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Spectrophotometric determination for chromium (III) and cobalt (II) with 4-(nitro phenyl azo imidazole) (NPAI) as organic reagent

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ABSTRACT

A sensitive and selective spectrophotometric method is proposed for the rapid determination of Chromium (III) and Cobalt (II) using (NPAI), as spectrophotometeric reagent. The maximum absorbance observed at 582 nm, and 556 nm for Cr(III) and Co(II) respectively. The molar absorptivity for Chromium (III) and Cobalt (II) complexes is ($1.1497x10^4$ and $1.0162x10^4$) $L.mol^{-1}.cm^{-1}$ respectively. The Mole ratio [M: L] was 1:1 for the Cr (III) complex and1:2 for Co (II) complexe. The linear range of (1-19) and (1-21) respectively along with limit of detection 0.132 and 0.12 µg mL^{-1}. Relative standard deviation for seven replication measurements (0.29% Cr and 0.27% Co),and the recovery range of (98.79) and(99) were obtained for Cr(III) and Co(II) ions ,and E_{rel}= -1.22 , -1 for Cr(III) and Co(II) respectively. The most important interference were due to Ni^{2+}, Ag^{1+}, Cu^{2+} and Hg^{2+}, suitable masking agents were used.

Keywords: Imidazole, Spectrophotometric determination of chromium (III) and Cobalt (II)

INTRODUCTION

Many organic reagents have attracted much attention as they are sensitive, chromogenic reagents in addition to being interesting complexing agents [1]. Large number of the spectrophotometric methods based on these reactions were developed and used in analytical chemistry [2].In chemical study of the imidazole shows that it is mixture of the pyridine and pyrole characteristics formulates many polarizational salts and as basic it is stronger than the pyridine. Imidazole is a ubiquitous reagent in chemical and biological systems [3].

Chromium and Cobalt are highly useful elements and used in various industrial processes and products, have resulted in an increased these elements content of environmental samples [4-6].

Chromium occurs in several chemical species and it is not biodegradable in the environment. Its species exist mainly in two different oxidation states in water, Cr (III) and Cr (VI), which have different effects on environmental poisoning, biological effects and human health. Chromium (III) is considered an essential element controlling glucose lipid and protein metabolism in mammals, while chromium (VI) is definitely highly toxic for biological systems, with mutagenic and potential carcinogenic properties [7]. The toxicity of Cr (VI) compounds derives from its ability to diffuse through cell membrane and oxidise biological molecules [8].

Most of the effects of chromium have been studied in relation to its occupational hazards. The increase in the discharge of industrial effluents and sewages is a cause of concern. The contamination of chromium in groundwater makes it improper for drinking. In view of such an environmental problem, constant monitoring and analysis of chromium becomes a necessity. In a continuation of the development of suitable methods for the determination of metals, especially in natural samples, a sensitive and selective method has been developed for the determination of chromium (III) in its pure form, natural samples, industrial effluents and alloys [9].

Cobalt metal powder is a fire hazard.Evidence indicates that minute quantities of cobalt may be detrimental to higher plant life, particularly in water and sand cultures. Cobalt toxicity is characterized by a chlorosis similar to that induced by lack of iron[10].The spectrophotometric determination of cobalt is usually preceded by a reaction with reagents such as bis (2, 4, 4-trimethyl penthyl) phosphinic acid [11], 5-(6-methoxy-2-benzothiazoleazo)-8-aminoquinoline [12], 2-amino-cyclopentene-1-dithiocarboxylicacid [13], ammonium 2-amino-1-cyclohexanedithiocarbamate [14], 2-(2-benzothiazolylazo)-2-*p*-cresol [15]. In this work a 4-(Nitro phenyl azoimidazole) (NPAI), was prepared by Azhar A. Ghali and Dhiaa Z. Mashkour [16] and used, as an analytical reagent for the micro determination of Cr(III) and Co(II). The method has been found to be simple, rapid and sensitive for the determination of these metal ions.

