IBN AL- HAITHAM J. FOR PURE & APPL. SCI VOL. 23 (3) 2010

Removal Interferences with Spectrophotometric Study for the Determination of Chromium, Vanadium and Their Application

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Abstract

The species of Cr (III), Cr (VI) in biological samples and V(IV), V(V) in foods & plants samples were determined by spectrophotometric methods. Integrated spectral studies of complexes [Cr (III, VI)-DPC], [Cr (VI)-bipy], [VO-SH], [V (V)-8-HQ] which included a study of the optimum conditions for the complexes formation by the investigation of the chemical and physical variables affecting each complex formation, the nature of complexes, the preparation of calibration curves of the complexes and treated the resulted data by modern statistical methods and study the interfering species. Interferences were removed to explain the reactions thermodynamically by determining $E°_{cell}$, K_{eq}. and ΔG values and includes a study of separating the interfering ions from chromium and vanadium ions by using ion exchange columns.

The linear ranges of determination for Cr (III), Cr (VI) and V(IV), V(V) were 0.5-8 $\mu g ml^{-1}$ with correlation coefficients of 0.9985 to 0.9995. The detection limit for Cr(III), Cr(VI), V(IV) and V(V) were found to be 20, 15, 50 and 100 $ng.ml^{-1}$, respectively. Precision was typically better than 1.5 %, based on triplicate injections. The satisfactory recovery of 98.9 % ~ 100.81 % for Cr (VI) could be obtained from blood and urine samples and of 99.24 % ~ 101.09 % for V (IV) could be obtained from foods samples. The results agreed with those obtained by spectrophotometric determination with standard addition method and with certified values of standard reference samples.

Introduction

The chemical specification of trace elements in biological and environmental samples is very important, because the effects of elements, especially trace heavy metals, on ecological and environmental systems are generally influenced by their chemical forms. Cr (III) is present as several hydroxide species, such as $CrOH^{2+}$, $Cr(OH)_2^{+}$, $Cr(OH)_3$ and $Cr(OH)_4$, $Cr_2(OH)_2^{4+}$ and $Cr_3(OH)_4^{5+}$. Cr (VI) may be present in the solutions CrO_4^{2-}, $Cr_2O_7^{2-}$, $HCrO_4^{-}$ and $HCr_2O_7^{-}$. Cr (VI) is reported to be toxic and carcinogenic to human even at relatively low concentration level [1]. Chromium is an essential nutrient required for normal glucose and lipid metabolism as it enhances the effect of insulin [2]. Insulin 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 [3,4], chromium is found in most fresh food and drinking water. Sources rich in chromium include bread, cereal, fresh vegetables, meats, spices, fish, brewers, yeast and beer [5].

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 abundance and 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 [6,7]. Vanadium is essentially required as a beneficial element that helps in carbohydrate metabolism prevention of some heart diseases [8]. 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. It is also useful as a supplement for type II diabetics, resulting in modest reductions of blood sugar and hepatic (liver) insulin resistance [9]. Vanadium is found in very small amounts in a wide variety of foods, including many cereals, fishes, fresh fruits and vegetables which contain this element more than 40 mg per gram of food. Foods rich in vanadium include mushrooms; black pepper, parsley, shellfish and dill seed [10], 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 carcinogenetic. A number of methods for the differential determination of chromium and vanadium by AAS [11-14], ion exchange [15-17], ICP-AES [18,19] and FIA technique [20,21] coupled to other method have been described. The spectrophotometric methods [22-28] of different species of Cr and V have been successfully performed with high sensitivity for the determination. The main purpose of this work was to establish a simple, sensitive and reproducible method for the determination of Cr(III), Cr(VI), V(IV) and V(V) by the description of an integrated spectral study of complex [Cr (III, VI)-DPC), Cr (VI)-bipy), (VO-SH) and (V(V)-8-HQ), respectively. The proposed method has been applied to the determination of chromium in the biological samples and vanadium in plants & foods with satisfactory results.

Experimental

Apparatus

A double-beam UV–Visible spectrophotometer model (UV-1650 PC) Shimadzu/ (Japan) interfaced with computer via a shemadzu UV-probe data system program was used for the absorbance measurements and pH meter Orion expandable ion analyzer model (EA 940) equipped with a glass combination electrode was used, quartz cells, (1cm), sensitive electronic balance (satorius, BL2105), cationic exchanger (IR-120 (Na^+))and anionic exchanger (IR-400 (Cl^-)).

Reagents

Cr(VI) 100 ppm: 0.02827g of $K_2Cr_2O_7$ (BDH); Cr(III) 100 ppm: 0.07692g of $Cr(NO_3)_3.9H_2O$ (Riedel-de-Haen); (VO^{+2}) 100 ppm: 0.04966g of $VOSO_4.5H_2O$ (BDH); (VO_2^+) 100 ppm: 0.017843 g of V_2O_5 (BDH); 1,5-Diphenylcarbazide, 2.58×10^{-2} M: 0.125g/100ml acetone (Fluka A.G); 2,2'-Bipyridine, 1mM: 0.015612g/100 ml distilled water (Fluka A.G); Thioglycolic acid HS-CH_2COOH, 3mM: 5ml/50ml distilled water, 8-Hydroxylquinoline 8-HQ, (BDH) 1mM: 0.01452g/ 100 ml chloroform (Fluka A.G)**;** H_3PO_4, 1:1 (V/V): 50 ml (15.717M)/50ml distilled water; H_2O_2 2M: 60.7ml (16.47 M)/500 ml distilled water (solvay). H_2O_2 was calibrated with $KMnO_4$; NaOH 1M: 4g/100 ml distilled water; H_2SO_4 1M: 27.864 ml (17.944 M)/ 500 ml distilled water**;** HCl 1M: 8.548 ml (11.63 M)/ 100ml distilled water**;** HNO_3 1M: 4.593 ml (21.774 M)/ 100ml distilled water**;** CH_3COOH 1M: 28.74ml (17.396 M)/ 500 ml distilled water**;** CH_3COONa 1M: 8.2 g/100 ml distilled water.

Preparation of 100ml Interfering Ion (100 μgml^{-1})

Co(II):- 0.04937g of $Co(NO_3)_2.6H_2O$, Cd(II):- 0.02584g of $Cd(NO_3)_2.3H_2O$, Cu(II):- 0.03842g of $Cu(NO_3)_2.3H_2O$, Ni(II):- 0.0495g of $Ni(NO_3)_2.6H_2O$, Mg(II):- 0.1013g of $MgSO_4.7H_2O$, Mn(II):- 0.0457g of $Mn(NO_3)_2.4H_2O$, $S_2O_3^=$:- 0.02214g of $Na_2S_2O_3.5H_2O$, Br^- :- 0.01084g of LiBr, I^- :- 0.01142g of NH_4I, $C_2O_4^=$:- 0.01523g of $Na_2C_2O_4$.

Treatment of samples

*Urine samples

The urine samples were treated with 2ml of perchloric acid 60% (v/v) for the purpose of the protein sedimentation [29].

***Blood samples [28, 29]**

The blood samples were treated with 5ml of H_2O_2 and 5 ml conc. HNO_3, the solution was heated until the excess acid was expelled. After drying, added 5 ml (1:1) HCl , 5 ml HNO_3 and 20 ml D.W were added after that was filtered the solution.

***Plants and foods samples [28, 29]**

The plants and foods samples were dissolved (mushroom, cereal and strawberry) in 50ml of a mixture (HCl: HNO_3) (1:1) (v/v) with heating to complete dissolve then the solution was filtered and diluted to 250 ml in volumetric flask with distilled water.

Preparation of Metal Complexes

Chromium–1,5-Diphenylcarbazide (DPC) complex

Cr(IV) reacts with 1,5-diphenylcarbazide in acidic medium to form a red-voilet color complex which exhibits a measure band absorbance at 542 nm. A concentration range of (0.5-8) ppm of Cr(VI) has been prepared by diluting a standard solution of 25 ppm concentration which adjusts at (pH=8-8.5) in basic medium (NaOH), in volumetric flask 50 ml, 1ml of diphenylcarbazide was added with stirring to the chromium solutions followed by 2.5 ml H_3PO_4 (1:1) and then diluted to the mark by distilled water. The [Cr(VI)-DPC] complex could be formed by starting with chromium (III) ions and oxidized to Cr(VI) after adding an excess sodium hydroxide (NaOH) followed by a 5 ml of 6% hydrogen peroxide (H_2O_2) [29].

