

Determination of micro amount of Cobalt (II) by Using Antipyriyl azo pyrogallol

Amal –S-Majeed* & Hussein-J-Mohammed** *Chemistry Department / Faculty of Education for Female / Kufa University

**Faculty of Dentistry / Kufa University

**E-mail : ibraiem _ af @ yahoo . com

المستخلص

تم تطوير طريقة طيفية جديدة و سريعة و حساسة في تقدير الكميات الضئيلة للكوبلت الثنائي . إعتمدت الطريقة على أساس تكوين معقد ١:١ فلز – كاشف مع الكاشف ٤- (٤'-بايروزولون أزو) بايروكالكول (APAP) يمتلك المعقد أعلى قمة إمتصاص عند الطول الموجي ٤٦٣ نانوميتر و معامل إمتصاص مولاري ١,٨ X ١٠^٤ لتر. مول-١. سم-١ . كانت العلاقة الخطية بين الإمتصاص عند الطول الموجي الأعظم و التراكيز تتراوح بين (٠,٠٥ – ١,٥) جزء في المليون أما الدقة و الضبط للطريقة فقد أعطت نتائج تراوحت بين أفضل من ١,٤٥ % بالنسبة إلى RSD و ٠,٦ % بالنسبة إلى الخطأ النسبي . و لبيان إنتقائية الطريقة تم دراسة تأثير عدد من الأيونات السالبة و الموجبة على إمتصاصية المعقد المتكون . كان ثابت الإستقرار للمعقد تحت الظروف الفضلى و درجة حرارة الغرفة ٥,٧١ X ١٠^٤ لتر. مول-١ . طبقت الطريقة المقترحة و بنجاح على نماذج ترابية و نماذج لمزيج محضر مختبرياً .

Abstract

A new , simple , sensitive and rapid spectrophotometric method is proposed for the determination of trace amount of cobalt (II) . The method is based on the formation of a 1:1 complex with 4-(4'-pyrazolon azo) pyrogallol (APAP) as a new reagent is developed . The complex has a maximum absorption at 463 nm and $\epsilon_{\max}$ of 1.8×10^4 L. mol⁻¹. cm⁻¹ . A linear correlation (0.05 – 1.5 $\mu\text{g. ml}^{-1}$) was found between absorbance at $\lambda_{\max}$ and concentration . The accuracy and reproducibility of the determination method for various known amounts of cobalt (II) were tested . The results obtained are both precise (RSD was better than 1.45 %) and accurate (relative error was better than 0.6 %) . The effect of diverse ions on the determination of cobalt (II) to investigate the selectivity of the method were also studied . The stability constant of the product was 5.71×10^4 L. mol⁻¹ . The proposed method was successfully applied to the analysis of dust and synthetic mixtures without any preliminary concentration or separation.

