Simultaneous Determination of Copper (II) and Cobalt (II) Ions by H-Point Standard Addition Method

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Abstract: *A new, simple, inexpensive and sensitive method for the simultaneous spectrophotometric determination of Cu(II) and Co(II) by H-Point Standard Addition method has been reported . 3-Hydroxy-3-(4-Methyl Phenyl) -1-(3-Chloro, 2- Methyl Phenyl) Triazene (HMCPT) was used as reagent at pH 6.7-7.2. This method is based on the difference in the absorbance of yellow complexes of above reagent with Cu(II) and Co(II) at different wavelength pairs. The result showed that Cu(II) and Co(II) can be determined simultaneously with concentration ratio of 3:1 and 1:3. This method was successfully applied to the determination of these metals in synthetic samples.*

Keywords: *H-point standard addition method, Copper, Cobalt, HMCPT.*

I. Introduction

Hydroxytriazenes are well established chelating agents as revealed by reviews appearing on them during last few years [1-2]. These compounds have been extensively used as analytical reagents[3-6]. 3-Hydroxy-3-(4-Methyl Phenyl) -1-(3-Chloro, 2- Methyl Phenyl) Triazene (HMCPT) have been synthesized by using standard method [7-9].

The survey of literature reveals that hydroxytriazenes have been recently used for both spectrophotometric and complexometric determination of transition and non transtion metals[10-12].

Cobalt is obtained from copper ore as by product. Both metals are essential trace elements for plants and animals[13]. Cobalt is a key constituent of vitamin B-12[14] and uses for formation of alloys[15]. Copper is also combined with other metals to make alloys. It is a good electrical conductor[16]and has diverse role in oxygen transport system[17.]

Simultaneous determination of copper and cobalt in different alloys is difficult by normal spectrophotometry due to overlap of spectra of cobalt and copper complexes. A number of selective techniques have been proposed for simultaneous determination of copper and cobalt. Some of the simultaneous determination methods of different metal ions are reported in the literature such as derivative spectrophotometry [18-20], GC-AES[21], different pulse polarography[22], derivative solid phase spectrometry[23], atomic emission spectometry[24], and chemometric based technique such as H-point standard addition[25] and the partial least square method [26].

These techniques have various limitations including high cost, requirement of tedious preliminary separation techniques, and excessive use of organic solvents. A large volume of solvents is requires for these techniques, which are expensive, hazardous to health, and harmful to the environment.

In 1988, Bosch Reig and Campins Falco delineated the fundamentals of H-point standard addition method (HPSAM) [27], with which two species with mostly or even totally overlapping spectra can be determined [28-32]. The HPSAM, as a modified version of the standard addition method, allow for the direct correction of both proportional and constant errors produced by the sample matrix. Where only the analyte concentration is required [33], absorbance increments can be used, eliminating blank bias error due to the use of an absorbent blank[34, 35]. HPSAM has also been applied to HPLC, spectrofluorimetry, synchronous spectrofluorimetry and to kinetic data analysis with an additional variant, time[36-39]. This method is also of use when unknown interfering substances are involved[40].

A few UV-Vis spectrophotometric applications have been developed for the simultaneous determination of copper and cobalt using a color reagent in the sample. However, UV-Vis spectrophotometry, one of the most widely used analytical methods, has been an attractive method for its rapidity, simplicity and broad application.

In this work, a selective H-point standard addition method has been developed for the simultaneous determination of copper and cobalt, employing 3-Hydroxy-3-(4-Methyl Phenyl) -1-(3-Chloro, 2- Methyl Phenyl) Triazene (HMCPT) as a chromogenic complexing agent in pH range 6.7-7.2.

II. Experimental

2.1 Preparation of Metal Solution-
All chemical used were of analytical reagent grade of Merck chemical companies. Doubly distilled water was used throughout. The stock $1*10^{-2}$ M cobalt solution was prepared to the solution to prevent hydrolysis. The solution was standardized with $1*10^{-2}$ M EDTA using mureside[41] as an indicator. Weaker solution was prepared by its appropriate dilution with double distilled water.

The stock $1*10^{-2}$ copper solution was prepared from the copper pentahydrate salt in a volumetric flask. The solution was standardized with $1*10^{-2}$ M EDTA using murexide[41] as an indicator.

2.2 Preparation of Reagent (HMCPT) Solution-
A $1*10^{-4}$ M Solution of reagent was prepared with appropriate amount of 3-Hydroxy-3-(4-Methyl Phenyl) -1-(3-Chloro, 2- Methyl Phenyl) Triazene HMCPT in alcohol. The solution was prepared on daily basis when needed.