EXPERIMENTAL SECTION

Experimental Apparatus:

(FTIR) Spectra (4000-400cm^{-1}) in KBr disk were recorded on a SHIMADZU FTIR-8400S Fourier Transform infrared. Spectrophotometer (Japan), absorption spectra was measured on aT80 UV-Vis spectrophotometer and absorbance was measured on Apel PD -303UV-visible spectrophotometer using 1 cm quartz cells. A model WTW multi 720 pH – meter was used to adjusted and measure the pH of the solution, Melting point was measured using SMP30 Stuart, UK.

Reagents and Solutions:

All the chemicals used were of analytical reagent grade, and were used without further purification. Ethanol was purchased from (GCC, England).

-1x10^{-3}M (NPAI) standard solution was prepared by dissolving (0.054) g in 250 ml of absolute ethanol.

-Stock Cr(III) solution ;A solution of Cr(III) (1000 µg.ml^{-1})was prepared by dissolving (0.5125)g of $CrCl_3.6H_2O$ (Merck) in (100 ml) deionized water. Other standard solutions of Cr (III) were prepared by dilution of stock solution with distilled water.

-Stock Co(II) solution ;A solution of Co(II) (1000 µg.ml^{-1})was prepared by dissolving (0.4037)g of $CoCl_2.6H_2O$ (BDH) in (100 ml) deionized water. Other standard solutions of Co (II) were prepared by dilution of stock solution with distilled water.

- The pH of the medium (2-9) were adjusted with ammonium acetate (0.01 mol L^{-1})–ammonia – glacial acetic acid buffer solution.

General procedure:

Into a 10 mL calibrated flask, transfer 1.5 mL of sample solution containing less than 100 µg.ml^{-1} of Cr(II) and adjust the pH to 6.5 with ammonium acetate buffer, add 1x10^{-3}M ethanolic (NPAI) solution and diluted to the mark with deionized water. The absorbance of the resultant solution was measured after 10 min at 582 nm at 25 C° against the corresponding reagent blank prepared under identical conditions but without Chromium. The same procedure for Cobalt (II) at pH 8 and the absorbance of the result solution after 10 min at 556 nm.

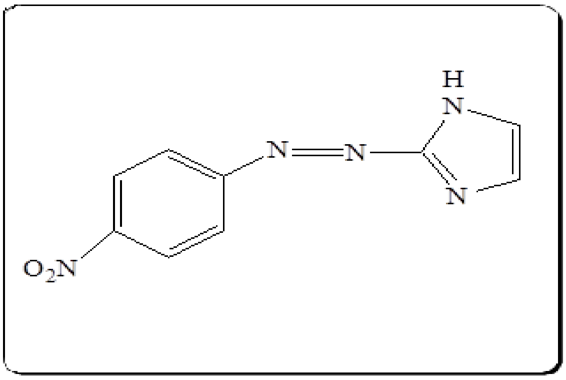


Fig.(1): Structure of the reagent (NBAI)

RESULTS AND DISCUSSION

FTIR Spectra of the Reagent (NBAI) and its complexes:

FTIR spectral data of the reagent (NBAI) and its complexes are summarized in Table (1) .The comparison between spectra of the reagent with those of the coordination complexes have revealed certain characteristic differences Azo reagent spectrum show. The wide band which has been observed at (3425) cm^{-1} in the spectrum of the free reagent was due to υ (N─H) of imidazole ring. The unchanged of this band in complexes means that the υ(N─H) group dose not participate in coordination[17].The V(C=N) of imidazole ring appear at 1589cm^{-1} in the spectrum of the reagent .This band shifts to lower frequency at(1532 and1550) cm^{-1} of Cr and Co complexs with change in shape[18]. These differences suggest alinkage of this ion with reagent.The ν (N=N) stretching vibration appears at (1342) cm^{-1} in the spectrum of the free reagent, this band appearing at (1500 and 1450) cm^{-1} in the prepared complexes spectra respectively. Both band shifted and reduced in intensity due to complexes formation [19].In the far IR spectra of complexes, there are new weak bands in the region of (400-750) cm^{-1} occurring in the spectra of complexes . These bands did not present in the spectrum of reagent.