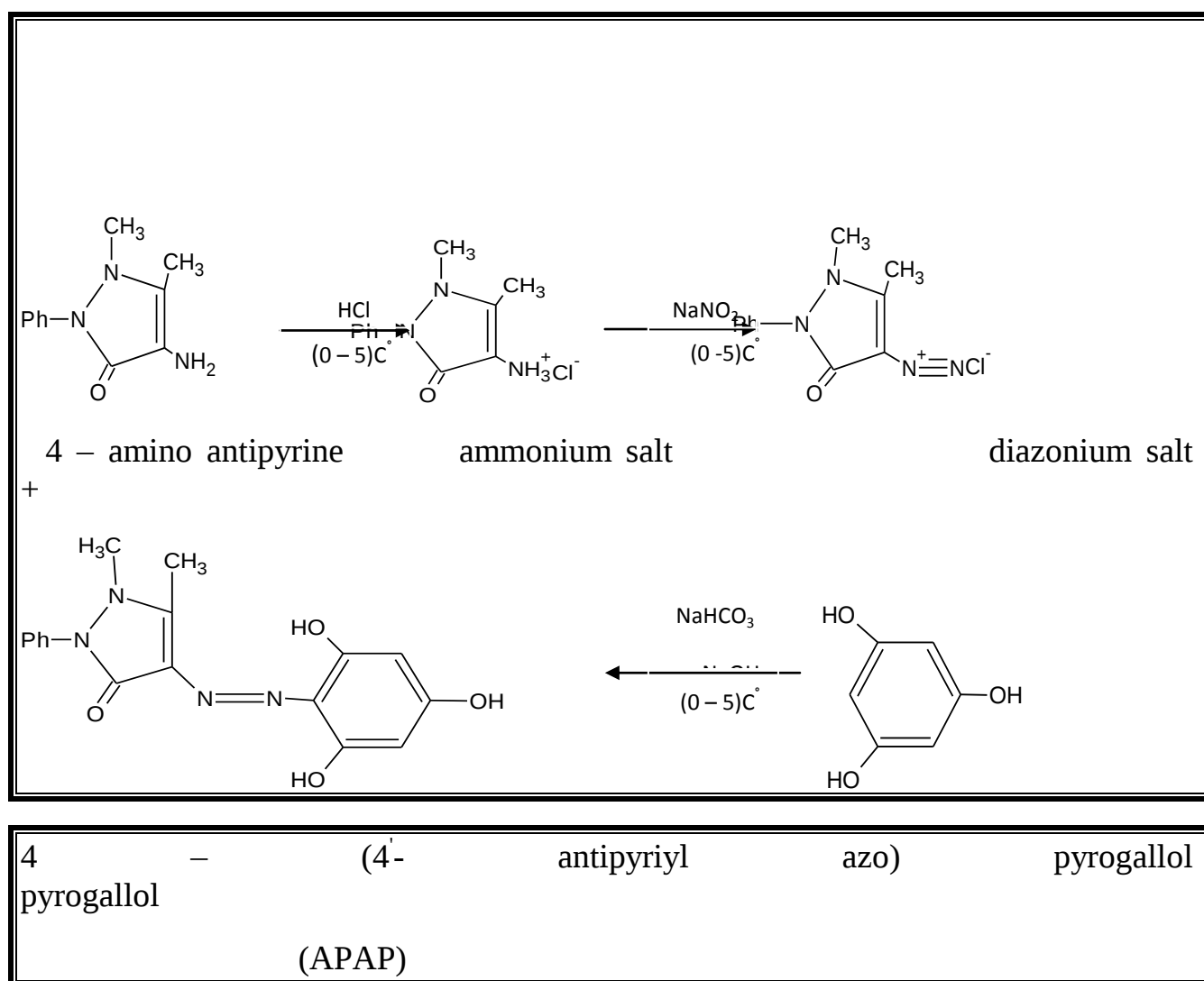
Introduction

Azo compounds have a great industrial importance⁽¹⁾ as well as biological activity⁽²⁻⁴⁾. They can also be used in subtractive photographic process and color pictures⁽⁵⁾ . Heavy metals in different place may cause a significantly serious damage on human health . In fact , some surveys clarified that the contents of certain toxic heavy metals , especially cobalt (II) in fat⁽⁶⁾ and liver⁽⁷⁾ , therefore , is essential for protection of the environment and of our health . In chemical analysis , metal chelation followed by solvent extraction and spectrophotometric detection is the preferred mode of analysis for a number of metal ions^(8,9) due to its rapidity , simplicity and wide applications . Pyrazolon azo forms colored water – insoluble complexes with a large number of metal ions⁽¹⁰⁾ . In the determination of trace or ultra – trace amounts of cobalt in environmental and biological samples , a preconcentration /separation procedure is required even when relying on the high sensitivity and selectivity of modern

instrumental techniques , such as reversed – phase high performance liquid chromatography (RP – HPLC)⁽¹¹⁾ , inductively coupled plasma mass spectrometry (ICP – MS)⁽¹²⁾ , atomic absorption spectrometry (AAS)^(13,14) and especially neutron activation analysis (NAA) , show good sensitivity but is limited because of expensive instrumentation and high cost for routine analysis . According to the best of our knowledge , this reagent hasnot been reported in the literature as being used for any cation determination . In this study , we wish to report this reagent as a selective reagent in spectrophotometric determination of micro amounts of cobalt (II) .

Experimental

Preparation of the reagent (APAR): The reagent was prepared by coupling reaction of diazonium salt of 4 – amino antipyrine with appropriate pyrogallol as coupling component in alkaline solution (scheme.1)



Scheme.1 preparation of reagent (APAP)

Apparatus: Spectrophotometric measurement were made with Shimadzu UV – visible – 1700 double beam spectrophotometer using 1.00 cm glass cells .

Measurements of pH were made using an Inolab, WTW, 720 pH – meter equipped with a glass – saturated calomel combined electrode ..