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

Chromium-2,2`-Bipyridine (bipy) Complex [29]

Cr(IV) reacts with 2,2`-bipyridine in acidic medium to form a light blue color complex which exhibits a measure band absorbance at 308nm.

A concentration range (0.5-8) ppm of Cr(VI) was prepared by dilution in 25 ml volumetric flask. An aliquot (5 ml) of this solution was transferred to separate funnel and acidified with 1ml of 1M sulfuric acid. Sufficient distilled water was added to bring the total volume to 20ml and then about 20 ml of ethyl acetate was added. The funnel and its contents were cooled at 10°C for 1/2 hour. After cooling, 1ml of a 3 % solution of hydrogen peroxide was added and also cooled at 10°C and immediately extracted by vigorously shaking the separation funnel for 30 second. After the layers being separated, the aqueous layer was discarded. The ethyl 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 by a vigorous shaking for 30 seconds. After the layers were separated, the aqueous layer was discarded and transferred the ethyl acetate layer to a 25 ml volumetric flask, and diluted to the mark with an additional ethyl acetate and measured the absorbance of sample at 308 nm buffer solution (pH=5.64).

Vanadium–Thioglycolic acid (SH) complex [30]

V(IV) reacts with thioglycolic acid in buffer solution from sodium acetate (pH=5.0-5.5) to form a very light blue color complex which exhibits a measure band absorbance at 225 nm. A concentration range of (0.5-8) ppm of V (IV) was prepared in 50 ml of volumetric flasks, 5 ml of 30 mM thioglycolic acid and 1ml of 0.15 M sodium acetate were added and the solution was adjusted at (pH=5.0-5.5), the solution was diluted to the mark by distilled water and after that was shacked, and measured the absorbance at 225 nm.

Vanadium-8-Hydroxyquinoline (8-HQ) complex [29]

V(V) reacts with 8-hydroxyquinoline in acidic medium (pH=3.5-4.5) to form a brown color complex which exhibits a measure band absorbance at 550 nm. A concentration range of (0.5-8) ppm of V(V) was prepared in 50 ml volumetric flasks, 1ml of 1M H_2SO_4 was added;

the solution was adjusted at (pH=3.5-4.5) and the solution was transferred to 100 ml separatory funnel. Then 5 ml of 1mM 8-HQ was added and immediately extracted by a vigorous shaking for 30 seconds. 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, and measured the absorbance at 550 nm.

Results and Discussion

Spectrophotometric Study of Chromium and Vanadium Complexes of Various Valences

This study includes the scanning of the spectrum of the reagents in the ultraviolet-visible region, by taking certain volumes of reagents in a measuring cell versus a blank. The comparison of the absorption spectra of [Cr(VI)-DPC], [Cr(VI)-bipy] and [VO-SH], [V(V)-8-HQ] complexes with reagents and metals as shown in figures (1), (2) respectively and figure (3) shows a comparison of the absorption spectra of the (Cr-DPC) 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.

Studying the Optimum Conditions for Complexes Formation

- **Effect of the reagents concentration**

A set of variable concentrations of reagents has been prepared to determine the optimum concentration to the highest absorption intensity. Fig. (4) Shows that the optimum concentration of DPC reagent in [Cr (III, VI)-DPC] complex was (25.8 mM), and the optimum concentration of (bipy) reagent in [Cr (VI)-bipy] complex was (0.6mM), Fig. (5) Shows that the optimum concentration of (SH) reagent in [VO-SH] complex was (3mM) and the optimum concentration of (8-HQ) reagent in [V (V)-8-HQ] complex was (1mM). The optimum concentration of reagents gave a regular increase to the signal which is appropriate for analytical purposes.

- **Effect of pH**

This effect has been studied by using a fixed concentration of both metal ions and reagent solutions, where a series of solutions have been prepared; in the first series, the complexes formation were studied at different types 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 includes 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 [Cr (III, VI)-DPC] complex was at (pH=8-8.5) in the presence of NaOH, fig. (6) shows that the maximum absorbance of the [Cr (VI)-bipy] complex was at (pH=4-4.5) in the presence of H_2SO_4 and fig. (7) shows that the maximum absorbance of the [VO-SH] complex was at (pH=5-5.5) in the presence of CH_3COONa and the maximum absorbance of the [V (V)-8-HQ] complex was at (pH=3.5-4.5) in the presence of H_2SO_4.

- **Effect of acids or base concentration**

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

Fig (8) shows that the optimum absorbance of [Cr (III, VI)-DPC] complex at the constant DPC reagent and ion concentration when 1ml of 1M NaOH solution was added and the optimum absorbance of [Cr (VI)-bipy] complex at the constant (bipy) reagent and ion concentration when 1ml of 1M H_2SO_4 was added solution, fig (9) shows that the optimum

absorbance of [VO-SH] complex at the constant (SH) reagent and ion concentration when 1ml of (0.15M) CH_3COONa solution was added and the optimum absorbance of [V (V)-8-HQ] complex at the constant (8-HQ) reagent and ion concentration when 1ml of (0.1M) H_2SO_4 solution was added.

Studying the Effect of the Physical Variable on Complexes Formation

- **Time Effect**

The absorbance was measured at different periods of time in the absence of light. It can be noticed from figure (10) that the complexes were fixed for long periods of time up to several hours through the constant absorbance of the complexes.

- **Light Effect**

The absorbance of [Cr(VI)-DPC] complex was measured at different periods of time in the presence of daylight and radiation light. The results show the absence of any influence of daylight and radiation light on the complexes stability for a period of time ranging from several minutes to several hours. As shown in figure (11).

- **Temperature Effect**

The effect of temperature on the [Cr(VI, III)-DPC], [Cr(VI)-bipy], [VO-SH] and [V(V)-8-HQ] complexes absorption as shown in figure (12). The results show that the analysis within room temperature (25-35)°C was appropriate where the [Cr-DPC], [VO-SH] and [V(V) - 8-HQ] complexes was stable and the time analysis at (10-15)°C were appropriate where the [Cr (VI)-bipy] complex was stable.

Nature of Complexes Formation

Applying the optimum conditions, which were obtained previously, the metals to reagents ratio in the [Cr (III, VI)-DPC], [Cr (VI)-bipy], [VO-SH] and [V (V)-8-HQ] complexes were obtained by following continuous variation method, where a series of solutions was prepared in which the formal concentration of the metal ions and reagents were held constant (0.5M) while varying volume ratios. The final volume was 10 ml for each solution. Fig. (13) shows the plot of the absorbance versus mole fraction of the reactants, (A) shows the Cr (III, VI) / DPC ration appeared to be 1:2 at pH=8-8.5 and λ_{max}=542 nm, (B) shows the Cr (VI) / bipy ration appeared to be 1:2 at pH=4-4.5 and λ_{max}=308 nm, (C) shows the V (IV) / SH ration appeared to be 3:2 at pH=5-5.5 and λ_{max}=225 nm and (D) shows the V (V) / 8-HQ ration appeared to be 1:2 at pH=3.5-4.5 and λ_{max}=550 nm. And fig. (14) shows the suggested structure of the complexes respectively.

Calibration Curves

A calibration curve was prepared from a series of standard solutions in the range (2-8) ppm, using the optimum conditions for the complexes formations. The absorbance measurements were made at 542 nm for the [Cr (III, VI) – DPC] complexe, 308 nm for the [Cr (VI) – bipy] complex, 225 nm for [V (IV)- SH] complex and 550 nm for the [V (V)-8-HQ] complex. Linear curves were obtained as shown in figure (15) A, B. Table (1) shows that treatment data resulted from modern statistical treatment [31-32].

Studying The Effect of Interfering Ions

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}).

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 selected 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 $C_2O_4^=$.