2.3 Preparation of Buffer Solution-
A fresh 1% perchloric acid and tris buffer solution was also prepared by dissolving it in minimum quantity of double distilled water and then diluting it with ethanol.

2.4 Apparatus-
Systronics-108 UV-Vis spectrophotometer was used to record the spectra. Systronics 324 pH meter was used to adjust the pH and 1 cm quartz cuvette was utilized for absorbance studies.

2.5 Synthesis of the Reagent-
3-Hydroxy-3-(4-Methyl Phenyl) -1-(3-Chloro, 2- Methyl Phenyl) Triazene (HMCPT) has synthesized per standard method. The general method is described below. The synthesis of the reagent was done in three steps.
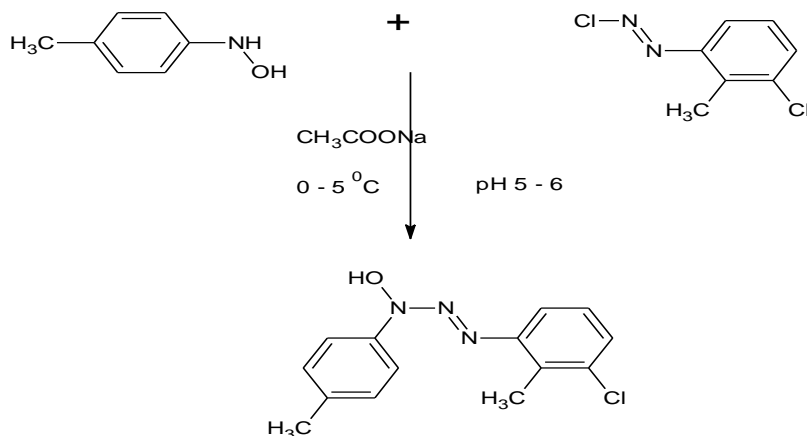
2.5.1 Reduction of p-nitrotoluene-

Step-1 Reduction of p-nitro toluene.
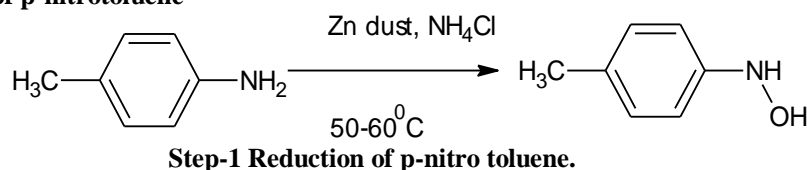
2.5.2 Diazotization of amino compound-

Step-2 Diazzotization of 3-Chloro,2-Methyl Aniline
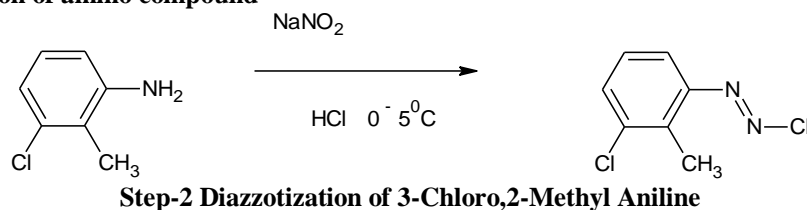
2.5.3 Coupling-

Step- 3 Coupling

The compound 3-Hydroxy-3-(4-Methyl Phenyl) -1-(3-Chloro, 2- Methyl Phenyl) Triazene (HMCPT) as a metallochronic was obtained as brownish yellow precipate, which was treated with activated charcoal and then recrystallised several times in ethanol. The final product was obtained in the form of light yellow needle shaped crystals. Melting point of all synthesized compounds were taken in open capillaries and found 110^OC. Resultant compound was subjected to four spot tests detection as described by Purohit[13-16]. This compound gave positive test with all the four reagents proving that the synthesized compound is a hydroxytriazene.

To check the purity of the compound CHN-analysis and IR studies have been done. CHN data has been given in table 1. IR-data of this compound has been given in table 2, showing the characteristic peaks of (O-H str.) (C-H str. Ar) (C-H str. CH_3) (N=N str.) (N-N str.) and (C-Cl str.) vibrations.