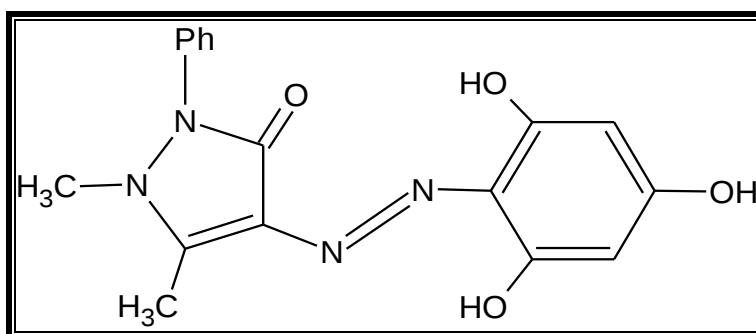
Reagents: All chemicals used were of analytical grades .

Cobalt (II) stock solution ($200\text{ }\mu\text{g} \cdot \text{ml}^{-1}$) Prepared by dissolving 0.220 g of cobalt chloride in 500 ml of distilled water , working standard of Co (II) solutions were prepared by simple dilution of the appropriate volume of the standard Co (II) solution ($200\text{ }\mu\text{g} \cdot \text{ml}^{-1}$) with distilled water **4 –(4- antipyriyl azo) pyrogallol (1 mM)** 0.085 g of reagent was dissolved in 250 ml of ethanol . **III / Foreign ion solutions ($10\text{ }\mu\text{g} \cdot \text{ml}^{-1}$)** These solutions were prepared by dissolved an amount of the compound in distilled water completing the volume in a volumetric flask .

General Procedure: To an aliquot of Co (II) taken separately in the *Beer's law* range given in Table.1 was added (APAP) reagent solution Table.1 and the pH was adjusted in the range given in Table.1 . The complexes formed were solubilized in water and diluted up to 10 ml in a standard flask . The absorbance of the resulting solution was measured at the respective absorption maxima against a reagent blank prepared under similar condition .

Results and Discussion

Properties of (APAP) and its metal chelate APAP is a tridentate with coordination of azo group nitrogen , hydroxyl group and carbonyl group ; it has the following structure :



structure of APAP

Owing to the large conjugated system , the compound showed excellent chelating ability to form inner metal chelates . APAP and its metal chelates can be easily solubilized in an aqueous solution .

Spectra: The result of this work indicated that the reaction of Co (II) with APAP at pH yield highly soluble product which can be utilized as a suitable assay procedure for Co (II) . This product has a maximum absorption at 463 nm at which the blank at this wave – length shows zero absorbance Fig. 1 was adopted in all subsequent

experiments The effect of various parameters on the absorbance intensity of the formed products were studied and the reaction conditions were optimized .