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

$$Cr_2O_7^= + 14H^+ + 6e^- \rightleftharpoons 7H_2O + 2Cr^{3+} \text{----(1)} \quad E=1.33V$$
$$6\times[VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O] \text{ -----(2)} \quad E= +1.00V$$

$$Cr_2O_7^= + 14H^+ + 6e^- \rightleftharpoons 7H_2O + 2Cr^{3+} \text{ ----(1)} \quad E=1.33V$$
$$\mp 6VO_2^+ \mp 12H^+ \mp 6e^- \rightleftharpoons \mp 6VO^{2+} \mp 6H_2O \text{ ----(2)} \quad E= \mp 1.00V$$

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

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 [33]:-

$$\text{Log } K = \frac{nFEcell}{2.303\,RT}$$

$$K_{eq} = 3.028\times10^{33}$$

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

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

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

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

In equation (3), the reaction was preferred thermodynamically because the value of E°_{cell} is positive and 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), ($\Delta G^\circ = -nFE^\circ_{cell}$).

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.

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

$5\times[VO^{2+} + 2H^{+} + e^{-} \rightleftharpoons V^{3+} + H_2O]$ -----(1) E= 0.34V

$MnO_4^{-} + 8H^{+} + 5e^{-} \rightleftharpoons Mn^{2+} + 4H_2O$ ----(2) E=+1.5V

$5VO^{2+} + 10H^{+} + 5e^{-} \rightleftharpoons 5V^{3+} + 5H_2O$ -----(1) E= 0.34V

$\mp MnO_4^{-} \mp 8H^{+} \mp 5e^{-} \rightleftharpoons \mp Mn^{2+} \mp 4H_2O$ -----(2) E= ∓1.5V

$Mn^{2+} + 5VO^{2+} + 2H^{+} \rightleftharpoons MnO_4^{-} + 5V^{3+} + H_2O$ ----(3) E°_{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 convert 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: -

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

$Cd^{2+} + 2e^{-} \rightleftharpoons Cd$ ------(2) E= - 0.4V

$2VO^{2+} + 4H^{+} + 2e^{-} \rightleftharpoons 2V^{3+} + 2H_2O$ ----(1) E= 0.34V

$\mp Cd^{2+} \mp 2e^{-} \rightleftharpoons \mp Cd$ -----(2) E= ±0.4V

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

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

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

$Br_2 + 2e^{-} \rightleftharpoons 2Br^{-}$ ----(2) E= +1.07V

$2VO^{2+} + 4H^{+} + 2e^{-} \rightleftharpoons V^{3+} + H_2O$ ----(1) E= 0.34V

$\mp Br_2 \mp 2e^{-} \rightleftharpoons \mp 2Br^{-}$ ----(2) E= ∓1.07V

$2Br^{-} + 2VO^{2+} + 4H^{+} \rightleftharpoons Br_2 + 2V^{3+} + 2H_2O$ ---(3) E°_{cell}= - 0.73V

What is noticed in equation (3), 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:-

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

$Mg^{2+} + 2e^{-} \rightleftharpoons Mg$ ------(2) E= -2.34V

$2VO^{2+} + 4H^{+} + 2e^{-} \rightleftharpoons 2V^{3+} + 2H_2O$ ------(1) E= 0.34V

$\mp Mg^{2+} \mp 2e^{-} \rightleftharpoons \mp Mg$ ------(2) E= ±2.34V

$Mg + 2VO^{2+} + 4H^{+} \rightleftharpoons Mg^{2+} + 2V^{3+} + 2H_2O$ ---(3) E°_{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 then they increased the percentage effect.

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 the determination of chromium and vanadium ions. The best method used to remove the interferences ions influence was **ion exchange** method which is illustrated in tables (4) and (5).

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 (2) but the negative ions were difficult to remove from the dichromate [$Cr_2O_7^{=}$] which is noticed, thus, it should be converted from dichromate ions into chromate ions in basic media, then reduce chromate ion Cr (VI) to Cr (III) by ethanol with heating [29] 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.

Vanadium ions was 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 [33]. 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.

To see **Amphoteric** behavior for vanadium [33], 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+}). Then 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).

Applications

The proposed method was applied to the quantitative determination of chromium and vanadium in biological samples (blood and urine for chromium, and plants and foods for vanadium).

Chromium and vanadium ions were determined in samples after treatment (2-4). The absorption was measured for the samples after treatment and after adding (0, Z, 2Z, 3Z) $mg.ml^{-1}$ of metal ions to (5ml) of samples in (25ml) volumetric flask. Fig. (16) and fig. (17) showed the relationship between chromium ions added to the samples (urine, blood) and fig. (18) showed the relationship between vanadium ions added to the samples (mushroom, cereal and strawberry) against the absorbance, the intercept point (C) represented the amount of metal ions. Recovery for total amount of metal ions and recovery for the amount of metal ions in sample only (from calibration curve) were calculated and the quantity of metal ions found in samples using spectrophotometric method (3-1) as shown in tables (6), (7) and (8) respectively.

Conclusions

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

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

interference by ions in samples with using ion-exchange columns to overcome the interfering ions.

- 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.

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Table (1): Outline for the results of the linear regression equation of the complexes

complexes	Slop (b) $b \mp S^*_b t$	Intersection (a) $a \mp S^*_a t$	R	R^2 %
Cr (VI) – DPC	0.32 ∓ 0.0073	0.0275 ∓ 0.0039	0.9985	99.7
Cr (III) – DPC	0.3098 ∓ 0.018	0.0448 ∓ 0.0095	0.9989	99.8
Cr (VI) – bipy	0.284 ∓ 0.0089	0.013 ∓ 0.049	0.9995	99.9
V (IV) – SH	0.327 ∓ 0.0185	0.0257 ∓ 0.0100	0.9989	99.8
V (V) – 8-HQ	0.2451 ∓ 0.013	0.0885 ∓ 0.072	0.9989	99.8

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

Table (2): 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

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
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		

Table (3): 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

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

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 (4): The percentage of interference effect before and after separation of Cr (VI) ions

Positive and negative ions interferences	Concentration of ions interferences with 4 ppm 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
I^-	4ppm	+19.44	+9.54
$S_2O_3^=$	4ppm	- 38.7	- 6.61
NO_3^-	4ppm	-50.4	-17.8

Table (5): The percentage of interferences effect before and after separation for V (IV) ions

Negative ions interferences	Concentration of ions interferences with 4 ppm 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

Table (6): 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	Z: 2.621	2.622	99.96	0.873	100.11
		2Z: 3.496	2Z: 4.367	4.37	100.93	0.871	100.34
		3Z: 5.244	3Z: 6.111	6.118	99.885	0.867	100.81
(2) non-exhibition	0.685	Z: 1.37	Z: 2.052	2.055	99.85	0.682	100.44
		2Z: 2.74	2Z: 3.418	3.425	99.796	0.682	101.03
		3Z: 4.11	3Z: 4.792	4.795	99.94	0.682	100.44

Table (7): 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

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Table (8): 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 2Z: 5.248 3Z: 7.872	Z: 3.935 2Z: 6.570 3Z: 9.185	3.936 6.560 9.184	99.975 100.15 100.01	1.311 1.322 1.313	100.076 99.24 99.924
(2) cereal samples	b*: 31.41 (dry)	0.924	Z: 1.848 2Z: 3.696 3Z: 5.544	Z: 2.773 2Z: 4.610 3Z: 6.467	2.772 4.620 6.468	100.04 99.78 99.98	0.925 0.914 0.923	99.89 101.09 100.11
(3) strawberry samples	c*: 93 (dry)	0.761	Z: 1.522 2Z: 3.044 3Z: 4.566	Z: 2.282 2Z: 3.806 3Z: 5.325	2.283 3.805 5.327	99.96 99.95 99.96	0.760 0.762 0.759	100.13 99.87 100.26

a*=Study 1 [34], b*=Study 2 [35], c*= Study 3 [36]

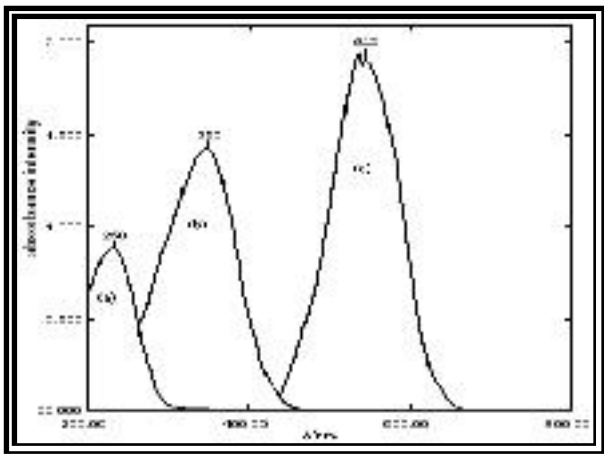

Fig. (1) A:Comparison of the absorption spectra of (a) reagent at (DPC=25.8 mM) (b) metal ion at (Cr (VI) =6ppm) and (c) complex at (Cr (VI) =6ppm, pH=8-8.5, λ_{max} =542nm, DPC=25.8mM).