Table 1. Physical Characteristics, M.P., C H N Values of the reagent

Molecular Formula	Melting Point (^{o}C)	Colour and shape of the crystal	% Analysis					
			Calculated			Experimental		
			C %	H %	N %	C %	H %	N %
$C_{14}H_{14}N_3OCl$	110	Light yellow needle	60.98	5.08	15.24	61.24	5.24	15.13

Table 2 IR data of the reagent(Cm^{-1})

O-H str.	C-H str. Ar	C-H str. CH_3	N=N str.	N-N str.	C-Cl str.
3618	3028	2920	1581	1454	682

III. General Procedure

3.1 Individual Calibration-

For the preparation of each standard sample solution, 3 ml of reagent solution and 0.6 ml of cu(II) or co(II) solution were added to a 10 ml flask. The volume was made up to the mark with alcoholic buffer solution of pH 6.7-7.2 and allowed to stand for 5 min. at 25^0C. A portion of solution was transferred into a 1cm quartz cell to measure the absorbance against reagent blank.

3.2 H-Point Standard Addition Method-

Appropriate volumes of the Cu^{+2} and Co^{+2} standard solutions and 3 ml of $1.0*10^{-4}$ M (HMCPT) taken in a 10 ml volumetric flask. Requisite amount of analyte were added for standard addition and made up to the mark with alcoholic buffer solution pH 6.7-7.2

Using HPSAM, the simultaneous determination of cu (II) and Co(II) was performed by measuring the absorbance at 404 and 420nm with the standard addition of analyte[Cu(II)] solution and graphed to ascertain the concentration of Co(II). Two straight lines for concentration and absorption were plotted and the values for the absorption and concentration at the intersection of these two lines (H-point) termed -C_H and A_H, respectively, were obtained by extrapolation. Copper(II) and cobalt(II) were determined simultaneously using the concentration ratios of Cu(II) and Co(II) varying from 3:1 to 1:3 in mixed samples. Synthetic samples containing different concentration ratios of copper(II) and cobalt(II) were prepared, and standard additions of Cu(II) up to 8 μgml^{-1} were made.

For the determination of cobalt content in a mixture solution procedure will be revised vice-versa by the addition of cobalt and plot the graph between both two lines. The extraplotation of the lines intersection determine the concentration of cobalt.

IV. Results And Discussion

4.1 Preliminary Study of System-

3-Hydroxy-3-(4-Methyl Phenyl) -1-(3-Chloro, 2- Methyl Phenyl) Triazene (HMCPT) is a very good reagent for the determination of trace amount of Cu(II) and Co(II). The absorption spectra of the colored Cu-HMCPT and Co-HMCPT showed maxima at 404nm and 420nm in fig1. The determination of Co(II) is difficult in the presence of Cu(II) by ordinary spectrophotometry due to overlapping of spectra. However after application of the optimal conditions and HPSAM, the system allows for the accurate and simple simultaneous determination of cu(II) and co(II) .
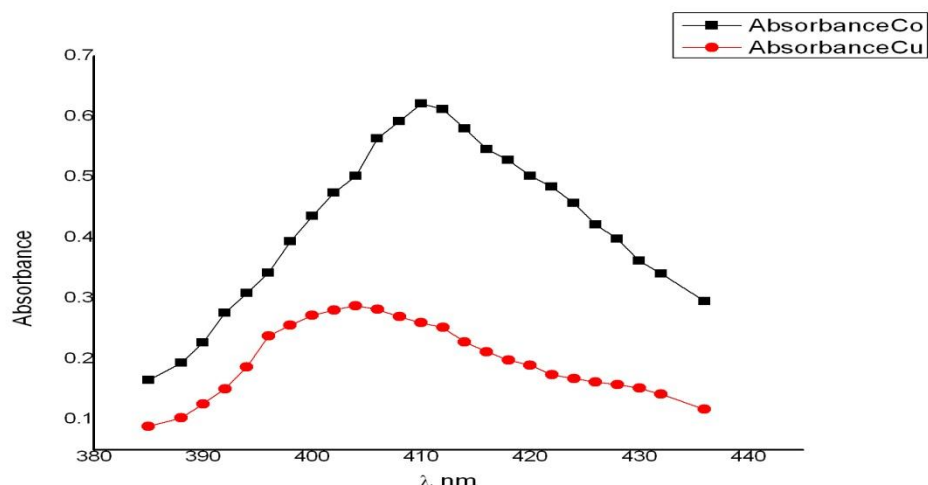
Fig. 1 Absorption spectra of (a)Co-HMCPT and (b)Cu(II)-HMCPT complex against reagent blank, Conditions 3ml of $1*10^{-4}$ M HMCPT and 0.6 ml of $1*10^{-5}$ Cu+2 and co+2 solution, pH 6.7-7.2 at 25^{0} C