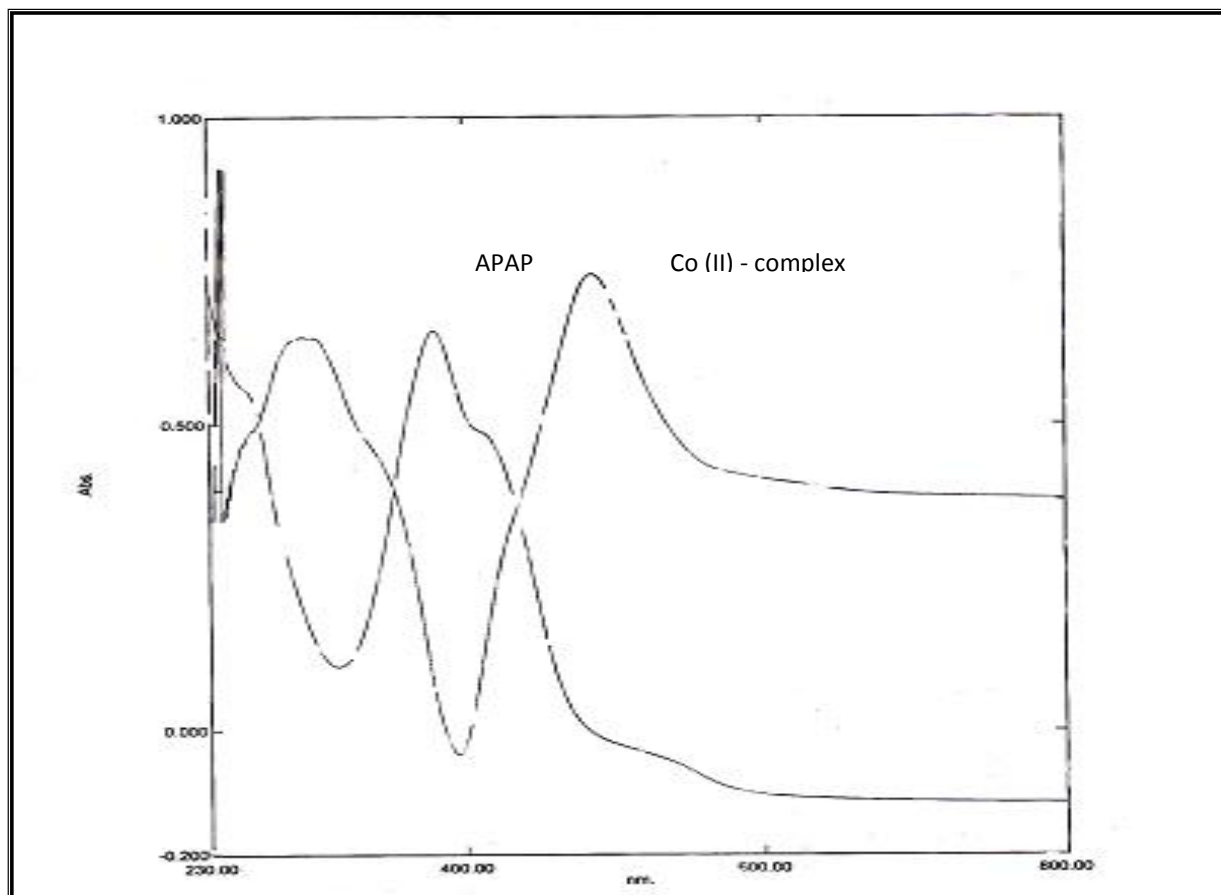


Fig.1: Absorption spectra of [Co (II) + APAP] treated as described under procedure and against a reagent blank and reagent blank against ethanol .

Effect of pH: The electronic absorption of APAR and its complex in ethanol have been recorded in the wavelength range (230 – 600) nm Fig. 1 . The electronic absorption of complex showed a red shift for ($\pi - \pi^*$) electronic transition band . [Co(L) . H₂O] shows one broad in visible region at 21.271 cm⁻¹ refer to ⁴T_{1g} (F) ²T_{1g} (F) that is in accordance with tetrahedral geometry of Cobalt metal ion⁽¹⁵⁾ .The pH of metal complex solutions was adjusted using dilute solutions (0.1 M) NaOH and (0.1 M) HCl , and the effect on absorbance was studied Fig. 2 . The absorbance of the complex was maximum and constant in the pH range given in Table. 1 .