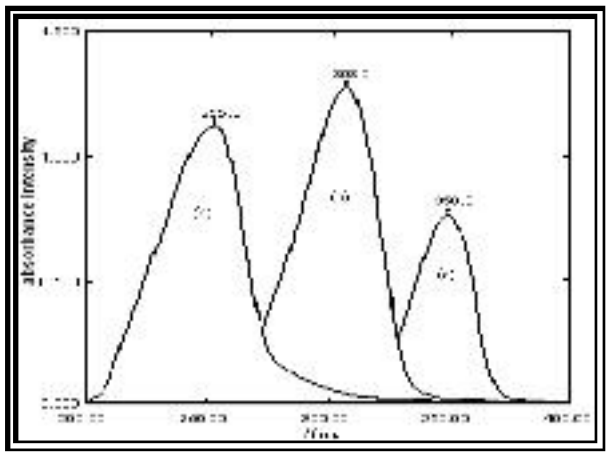

Fig. (1) B:Comparison of the absorption spectra of (a) metal ion at (Cr (VI) =8ppm) (b) reagent at (bipy=0.6mM) and (c) complex at (Cr (VI) =8ppm, pH=4-4.5, λ_{max}=308nm, bipy=0.6mM).

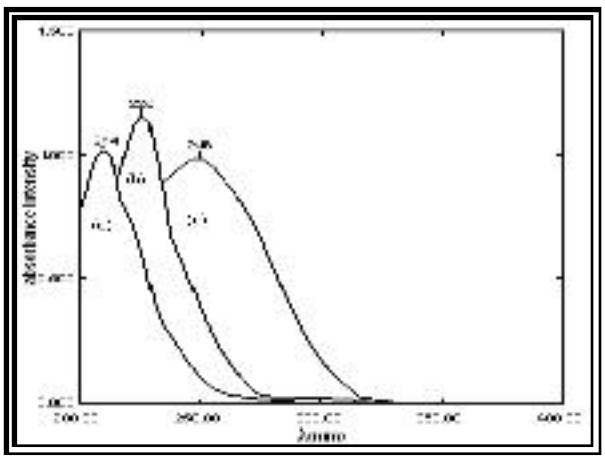

Fig. (2) A:Comparison of the absorption spectra of (a) metal ion at (V (IV) =8ppm) (b) complex at (V (IV) =8ppm, pH=5-5.5, λ_{max}=225nm, SH=3mM) and (c) reagent at (SH=3mM).

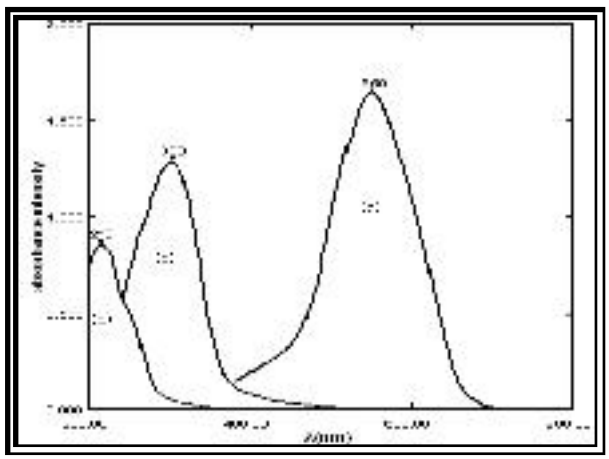

Fig. (2) B:Comparison of the absorption spectra of (a) metal ion at (V (V) =8ppm) (b) reagent at (8-HQ=1mM) and (c) complex at (V (V) =8ppm, pH=3.5-4.5, λ_{max}=550nm, 8-HQ=1mM).

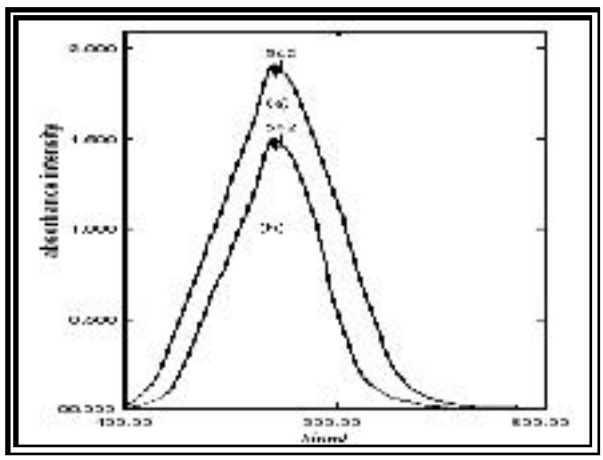

Fig. (3): Comparison of the absorption spectra of complex (a) starting with Cr(VI) at (Cr(VI)=8ppm, pH=8-8.5, λ_{max}=542nm, DPC=25.8mM) (b)starting with Cr(III) at (Cr(III)=8ppm, pH=8-8.5, λ_{max}=542nm, DPC=25.8mM)

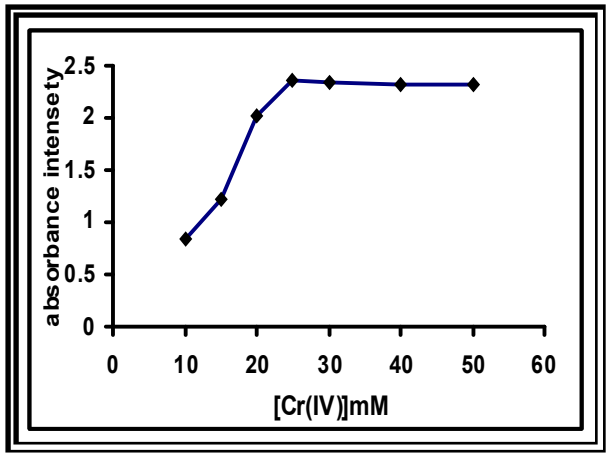

Fig. (4) A: Effect of reagent concentration on the absorbance Intensity of the complex [Cr (VI)-DPC] at (Cr (VI) =6ppm, pH=8-8.5, λ_{max} =542nm, DPC=25.8mM)

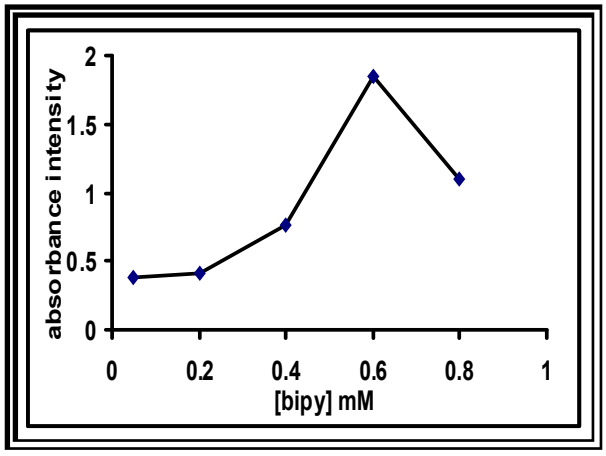

Fig. (4) B: Effect of reagent concentration on the absorbance Intensity of the complex [Cr (VI)-bipy] at (Cr (VI) =8ppm, pH=4-4.5, λ_{max}=308nm, bipy=0.6mM).