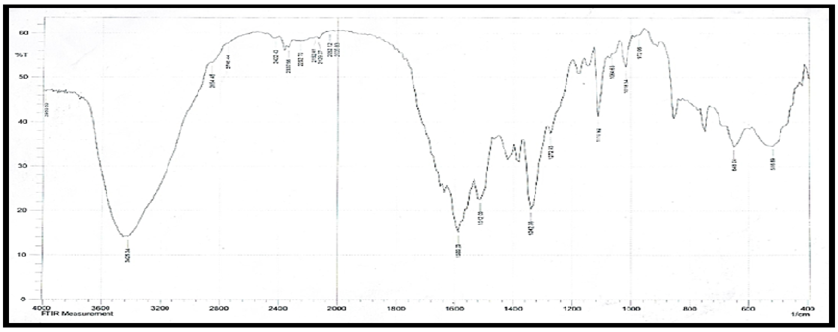
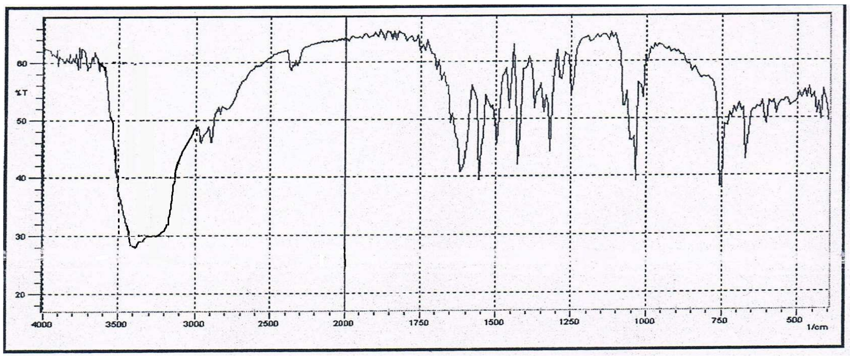


Fig (2):-FTIR Spectrum of the reagent (NBAI)



Fig(3):-FTIR Spectrum of the Cr complex

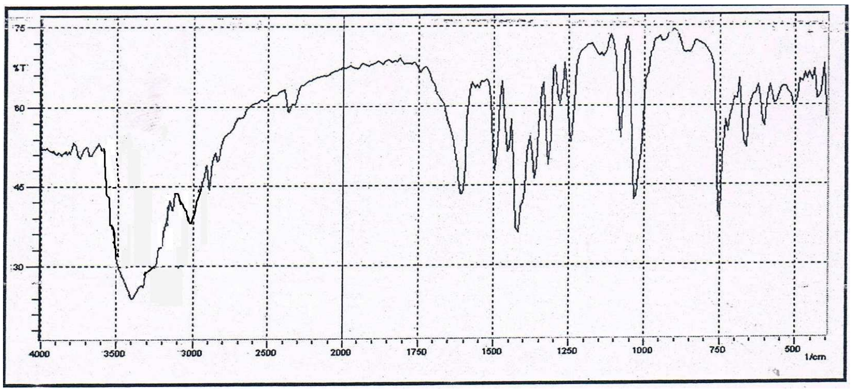


Fig (4):-FTIR Spectrum of the Co complex

Absorption spectra and characteristics of the complex:

The UV- Vis spectrum of an ethanolic solution of the reagent (NBAI) (1x10^{-3} M) showed peak (λ max) was observed at the (332 nm) due to the (π-π*) from aromatic ring through the azo group (charge transfer) was referred to the n- π* transition of intermolecular charge- transfer taken place from benzene through the azo group(-N=N-) Interaction of the metal ions Cr(III) and Co(II) with the reagent has been studied in aqueous ethanolic solution . A bathchromic shift of Cr(III) and Co(II) complexes show the absorption maxima of 582 and 556 nm referred to (charge transfer) with molar absorptivities (ε) of 1.27142×10^{-4} L.mol^{-1}.cm^{-1} and 1.27484×10^{-4} L.mol^{-1}.cm^{-1} obtained respectively while the reagent gave the absorption maxima of 332 nm as depicted in Fig. 5. The wave length different(Δ λ_{max}) is (250-224 nm) ,a great bathochromic shift in the visible region has been detected in the complex solutions spectra with respect to that of the free reagent. The high shift in the (λ_{max}) gave a good indication for complex formation.

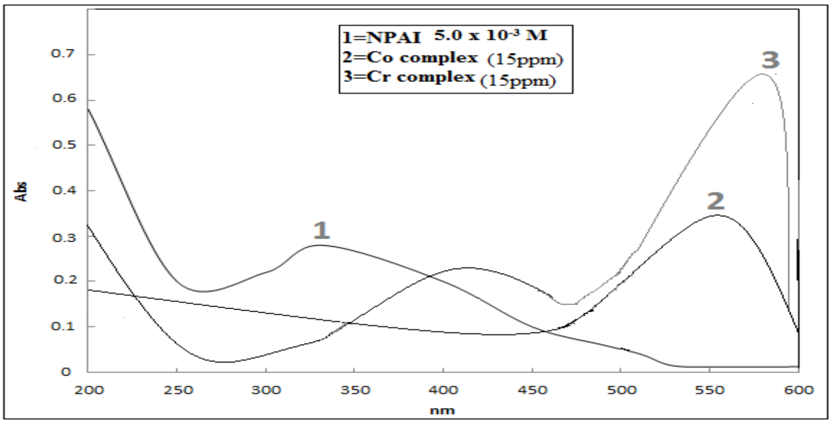


Fig.(5): Absorption spectra Reagent (NBAI) = 5.0 x 10^{-3} M (1) Cr(III)-(NBAI) complex{[15 ppm] in pH=6} and (2) Co(II)-(NBAI) complex{[15 ppm] in pH=8}

Optimization of Procedure:

Effect of pH

The effect of pH on formation of the (Cr(III) ,Co(II))- (NBAI) complexes was determined by recording their absorbance signals at λ_{max} ,over the range of 2-10 ,using different pH buffer solution (NH_3+ CH_3COOH). The results are shown in Fig.6.

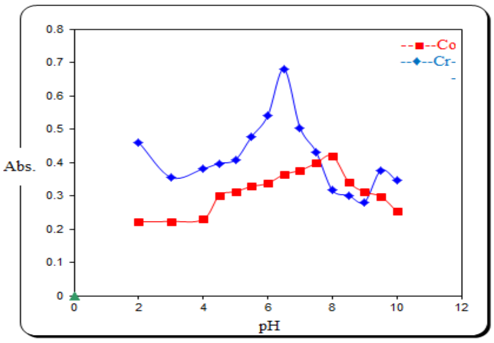


Fig.(6): Effect of pH on the formation of (NBAI)-M complexes formed with (Cr(III) and Co(II).

As can be seen in Fig.(6), the absorbance first increased with increasing pH and reached a maximum at pH 6 for Cr(III) and 8 for Co(II) complexes . The absorbance gradually decreased because of partial dissociation of the complexes at higher pH. Therefore, pH 6 and 8 were selected as the optimum pH's for complete formation of for Cr(III)andCo(II)complexes, respectively.