4.2 Optimization of Conditions-

The working conditions were optimized by studying the effect pH of solution, concentration of the reagent and other conditions. Formation of Cu(II)-HMCPT and Co(II)-HMCPT complex was affected by hydrogen ion concentration. Absorbance for both complexes was studied over a wide range of pH from 3-10 using buffers perchloric acid and tris buffer, potassium dihydrogen phosphate- potassium monohydrogen phosphate. The studied show that maximum absorbance is in the pH range 6-8 for Cu-HMCPT and 6-9 for Co-HMCPT complex as shown in Fig. 2. The absorbance of both Cu-HMCPT and Co-HMCPT increases up to pH 6-8, after which the absorbance decreases. Therefore, 6.7-7.2 pH range was selected for optimum ph using perchloric acid and tris buffer solution.
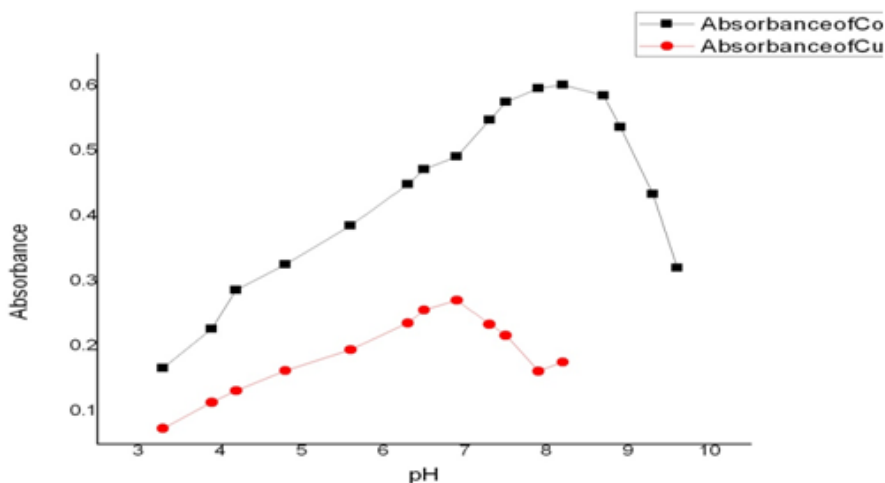
Fig-2 Effect of pH on the Absorbance of CU-HMCPT and Co-HMCPT Complexes

The effect of the temperature on the reaction was studied in the range of 15-35^{0} C. The results show that up to 25°C the absorbance of both Cu- HMCPT and Co- HMCPT increases, remaining nearly constant or decreasing slightly at higher temperatures. Therefore, 25^{0}C was selected as the optimum temperature. The decrease in absorbance may be due to the lower stability of these complexes at higher temperatures.
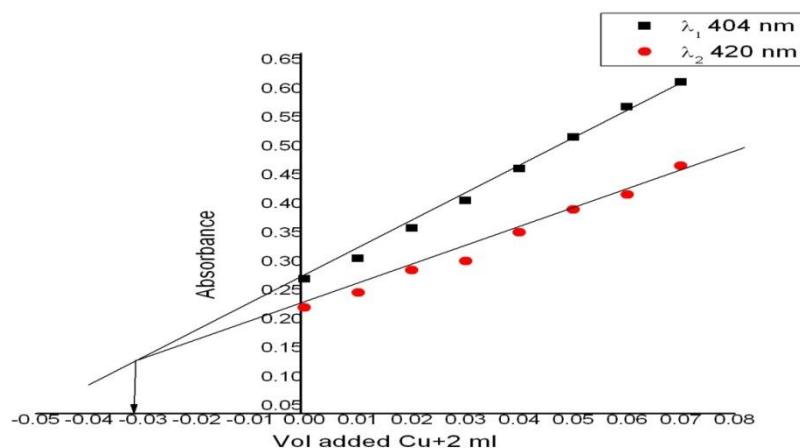
4.3 H-point standard addition method-

This is used for an unknown sample containing an analyte A and an interferent B. In this work either cu(II) can be considered as the analyte and co(II) as interferent(interfering ion) or vice versa. The main requirement of HPSAM is the selection of two wavelengths y^1 and y^2 at which the B Co(II)should have same absorbance and difference between the slopes of two straight lines must be as large as possible in order to get more accurate results. When Cu(II) was considered as the analyte, the pair of wavelength selected was 404 and

410nm, which gave the greatest slope increment and good accuracy, Then known amount of cu(II) were successively added and absorbance(A) were recorded at the two wavelengths. These can be expressed as the two equations given below-

$$A_{404}= M_{404}Ccu_{(II)} +bo+b \qquad \qquad (1)$$
$$A_{410}=M_{410}Cco_{(II)} +Ao+A' \qquad \qquad (2)$$

The two straight lines obtained intersect at the h-point (-Ccu, Aco)