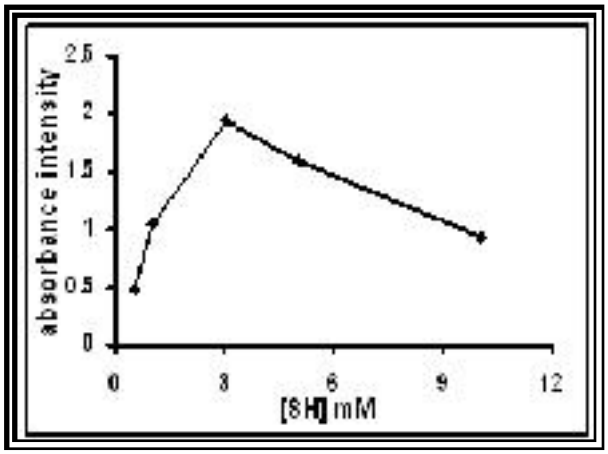

Fig. (5): A-Effect of reagent concentration on the absorbance intensity of the complex [VO-SH] at (V (IV) =8ppm, pH=5-5.5, λ_{max}=225nm, SH=3mM)

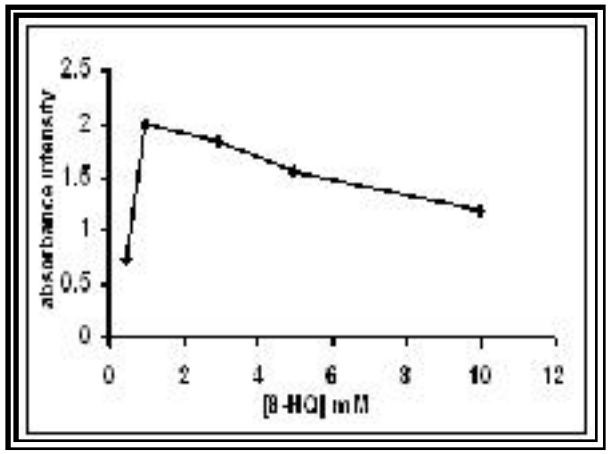

Fig. (5): B-Effect of reagent concentration on the absorbance intensity of the complex [V(V)-8-HQ] at (V(V)=8ppm,pH=3.5-4.5,λ_{max}=550nm, 8-HQ=1mM).

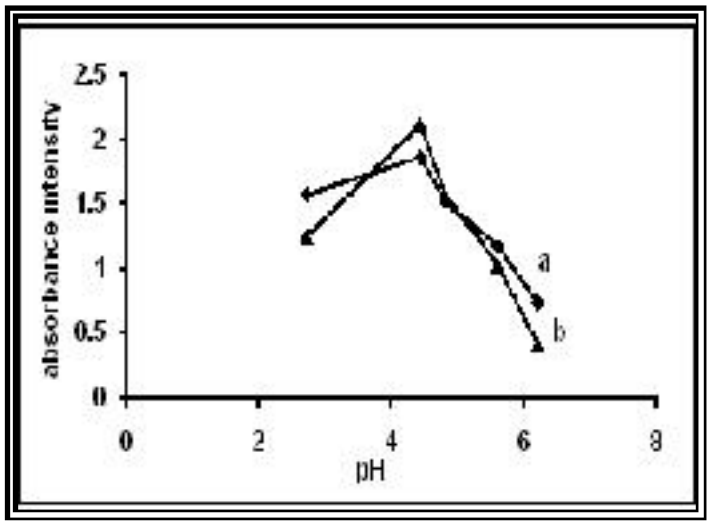

Fig. (6): Effect of pH solution on the absorbance intensity of the complex [Cr (VI)-bipy] (a) existence both Cr(VI) ion and reagent solution with H_2SO_4 at (λ_{max} =308 nm) (b) existence reagent only at (λ_{max} =350nm).

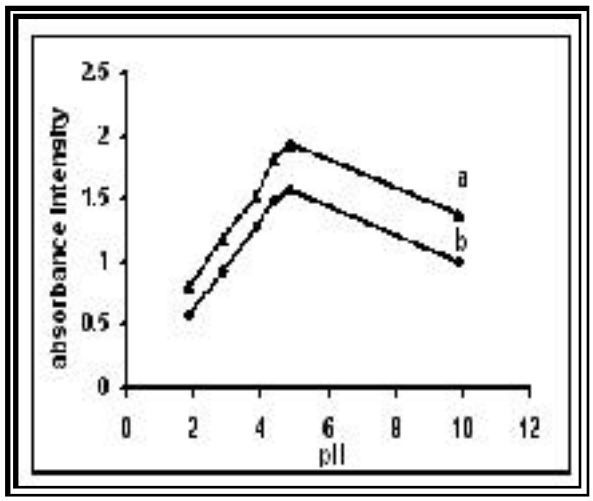

Fig. (7): A-Effect of pH solution on the absorbance intensity of the complex [VO-SH] (a) existence both V (IV) ion and reagent solution with CH_3COONa at λ_{max}=225 nm (b) existence reagent only λ_{max}=246 nm.

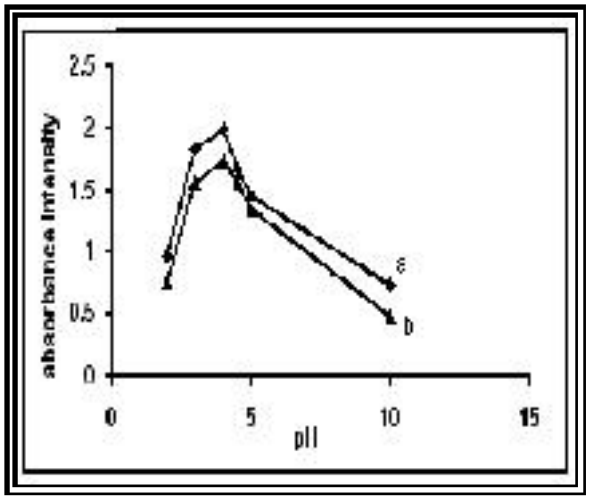

Fig. (7): B-Effect of pH solution on the absorbance intensity of the complex [V (V)–8-HQ] (a) existence both V (V) ion and reagent solution with H_2SO_4 which prepare λ_{max}=550nm (b) existence reagent only λ_{max}=300 nm.

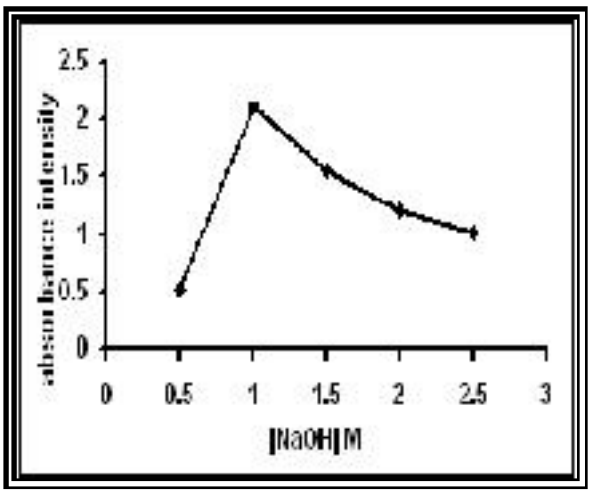

Fig. (8): A-Effect of NaOH concentration on the absorbance intensity of the complex [Cr (VI)-DPC] at (Cr (VI) =6ppm, pH=8-8.5, λ_{max} =542nm, DPC=25.8mM)

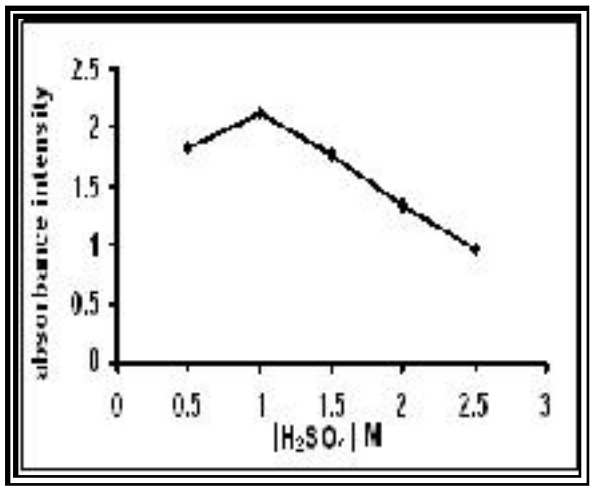

Fig. (8): B- Effect of H_2SO_4 concentration on the absorbance intensity of the complex [Cr (VI)-bipy] at (Cr (VI) =8ppm, pH=4-4.5, λ_{max}=308nm, bipy=0.6mM).