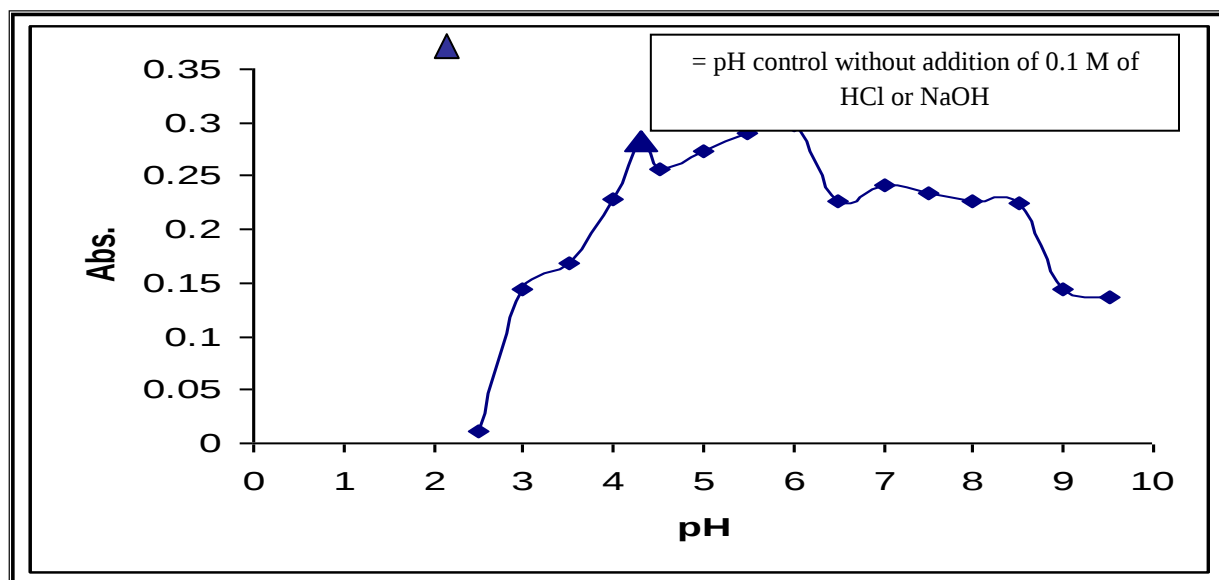


Fig.2: Effect of pH

Table.1 :- Analytical characteristics of Co (II) – complex.

Characteristic	Co (II) – complex
Absorption maximum (nm)	463
Beer's law range (ppm)	(0.05 – 1.5)
pH range	(4 – 6)
Sandell's sensitivity $\mu\text{g} \cdot \text{cm}^{-2}$	0.0034
Molar absorptivity ($\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$)	1.8×10^4
Stability constant ($\text{L} \cdot \text{mol}^{-1}$)	5.71×10^4
Formation constant	2.1×10^2
Free energy ($\text{KJ} \cdot \text{mol}^{-1}$)	-12.9935

Effect of (APAP) concentration: Various concentration of 4-(4'-antipyril azo) pyrogallol was added to fixed concentration of Co (II) 2.5 ml of 1 mM (APAP) solution was sufficient and gave minimum blank value was increased causing a decrease in the absorbance of the sample. Therefore 2.5 ml of 1 mM of APAP was used in all subsequent experiment Fig. 3 .