The stability of the complexs at different times and different temperatures

The absorbance of the complexes reaches a maximum value within 10 min are sufficient for the maximum absorbance of Cr(III) and Co(II) ,respectively, and remains stable for 24 hour. The effect of the temperature for the complexes was studied in the range (20-70) C^0, the maximum and constant absorbance were obtained in the range (20-50)C^0 for Cr(III) and (20-40)C^0 for Co(II),it was decrease in the temperature more than (50C^0 for Cr(III) and 40C^0 for Co(II)) because the complexes will be dissociated or evaporated in these temperatures.

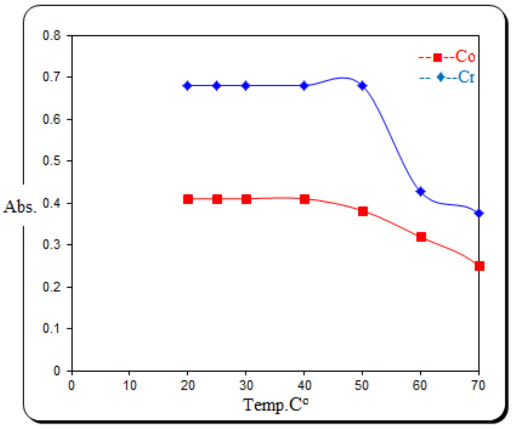


Fig.(7): Effect of the temperature on the absorbance for ((NBAI)- M complexes formed with Cr (III)and Co (II))

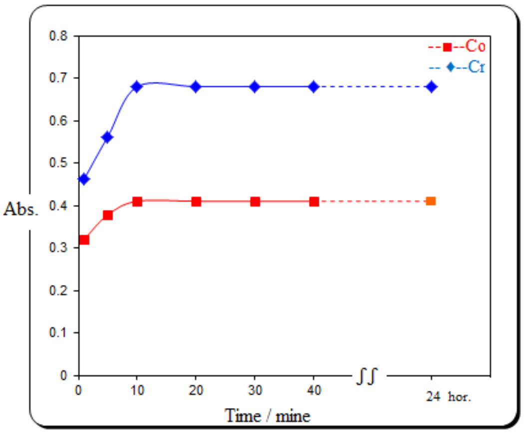


Fig.(8): Effect of time on the absorbance for ((NBAI)- M complexes formed with Cr (III)and Co (II)).

Composition of complex and stability constant:

The composition and the stability constant were evaluated by both of the continuous variation and the mole ratio methods (fig.9-14). Both methods showed that the molar ratio of(Cr(III) ions is 1:1 (metal : ligand)at pH 6 and Co(II) ions is 1:2 (metal : ligand)at pH 8) to reagent (**NBAI**). The stability constant is found to be $1x10^{10}$ $L.mol^{-1}$ and $5.1x10^{9}$ $L.mol^{-1}$ for Cr(III) and Co(II) respectively, and (α) of complexs were found to be (0.13 $L.mol^{-1}$) and (0.16 $L.mol^{-1}$) respectively by using the following equations[20]:

$$K_{st} = \frac{1}{K_{inst}} \qquad \ldots\ldots\ldots\ldots(1)$$

$$K_{inst} = \frac{(\alpha C)(n\alpha C)^{n}}{C(1-\alpha)} \quad . \quad \alpha = \frac{A_m - A_s}{A_m} \qquad \ldots\ldots\ldots\ldots(2)$$

Where:
α=degree of dissociation.
c =total concentration of the complex,
n =mole ratio =(1 to Cr(III),2 to Co(II)) .
Am= absorbance of a solution containing reagent two times excess than the amount of Chromium and Cobalt.
As= absorbance of a solution containing a stoichiometric amounts [reagent][Chromium and Cobalt]