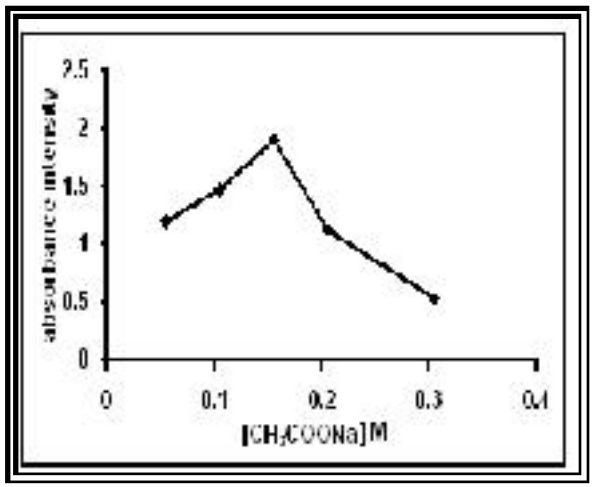

Fig. (9): A- Effect of CH_3COONa concentration on the absorbance intensity of the complex [VO-SH] at (V (IV) =8ppm, pH=5-5.5, λ_{max}=225nm, SH=3mM)

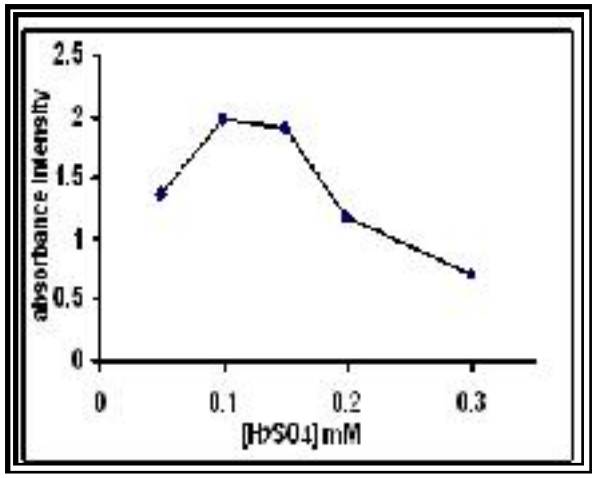

Fig. (9): B-Effect of H_2SO_4 concentration on the absorbance intensity of the complex [V(V)- 8-HQ] at (V(V) =8ppm, pH=3.5-4.5, λ_{max}=550nm, 8-HQ=1mM).

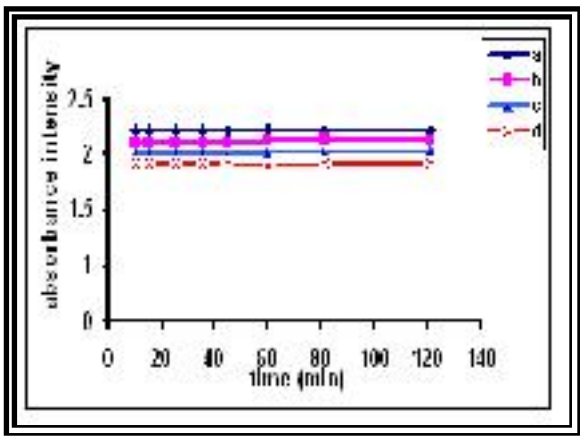

Fig. (10): Effect of time on the absorbance intensity of the complexes (a) [Cr (III, VI) - DPC] at (Cr (VI) =6ppm, pH=8-8.5, λ_{max} =542 nm, DPC=25.8mM), (b) [Cr (VI)-bipy] at (Cr (VI) =8ppm, pH=4-4.5, λ_{max}=308nm, bipy=0.6mM), (c) [VO-SH] at (V (IV) =8ppm, pH=5-5.5, λ_{max}=225nm, SH=3mM) and (d) [V (V)- 8-HQ] at (V (V) =8ppm, pH=3.5-4.5, λ_{max}=550nm, 8-HQ=1mM).

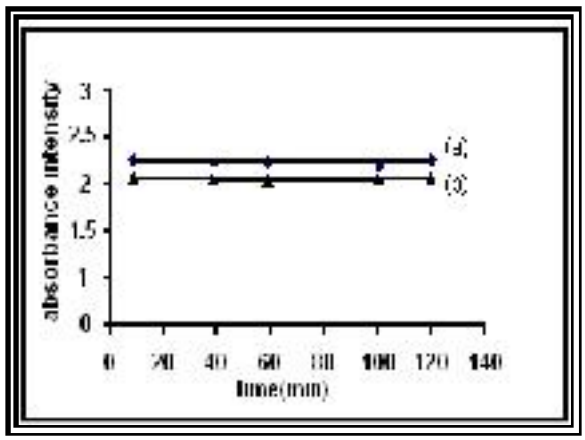

Fig. (11): Effect of light on the absorbance intensity of complex [Cr (VI)-DPC] at (Cr (VI) =6ppm, pH=8-8.5, λ_{max} =542nm, DPC=25.8mM) (a) daylight effect (b) radiation light effect.

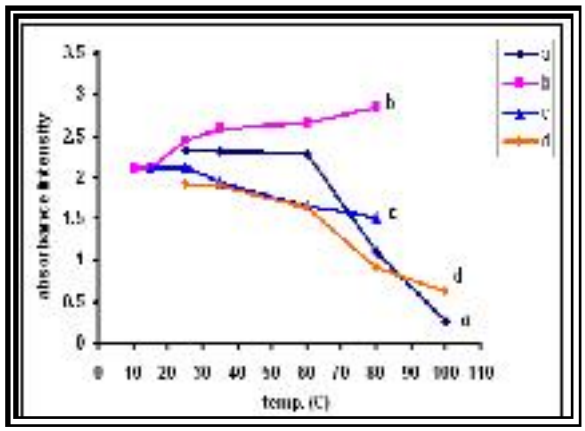

Fig. (12): Effect of temperatures on the absorption intensity of the complex (a) [Cr (VI)-DPC] at (Cr (VI) =6ppm, pH=8-8.5, λ_{max}=542nm, DPC=25.8mM), (b) [Cr (VI)-bipy] at (Cr (VI) =8ppm, pH=4-4.5, λ_{max}=308nm, bipy=0.6mM), (c) [VO-SH] at (V (IV) =8ppm, pH=5-5.5, λ_{max}=225nm, SH=3mM) and (d) [V (V) - 8-HQ] at (V (V) =8ppm, pH=3.5-4.5, λ_{max}=550nm, 8-HQ=1mM).