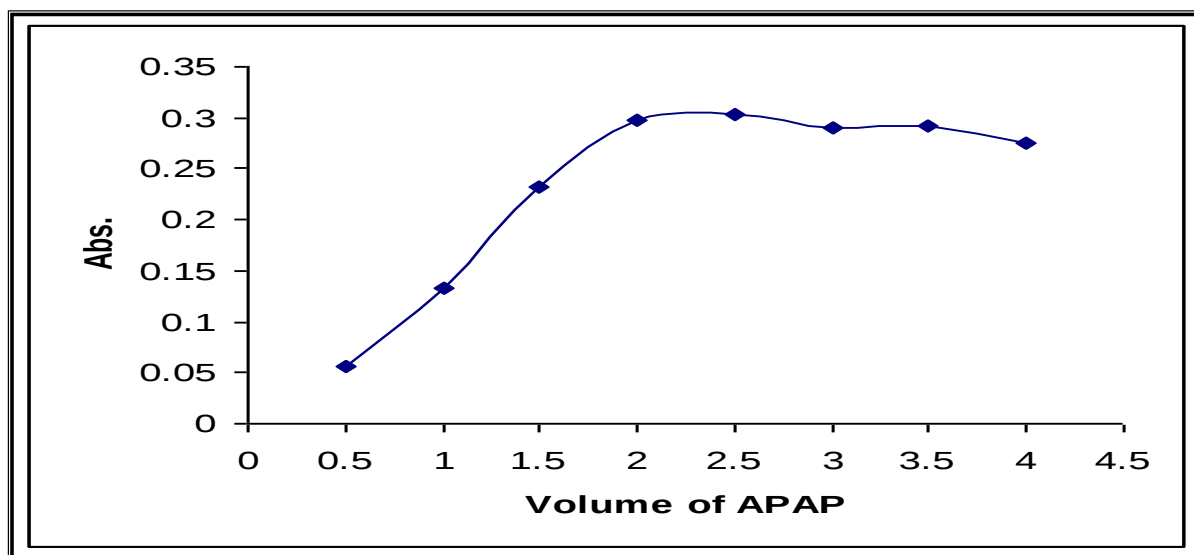


Fig.3: Effect of (APAP) concentration

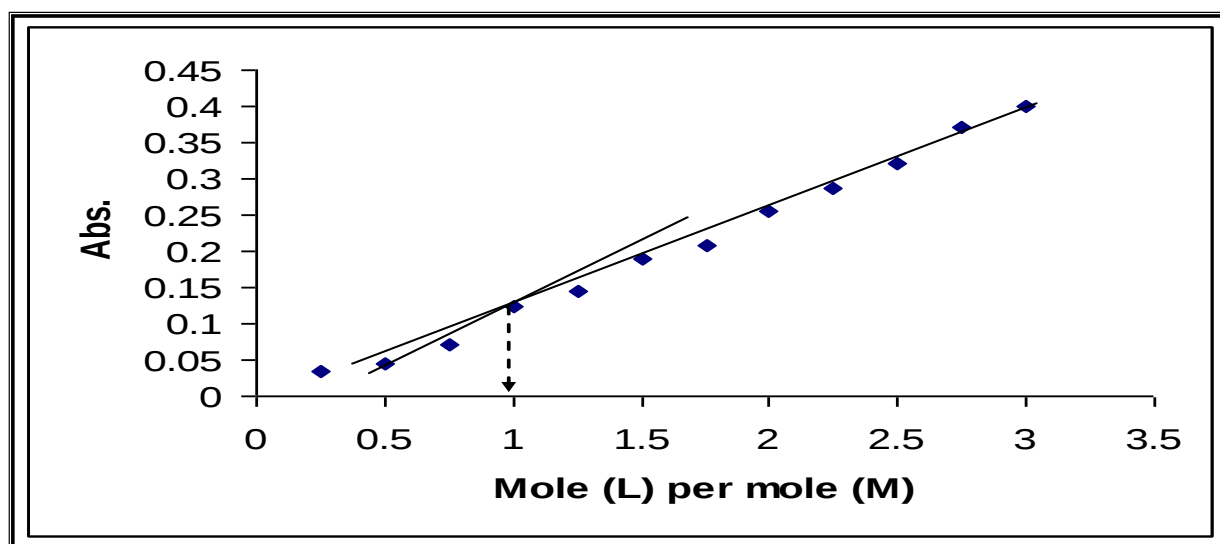


Fig.4: Mole ratio method for Co (II) – complex

Effect of reaction time: The colour intensity reached a maximum after the Co (II) has been reacted immediately with APAP and became stable after one minute , therefore one minute development time was selected as optimum in the general procedure . The colour obtained was stable for a least 24 hours .

Effect of temperature: The effect of temperature on the colour intensity of the product was studied . In practice , the same absorbance was obtained when the colour was developed at room temperature (25 – 30) C°, but when the volumetric flask were placed in a water – bath at (40 – 60) C° a loss in colour intensity and stability were observed , therefore it is recommended that the colour reaction should be carried out at room temperature for complex

Calibration graph: The calibration equation for (0.05 – 1.5 µg per ml , 0.05 – 1.5 ppm) Co (II) is $Y = 0.2002X + 0.0415$ ($R^2 = 0.9079$) . Since the coloured complex is stable for 24 hrs , the method can be applied to large series of samples . The molar absorptivity and sandells sensitivity are given in Table.1 .

Accuracy and Precision [synthetic samples]: To determine the accuracy and precision of the method, cobalt (II) was determined at two different concentrations. The results are shown in Table.2, indicate that satisfactory precision and accuracy could be attained with proposed method.

Table.2 :- Accuracy and precision of the proposed method

Amount taken of Co (II) per ppm	E* %	R. S. D. %
0.5	0.6	1.45
1	0.2	0.56

*for six determinations

Composition of the complex and free energy: The composition of complex was studied in the excess of reagent solution by the mole-ratio method. A break at a 1:1 (M:L) mole ratio suggested the formation of complex where M= Co(II) and L= APAP under the given condition Fig 4. The formation constant of the reaction product was calculated according to the equation⁽¹⁶⁾. Also the free energy changes (G) were calculated according to the following equation; $\Delta G = -2.303RT \log K_f$ Where R= gas constant = 8.3 J/degree.mole, T= absolute temperature = °C + 273 Using the above equation ΔG was found to be -12.9935 KJ.mole⁻¹. The negative value of ΔG indicates that the reaction is spontaneous

Interferences: The effect of diverse ions in the determination metal ion was studied. To test of diverse ions were determined by the general procedure, in the presence of their respective foreign ions Table 3. The metal ion can be determined in the presence of a 50 or more fold excess of cation and anion. In the experiment, a certain amount of standard Co (II) solution, coexisting ion solution and masking agent (or absence of masking agent) were added. It is found that Ag^+ , Cs^+ , I^- , Br^- , CO_3^{2-} , SO_4^{2-} and $C_2O_4^{2-}$ not interfere where as Pt^{2+} , Pd^{2+} , Cu^{2+} , Hg^{2+} , Pb^{2+} , Ni^{2+} , Cd^{2+} , Cr^{3+} and Fe^{3+} interfere seriously. However, their interferences are masked efficiently by addition 0.5 – 1.5 ml of 0.1 M of mixture of $NaNO_2 + NaNO_3 + KCl$, Table.4.

