in blood only (from calibration curve) was calculated and the quantity of Cr found in blood sample using spectrophotometric method (2-5-1) as shown in table (3-19).

Table (3-19): ***Spectrophotometric determination of Cr (VI) ion in blood samples.***

The presence of Cr in different blood samples	***The quantity of Cr found in blood sample only (practical) mg.ml^{-1}*** v	***The amount of standard chromium added to the blood sample (theoretical) mg.ml^{-1}*** y	***The quantity of Cr found (practical) [in blood sample + quantity of Cr added (theoretical)]*** x_1	***The quantity of total Cr (blood sample + the amount of Cr added) (theoretical)*** x_2	***Recovery for the total amount of chromium*** $\frac{x_1}{x_2} \times 100$	***The quantity of Cr found in blood sample mg.ml^{-1}*** $(x_1 - y)$	***Recovery for the Cr found in blood sample*** $\frac{v}{x_1 - y} \times 100$
(1) exhibition	*0.902*	***Z:*** *1.804*	***Z:*** *2.707*	*2.708*	*99.96*	*0.903*	*99.98*
		2Z: *3.608*	***2Z:*** *4.520*	*4.510*	*100.22*	*0.912*	*98.90*
		3Z: *5.412*	***3Z:*** *6.313*	*6.314*	*99.98*	*0.901*	*100.11*
(2) non-exhibition	0.572	***Z:*** *1.144*	***Z:*** *1.715*	*1.716*	*99.94*	*0.571*	*100.18*
		2Z: *2.288*	***2Z:*** *2.863*	*2.860*	*100.10*	*0.575*	*99.48*
		3Z: *3.432*	***3Z:*** *4.003*	*4.004*	*99.98*	*0.571*	*100.18*

3-D-2. Determination of vanadium (IV) ions in some plants and foods:-

Vanadium ion was determined in some plants and foods after treatment (2-6), the absorption was measured of the samples after treatment and after adding (0, Z, 2Z, 3Z) $mg.ml^{-1}$ of vanadium ion to 5ml samples in 25ml volumetric flask. Figures (3-47), (3-48) and (3-49) show the relationship between vanadium (IV) ions added to the samples against the absorbance. The intercept point (C) represents the amount of vanadium ion.

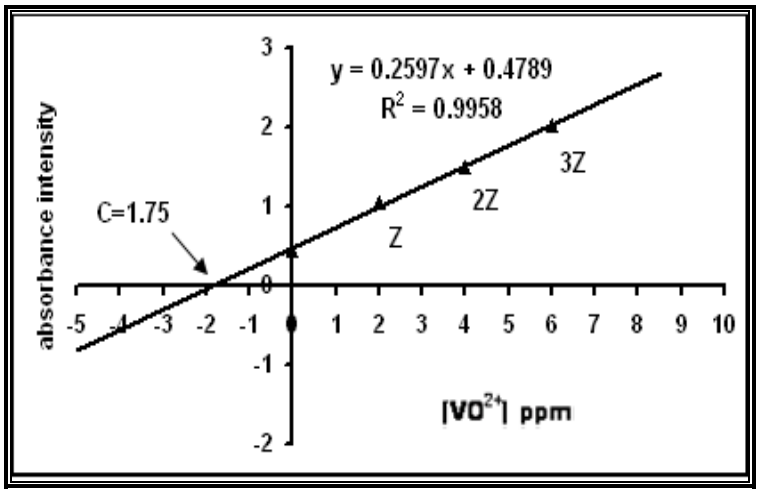


Figure (3-47): Standard addition curve for the determination of vanadium ion in mushrooms sample (1) through the relationship between the amount of vanadium added and the amount of absorbance intensity.

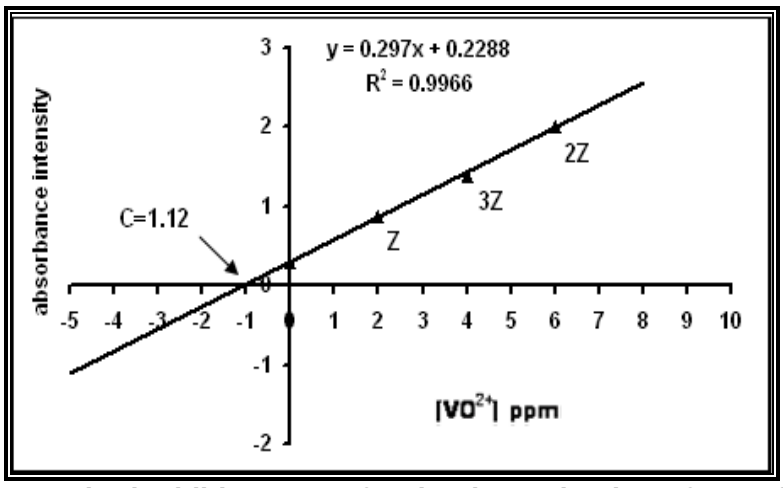


Figure (3-48): Standard addition curve for the determination of vanadium ion in cereal sample (2) through the relationship between the amount of vanadium added and the amount of absorbance intensity.