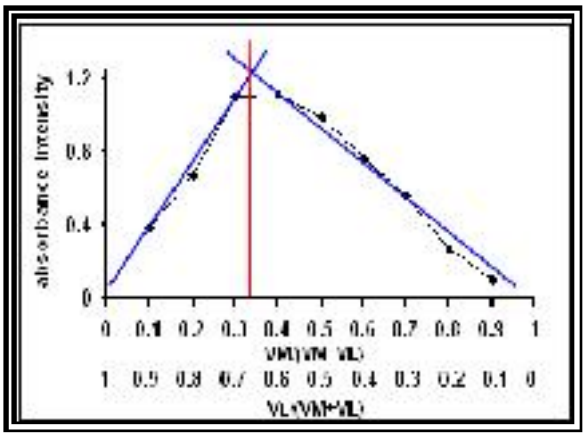

Fig (13): A- Continuous variation plot for the complex [Cr (VI)-DPC] at (Cr (VI) =0.5M, DPC=0.5M)

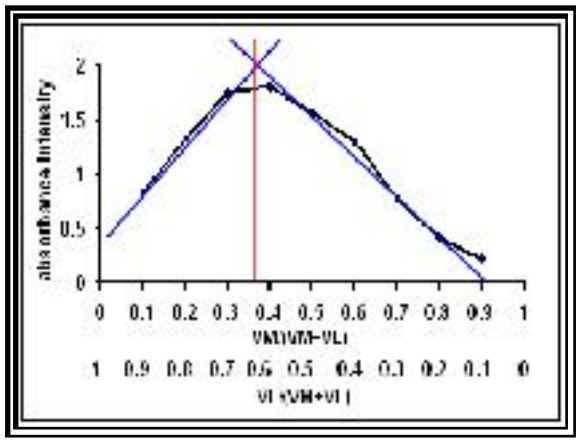

Fig (13): B- Continuous variation plot for the [Cr(VI)-bipy] at (Cr(VI)=0.5M, bipy=0.5M)

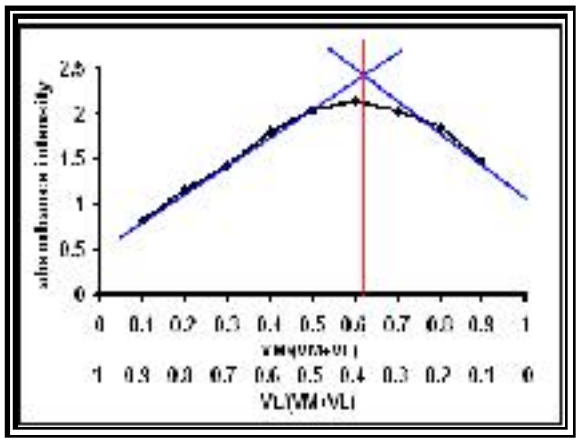

Fig. (13): C-Continuous variation method for the complex [VO-SH] at (V (IV) =0.5M, SH=0.5M)

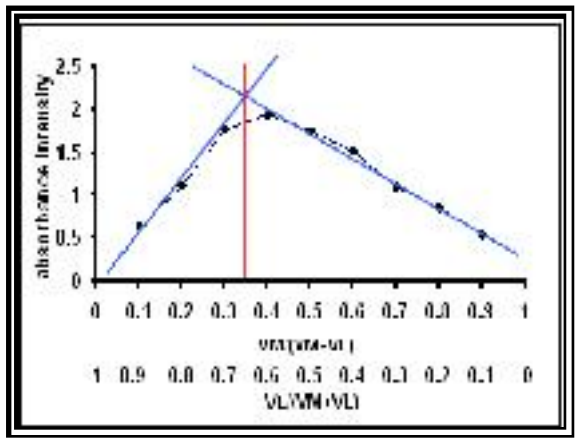

Fig. (13): D- Continuous variation plot for the complex [V(V)- 8-HQ] at (V(V)=0.5M, 8-HQ=0.5M)

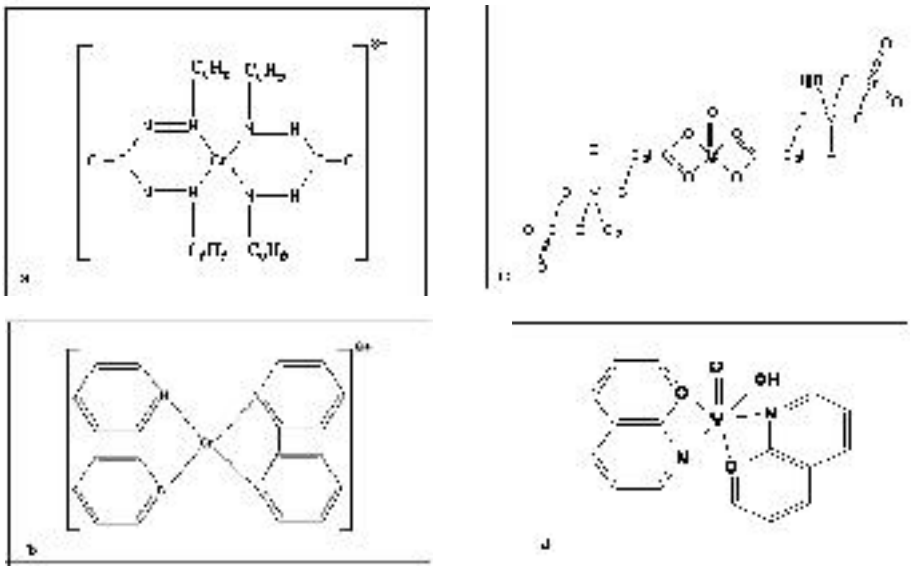

Fig. (14): The suggested structure of the complexes (a) [Chromium-1, 5-diphenylcarbazone] at 1:2 ratios, (b) [Chromium (VI)-2, 2'-bipyridine] at 1:2 ratios, (c) [VO-thioglycolic acid] at 3:2 ratios and (d) [Vanadium (V)-oxine] at 1:2 ratios

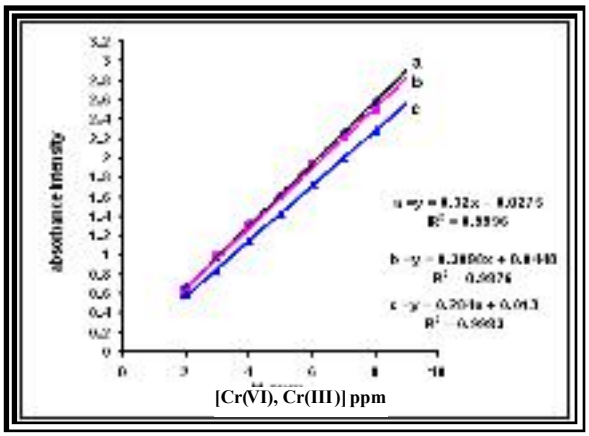

Fig. (15): A-linear calibration curve for determination of (a) Cr (VI) ion with DPC reagent, (b) [Cr (III)] ion with DPC reagent, (c) Cr (VI) ion with 2, 2'-bipyridine reagent.

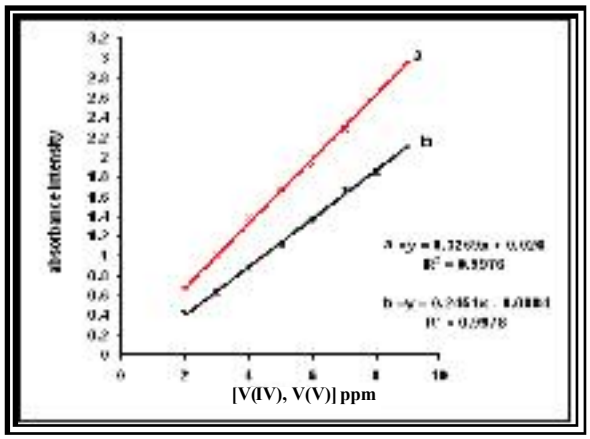

Fig. (15): B-linear calibration curve for determination of (a) V (IV) ion with thioglycolic acid reagent and (b) V (V) ion with 8-HQ reagent

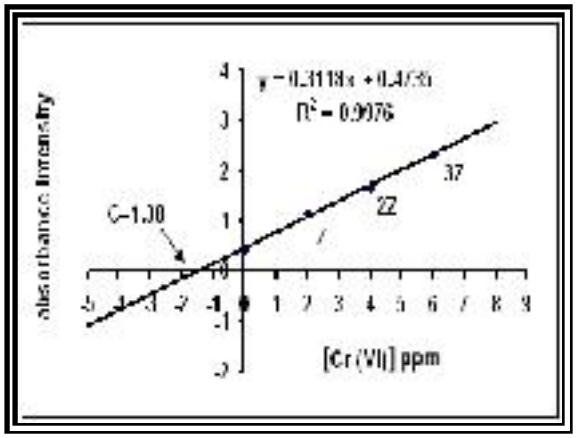

Fig. (16): A- Standard addition curve for the determination of Chromium in exhibition urine sample (1) through the relationship between the amount of chromium added and the amount of absorbance intensity.