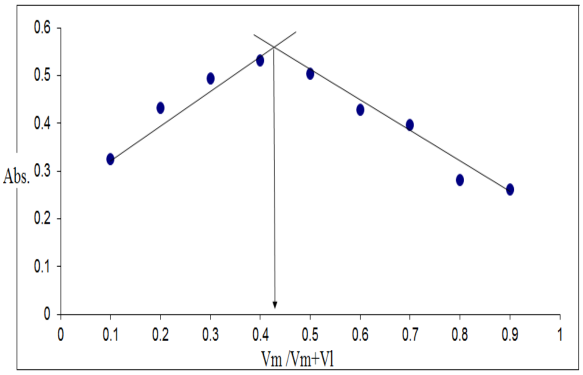


Fig (9): Continuous variation method for Cr complex with (NBAI) at pH=6

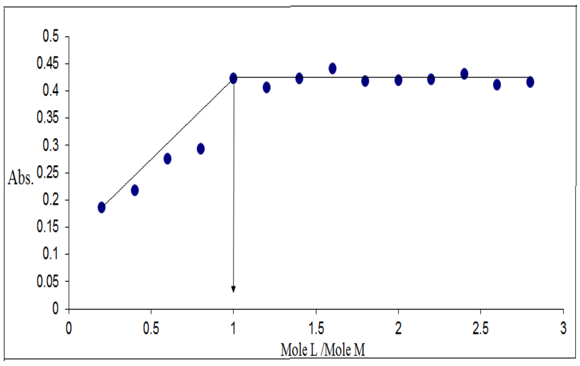


Fig (10): Mole ratio method for Cr complex with (NBAI) at pH=6

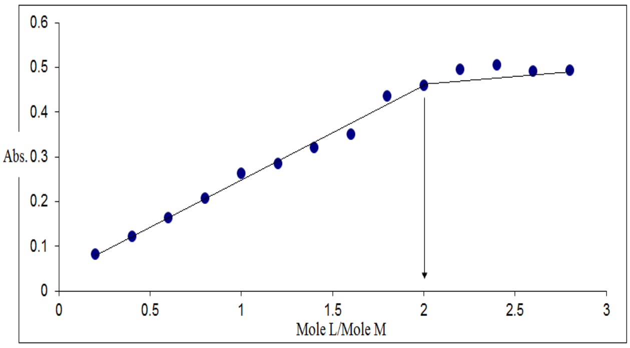


Fig (12): Mole ratio method for Co complex with (NBAI) at pH=8

Suggestion of structural formula of complexes:

From the obtained results of metal to reagent ratio FTIR-Spectrum, and depending on Imidazol compounds properties; the following structure can be suggested :

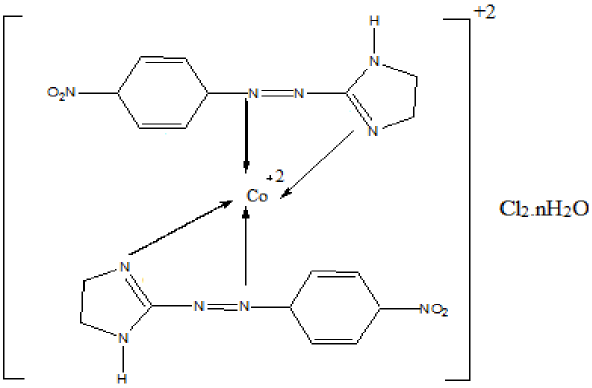


Fig (13):- Suggestion of structural formula for Co complex

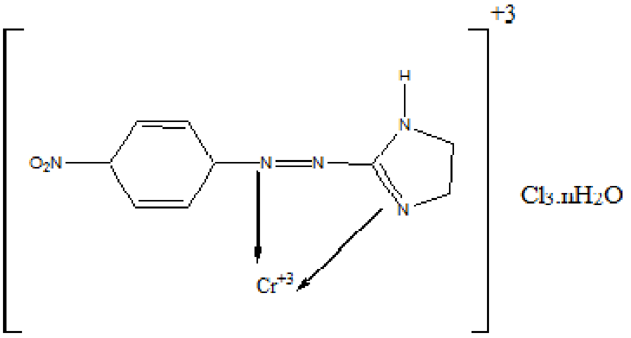


Fig (14):- Suggestion of structural formula for Cr complex

Analytical characteristics:

The calibration curve made as described in the experimental procedure and good correlation coefficient was found .fig. (9, 10, 11 and 12) the some analytical parameters for this Spectrophotometric determination of Cr(III) and Co(II) using this reagent summarized in table (1):

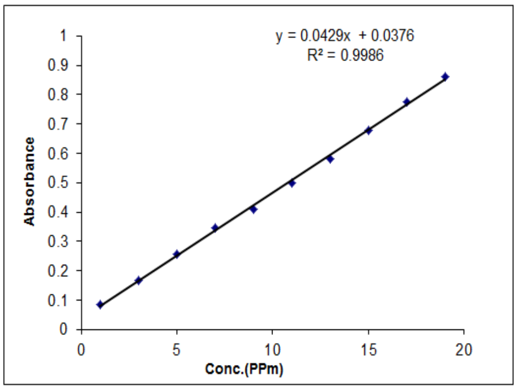


Fig.(15):Calibration curve of Cr Complex

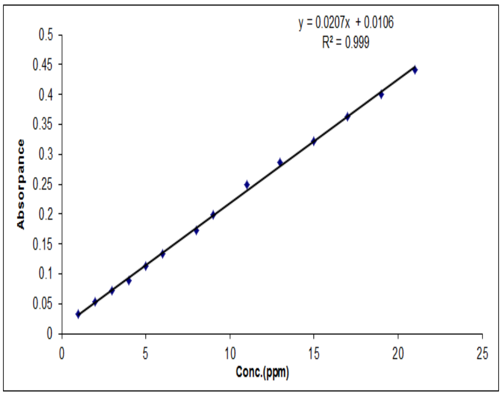


Fig.(16):Calibration curve of Co Complex

Table (1): Analytical data and some analytical parameters of the proposed method for determenation of Cr(III) and Co(II) (N=no. of determination)

Analytical Parameter	Cr (III) / ppm	Co (II) / ppm
λ_{max} (nm)	582	556
Regression equation	Y=0.0429X+0.0376	Y=0.0207X+0.0106
Molar absorptivity(L.mol^{-1}.cm^{-1})	1.1497x10^{4}	1.0162x10^{4}
Sandell Sensitivity(μg.cm^{-2})	0.0233	0.0483
Correlation coefficient(r)	0.9986	0.999
Detection Limit(D.L)	0.132	0.12
Linear dynamic range	1-19	1-21
Standerd deviation	0.002	0.0011
Relative Standard. Deviation %	0.29 (N=7)	0.27 (N=7)
Percent Relative error %	-1	-1.22
Percent Recovery %	99	98.79
Composition of complex (M: L)	1:1	1:2

These results indicating that this method is highly precise and suitable for the determination of Cr (III) and Co (II) spectrophotometrically.

Interference studies Chromium (III) and Cobalt (II) complexes:

The ions (Cu, Ni, Ag, Hg) were formed the complexes with the reagent(**NBAI**) during its reaction with Chromium and Cobalt, the effect of these ions are studied, as in table (2, 3).

Table (2): Effect of foreign ions on the determination of Cr (III) in concentration (15) ppm and suitable masking agents

Foreign ion 100 ppm	Masking agent( )ml ‚[ ]M	Error%
Cu^{2+}	Oxalic acid (0.5)[0.01]	-0.004
Ni^{2+}	Ascorbic acid (0.2)[0.1]	0.05
Hg^{2+}	Tartaric acid (0.1) [0.01]	0.006
Ag^{1+}	Sodium fiuoride (1.0)[0.01]	-0.003
Co^{2+}	Ascorbic acid (0.1)[0.1]	0.001

Table (3): Effect of foreign ions on the determination of Co(II) in concentration (15)ppm and suitable masking agents