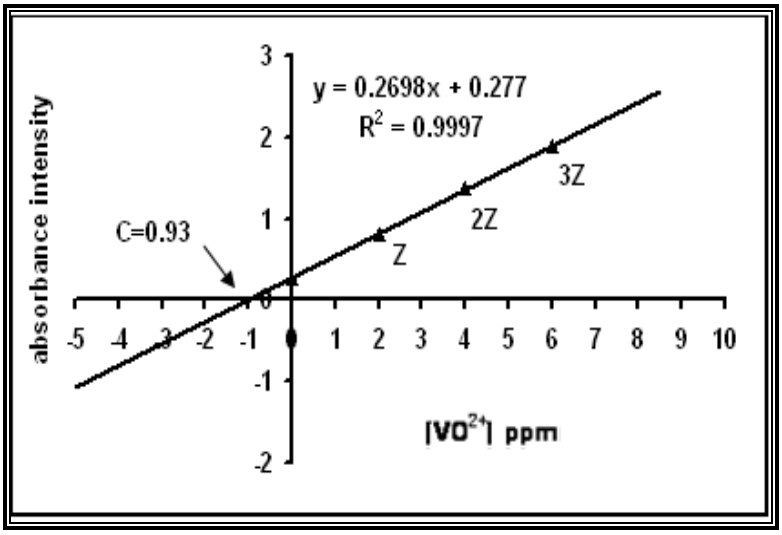


Figure (3-49): Standard addition curve for the determination of vanadium ion in strawberry sample (3) through the relationship between the amount of vanadium added and the amount of absorbance intensity.

Recovery for total amount of Vanadium and recovery for the amount of vanadium in foods only (from calibration curve) was calculated and the quantity of V found in foods samples using spectrophotometric method (2-5-3) as shown in table (3-20).

***Table (3-20)*: Spectrophotometric determination of V (IV) ion in foods samples.**

The presence of V in foods samples	Recoded value µg.kg^{-}	The quantity of V found in food samples only (practical) mg.ml^{-1} v	The amount of standard vanadium added to the food samples (theoretical) mg.ml^{-1} y	The quantity of V found (practical) [in food samples + quantity of V added (theoretical)] x_1	The quantity of total V (food samples + the amount of V added) (theoretical) x_2	Recovery for the total amount of vanadium $\frac{x_1}{x_2} \times 100$	The quantity of V found in food samples mg.ml^{1} $(x_1 - y)$	Recovery for the V found in food samples $\frac{v}{x_1 - y} \times 100$
(1) mushroom samples	a*: 50-2000 (dry)	1.312	Z: 2.624	Z: 3.935	3.936	99.975	1.311	100.076
			2Z: 5.248	2Z: 6.570	6.560	100.15	1.322	99.24
			3Z: 7.872	3Z: 9.185	9.184	100.01	1.313	99.924
(2) cereal samples	b*: 31.41 (dry)	0.924	Z: 1.848	Z: 2.773	2.772	100.04	0.925	99.89
			2Z: 3.696	2Z: 4.610	4.620	99.78	0.914	101.09
			3Z: 5.544	3Z: 6.467	6.468	99.98	0.923	100.11
(3) strawberry samples	c*: 93 (dry)	0.761	Z: 1.522	Z: 2.282	2.283	99.96	0.760	100.13
			2Z: 3.044	2Z: 3.806	3.805	99.95	0.762	99.87
			3Z: 4.566	3Z: 5.325	5.327	99.96	0.759	100.26

a*=Study 1 [(160)], b*=Study 2 [(161)], c*= Study 3 [(162)]

Recommendations and Conclusion: -

In the light the present study the following conclusions were drawn:-

1. The feasibility of the UV-Vis spectroscopic study to determine the trace elements in biological samples.

2. The possibility of using thermodynamic calculations (E_{cell}, K_{eq}. and ΔG) to determine the way in which the interfering ions can affect the determination of Cr (VI) and V (IV).

3. The method was applied successfully for the determination of trace amount of Cr(III), Cr(VI), V(V) and V(IV) in biological samples and foods with no effects or it had a little interferences by ions in samples with using ion-exchange columns to overcome the interfering ions.

4. The possibility of extending the ideas and results obtained from this work to study the medical, pharmaceutical and biological samples due to their simplicity, speed, high sensitivity (low detection limit) and economy, in addition to the high accuracy since the results showed that the complex formation system was the most suitable one to determine the chromium and vanadium ions in biology and living without the need for pretreatment.

Chapter Three

Results & Discussion

Part
(A)

Spectrophotometric Study of Chromium and Vanadium Complexes of various valences

Part (B)

Calibration Curves

Part (C)

Interferences

Part (D)

Applications