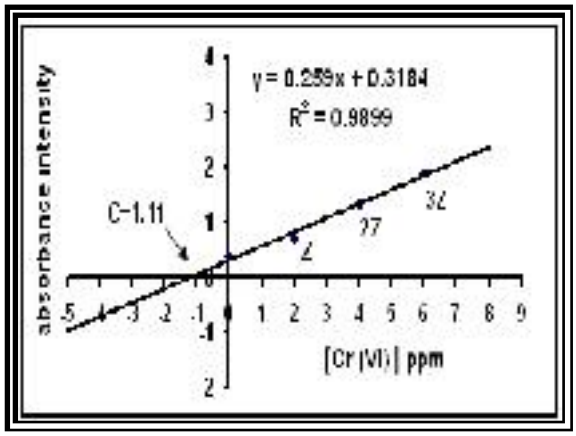

Fig. (16): B- Standard addition curve for the determination of chromium in non-exhibition urine sample (2) through the relationship between the amount of chromium added and the amountof absorbance intensity

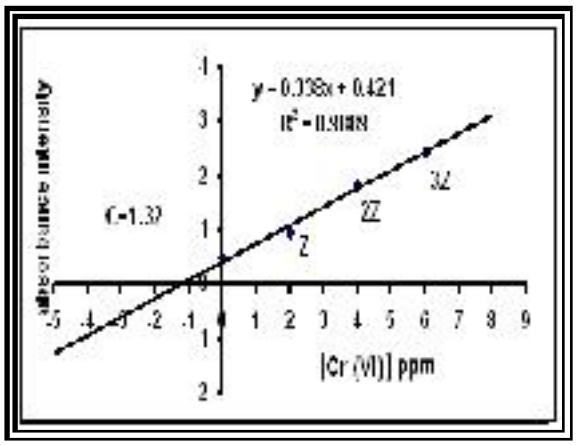

Fig. (17): A- Standard addition curve for the determination of chromium in exhibition blood sample (1) through the relationship between the amount of chromium added and the amount of absorbance intensity

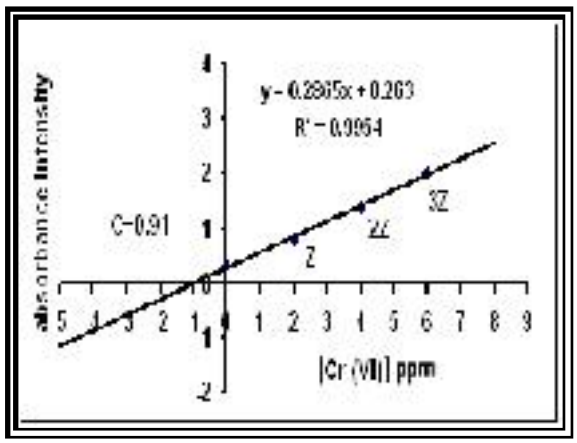

Fig. (17): B- Standard addition curve for the determination of chromium in non-exhibition blood sample (2) through the relationship between the amount of chromium added and the amount of absorbance intensity.

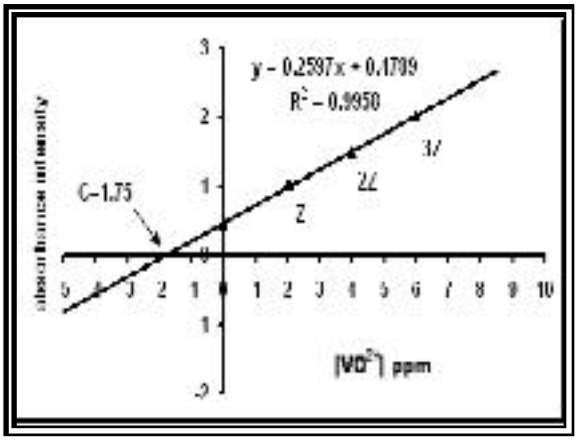

Fig. (18): A- Standard addition curve for the determination of vanadium ion in mushrooms sample (1) through the relationship between the amount of vanadium added and the amount of absorbance intensity

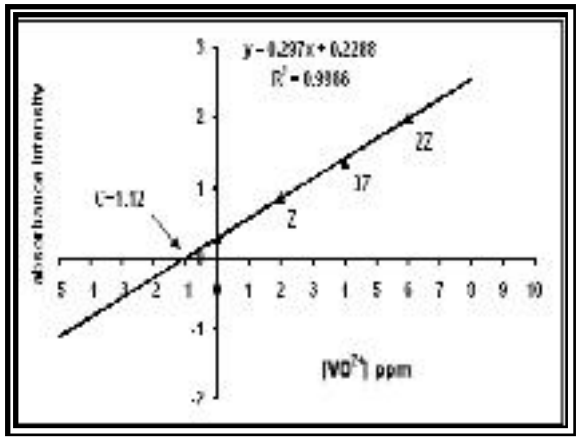

Fig. (18): B- Standard addition curve for the determination of vanadium ion in cereal sample (2) through the relationship between the amount of vanadium added and the amount of absorbance intensity.

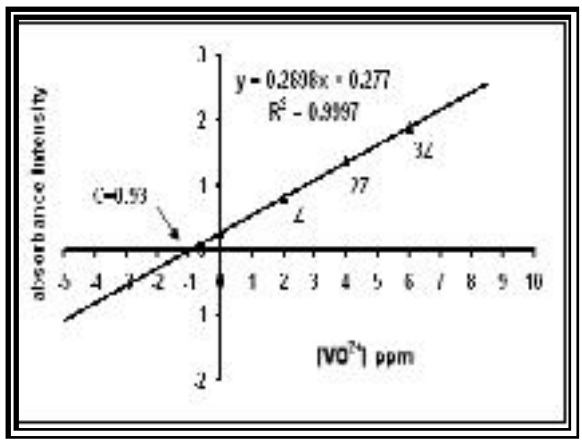

Fig. (18): C- Standard addition curve for the determination of vanadium ion in strawberry sample (3) through the relationship between the amount of vanadium added and the amount of absorbance intensity.

ازالة المتداخلات ودراسة طيفية لتقدير الكروم والفناديوم وتطبيقات

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الخلاصة

قدر الكروم الثلاثي والسداسي في النماذج الحية وتقدير الفناديوم الرباعي والخماسي في النباتات والاطعمة طيفيا عن طريق تكوين المعقدات [Cr (III, VI)-DPC], [Cr (VI)-bipy], [VO-SH], [V (V)-8-HQ] كما درست الظروف الفضلى لتكوين المعقد من حيث دراسة المتغيرات الفيزيائية والكيميائية كافة وتأثيرها في ثبوتية المعقد،و دراسة طبيعة المعقدات، وتحضير منحنيات المعايرة للمعقدات المحضرة ،واجراء المعالجات الأحصائية الحديثة للبيانات التحليلية الناتجة كما درست تأثير المتداخلات وقد فسرت ميكانيكية التفاعلات من الناحية الداينمية الحرارية من خلال حسابات $E°_{cell}$, $K_{eq.}$, ΔG كما درست امكانية ازالة هذه المتداخلات الأيونية باستخدام اعمدة التبادل الأيوني.

حضر منحني المعايرة لتقدير Cr(III), Cr(VI), V(IV), V(V) بمدى (0.5-8) مايكروغرام.مل$^{-1}$ومعامل الارتباط 0.9995 -0.9985 وقد وجد ان حد الكشف لتقدير Cr(III), Cr(VI), V(IV), V(IV) 20، 15، 50، 100 نانوغرام/مل$^{-1}$ على التوالي، وكانت نسبة الأسترداد المئوي لتقدير الكروم السداسي في انموذجات الدم والأدرار= 98.9% ~100.81% والأسترداد المئوي لتقدير الفناديوم الرباعي في النباتات والأطعمة =101.09% ~ 99.24% وقد تم الحصول على تطابق عال للنتائج التي تم الحصول عليها بالطريقة الطيفية وطريقة الأضافات القياسية.