Fig-4 H-Point Standard Addition Plot for the Simultaneous determination of Cu and Co , Conditions- 0.03ml of $1*10^{-5}$M Cu^{+2}, 0.03ml of $1*10^{-5}$ M Co^{+2}, CHMCPT=$3*10^{-4}$M, pH=6.7-7.2 at 25^{0}C

To achieve the simultaneous determination of Co^{+2} and Cu^{+2} in a sample, several synthetic mixtures with different concentration ratios of Cu^{+2} and Co^{+2} were analyzed using HPSAM. Results of the analysis of the different mixtures in the proposed system revealed a dynamic range of 10-70 and 10-70µg ml-1 for Cu^{+2} and Co^{+2} ions, respectively.

4.4 Accuracy of the Method-

In addition, several experiments were carried out on a series of samples containing a fixed amount of cobalt(II) with varying amounts of copper(II) (Fig. 5), accomplished by the addition of standard solutions of the varied ion. Figures 5 show the determination of Cu^{-2} and Co^{-2} ions in the samples at concentrations of 10-70 and 10-70µg ml^{-1}, respectively, to be independent of each other and accurate, thereby confirming the applicability of the proposed procedure.
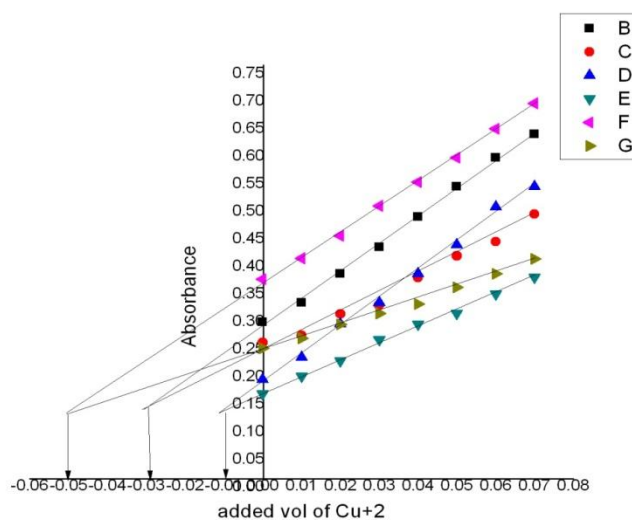
Fig-5 H-Point Addition plot for the simultaneous determination of copper and cobalt under optimized conditions, a constant concentration of cobalt (0.03ml) and copper concentration of (i) 0.01 (ii) 0.03 (iii) 0.05ml.

4.5 Diverse Ion Effect-

We investigated the influence of the presence of several cations and anions on the determination of Cu^{+2} and Co^{+2} ions by HPSAM under optimum conditions. The absorbance of anions and cations was studied with Cu^{+2} and Co^{+2} equivalents to five fold and ten fold concentration, respectively. The ions which interfered at one of the three levels were not screened further, whereas those which did not interfere at equivalent concentration or more were further screened at higher concentration. Most of the anions did not interfere at 10ppm and 50ppm concentration as Na^+, NO_2^-, K^+, SCN^-, Br^-, NO_3^-, SO_4^{-2}, Cl^-, NH_4^{+1}. The anion Br^-, NO_3^- K^+, Cl^-, SCN^- SO_4^{-2} is also not interfering at 100ppm concentration. The tolerance limit was found for anion is 100ppm and more concentration.

The interference study has been done with cation with presence of Co^{+2} and Cu^{+2}. The obtained that Ca^{+2}, Mn^{+2} and Zn^{+2} did not interfere at 10ppm, 50ppm concentration solution. Cation Ni^{+2}, Hg^{+2}, Ba^{+2}, Cd^{+2}, Pb^{+2} are interfering with all three concentration level. The result of interference study is that the Ni^{+2}, Hg^{+2} and Cd^{+2} is highly effect the absorbance.

Application of the Method-

The proposed method was successfully applied to the determination of cobalt and copper in synthetic samples.

The good agreement between the obtained results and the known values in water samples indicate the applicability of the HPSAM for the simultaneous determination of copper and cobalt in complex samples.

V. Conclusions

A H-point standard addition method has been used in simultaneous determination of cobalt(II) and copper(II) ions using 3-Hydroxy-3-(4-Methyl Phenyl) -1-(3-Chloro, 2- Methyl Phenyl) Triazene (HMCPT) as a metallochronic reagent at pH 6.7-7.2. The high degrees of reproducibility and valuable dynamic range as well as simplicity are the advantages of the proposed method. The proposed method is comparable to HPSAM using the PAN reagent for determination of cobalt and zinc in a sample[42].

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