Table.3 :- Effect of foreign ions

Seq.	Foreign ion (10 ppm)	%E
------	----------------------	----

1	Cs^+	zero
2	Ag^+	2.31
3	Cu^{2+}	34.65
4	Ni^{2+}	39.27
5	Pt^{2+}	10.56
6	Pd^{2+}	25.41
7	Cd^{2+}	13.53
8	Pb^{2+}	15.84
9	Cr^{3+}	9.24
10	Fe^{3+}	11.22
11	Hg^{2+}	11.55
12	I^-	- 0.33
13	Br^-	0.33
14	CO_3^{2-}	- 0.66
15	SO_4^{2-}	- 0.99
16	CN^-	- 40.59
17	$\text{C}_2\text{O}_4^{2-}$	- 3.30

Table.4 :- Effect of masking agents

Sequence	Foreign ion	Masking agent	%E
	(10 ppm)	NaNO ₂ + NaNO ₃ + KCl	
1	Cu ²⁺	1.5 ml + 1.0 ml + 1.0 ml	Zero
2	Ni ²⁺	1.0 ml + 1.0 ml + 1.0 ml	Zero
3	Pt ²⁺	0.5 ml + 1.0 ml + 0.5 ml	-1.98
4	Pd ²⁺	1.0 ml + 1.0 ml + 1.0 ml	-0.66
5	Cd ²⁺	1.0 ml + 1.0 ml + 1.0 ml	0.99
6	Pb ²⁺	0.5 ml + 1.0 ml + 0.5 ml	Zero
7	Cr ³⁺	1.5 ml + 1.5 ml + 1.0 ml	-0.33
8	Fe ³⁺	1.0 ml + 1.0 ml + 1.5 ml	0.33
9	Hg ²⁺	1.0 ml + 1.0 ml + 1.5 ml	0.99

References

1. M. Dimmler , H. Eilingsfeld, G. Hasen, Ger. Offen. 2,748,978; C. A. , 91, 75693, (1979).
2. S. Patai, "The Chemistry of Hydrazo , Azo and Azoxy Group" Part I, Wiley, New York (1975).
3. I. M. A. Awad. J. Chem. Technol. Biotechnol, 53, 227, (1992).
4. A. S. A. Zidan, A. I. El-Said, M. S. El-Meligy, A. A. M. Aly, O. F. Mohammed, J. Therm. Anal. 62, 665 (2000).
5. I. M. A. Awad, Phosphorus Sulfur Silicon. 114, 17 (1996).
6. H. Mussalo, S. S. Salmela, A. Leppanen, and H. Pyysalo, Arch. Environ. Health, 41, 49 (1986).
7. S. Iwao, K. Tsuchiya, and M. Sugita, Arch. Environ. Health, 38, 156 (1983).
8. W. J. Simmons, Anal. Chem, 45, 1947 (1973).
9. M. P. San Andres, M. L. Marina, and S. Vera, Talanta 41, 179 (1994).
10. M. F. Abo El-Ghar, N. T. Abdel-Ghani, Y. Badr, and O. M. El-Borady, ISESCO Sci and Tech Vision, 3, 58 (2007).
11. C. Zhang, J. Miura, and Y. Nagaosa, Anal. Sci, 21, 1105 (2002).
12. K. A. Wagner, R. McDaniel, and D. Self. J. AOAC Int, 84, 1934 (2001).
13. R. Dobrowolski, and J. Mierzwa, J. Anal. Chem, 344, 340 (1992).

14. Zh. G. Zhu, G. X. Wang, and J. Chin, 19, 210 (1999).
 15. G. G. Mohamed . Spectro.Chim. Acta , part A, 57, 411(2001).
- N. El – Enany ; F. Bdel and M. Rizk , J. Chin. Chim. Soc. 54, 941 (2007)