Foreign ion 100 ppm	Masking agent( )ml ‚[ ]M	Error%
Cu^{2+}	Tartaric acid (0.5)[0.04]	0.003
Ni^{2+}	Citric acid (0.8)[0.3]	0.001
Hg^{2+}	Ascorbic acid (0.1) [0.04]	0.003
Ag^{1+}	Sodium fiuoride (2.0)[0.03]	0.003
Cr^{3+}	Oxalic acid (0.7)[0.1]	0.003

CONCLUSION

In this work 4-(Nitro phenyl azo imidazole) was used to determination of micro amounts of Cr (III) and Co (II). The molar absorptivity of this complexes are 1.1497×10^4, 1.0162×10^4 $L.mol^{-1}.cm^{-1}$respectirelly.Most foreign ions do not interfere with ions study when masked using different masking agents . Because the (NPAI) can rapidly react with Cr(III) and Co(II) at room temperature , this method can determine these ions spectrophotometrically without heating or extraction . It is sensitive, selective, rapid , easy and convenience method for determined the ions Cr(III) and Co(II).

REFERENCES

[1] T. J. AL-Hasani and A. J. A. J. Jarad, Ibn AL-Hatham *J .for Pure and Appl. Sci*, **2010**, 23(1), 99-214.
[2] Kh. J. Al-adely and Y,O,Mussa, National Journal of Chemistry, **2009**, 33, 104-113.
[3] M. Ali, M.S. Mohammad and H. N. Kudhair , *J. AL-Qadisiya pure Sci.* ,**2007**,12(2),133-141.
[4] M. Jreew, K. H. Kadhim and A. N. Al-Sharefy, *National Journal of Chemistry*, **2006**, 24, 608-619.
[5] L. L. Wang, J.Q. Wang, Z.X. Zhengb and P. Xiao, *Journal of Hazardous Materials*, **2010**, 177,114–118.
[6] E. K. Paleologos, M. I. Prodromidis, D. L.Giokas, A. Ch. Pappas, M. I. Karayannis, *Analytica Chimica Acta*, 2002, 467, 205–215.
[7] S. Chen, X. Zhang, L. Yu, L. Wang and H. Li, *Spectrochimica Acta Part A*,**2012**,88 ,49- 55.
[8] R. E. Shaffer, J. O.Cross, S. L. R. Pehrsson, and W. T Elam, *Analytica Chimica Acta* ,**2001**, 442, 295.
[9] K. G. Kumar and R. Muthuselvi, *Journal of Analytical Chemistry*, **2006**, 61, 1, 28-31.
[10] N. Veerachalee, P. Taweema and A. Songsasen, Kasetsart *J. (Nat. Sci.)*, **2007**, 675- 680.
[11] R. Reddy and P.V.R.B. Sarma, **1994**, *Talanta*, 41, 1335.
[12] S. Zhao, X. Xia and Q. Hu, *Anal. Chim. Acta*, **1999**, 391,365-371.
[13] Safavi, H. Abdollahi, M.R.H. Nezhad and R. Kamali, *Spectrochim. Acta*, **2004**, 60, 2897-2901.
[14] T. Khayamian, A. A. Ensafi and B. Hemmateenejad, *Talanta*, **1999**, 49, 587-596.
[15] M.S. Carvalho, C.S.I. Fraga, K.C.M. Neto and E.Q.S. Filho, *Talanta*, **1996**, 43, 1675.
[16] A. Ghali and Dh. Z.Mashkour, R. C. Dennig and J. Thatcter , *J.Amer.Chem.Soc*.**1986**, 90, 5917.
[17] S. I.Gusev, M.V. Zhvakina, and I.A. Kozhevikov, ZH.Analit. *Khim.* **1974,** 26,859.
[18] L. Mangsup, S. Siripaisarnpipat and N.Chaichit, *Anal. Sci.***, 2003,**19,1345.
[19] W.C. Vosburgh, and G. R. Cooper, *J. Am. Chem. Soc.*, **194, 1**63,437.