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Development of An Extractive Spectrophotometric Method for Determination of Cr (III) Using 2, 4-Dimethyl -3H- 1, 5 Benzodiazepine

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ABSTRACT

A new analytical reagent 2, 4-dimethyl -3H- 1, 5 benzodiazepine (DBA) is proposed for the extraction and spectrophotometric determination of Cr (III). The Reagent was synthesized and characterized by IR, NMR, elemental analysis as well as Mass spectrometry. DBA reacts with Chromium to give red colored complex which can be quantitatively extracted into n-butanol at pH 8.8. The organic extract shows maximum absorption at 500nm where absorption due to similarly prepared reagent blank is negligible. The beer's law is followed in the concentration range 1-10 µg L^{-1} of Cr (III). The molar absorptivity and Sandell's sensitivity of Cr (III) -DBA complex is 7460 Lit $mol^{-1}cm^{-2}$ and 0.02427 mg $cm^{2\,-1}$ respectively. The proposed method is rapid, sensitive, reproducible, and accurate and has been satisfactory applied for determination and separation of Chromium (III) in commercial mixtures, pharmaceutical samples and alloys.

Keywords: Chromium (III), Spectrophotometric determination, DBA reagent.

INTRODUCTION

The symbol of Chromium is Cr and atomic number 24. is steely grey, lustrous hard and brittle metal [8] Ferrochromium alloy is commercially produced from chromite by silicothermic reaction and chromium metal by roasting and leaching process followed by reduction with carbon and aluminum. Chromium has high value for its high corrosion resistance and hardness. Trivalent chromium ion is an essential nutrient in trace amounts in humans for insulin, sugar and lipid metabolism. Hexavalent chromium is toxic and carcinogenic. [1] The increase in discharge of industrial sewages and effluents is a cause of concern. The contamination in groundwater makes it improper for drinking. In view of such environmental problem continues monitoring and analysis of the metal becomes necessity. Though a number of methods are available for determination of chromium (VI), only limited methods are available for determination of chromium (III). The available techniques for Cr determination, e.g., ion chromatography (IC), atomic absorption spectrometry (AAS), inductively coupled plasma-optical emission spectrometry (ICP-OES), inductively coupled plasma-mass spectrometry (ICP-MS) and etc, are expensive and require technical skills. Simple detection method for heavy metal contaminants available for in situ analysis has gained much interest. [3, 4-7, 9-12]

A spectrophotometric determination of Chromium (III) is based on the reaction of these ions with 2,4 dimethyl-3H-1,5 benzodiazepine, to give a red – colored product showing a maximum absorbance at 520

nm, with molar absorptivities is 4945 L mol^{-1} cm^{-1} for Chromium (VI) and Sandell's sensitivity of 0.01204 mg $cm^{2\ -1}$ [2]. The present paper describes the preparation of 2,4 dimethyl -3H-1,5 benzodiazepine, is a sensitive and selective reagent for the spectrophotometric determination of micrograms quantities of Chromium (III) without need for a preliminary steps.

MATERIALS AND METHODS

Instruments: A Shimadzu 2450 UV-Visible spectrophotometer with 1.0 cm quartz cell was used for absorbance studies. An Elico LI-120 digital pH-meter was used for pH adjustments. The experimental conditions are maintained as presented in Table 1.

Table 1. Experimental conditions

Condition	Results
Absorption Maxima	500nm
Solvent	n- butanol
pH range	
Equilibration time	1.0 min
Stability of Chromium- reagent	48 h
Beer's range	1 to 10 mg cm3 $^{-1}$
Molar absortivity	7460 Lit $mol^{-1}cm^{-2}$
Sandell's sensitivity	0.02427 mg/ cm^{2} -1
Mole ratio of Cr :reagent	1:1

Synthesis of Reagent: The reagent was synthesized by mixing 1 mole of O- phenylenediamine and 2 moles of Acetyl acetone in Ethanol. The above mixture is refluxed for 2 h in round bottom flask. The solution thus obtained is poured in ice. Solid is formed, which is purified with ethanol. It is then characterized and used for extractive spectrophotometric determination of Cr (III). A stock solution of reagent with concentration 0.05% was prepared in methanol. The scheme of reaction is as shown in fig.1.

Reaction:

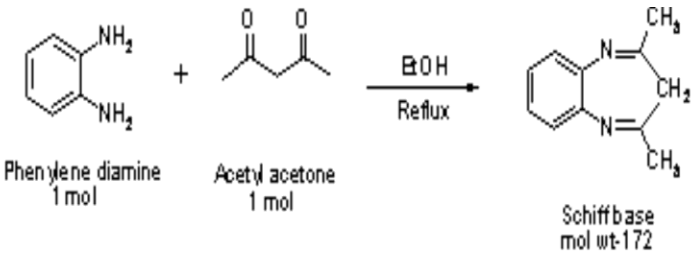

Fig 1. Synthesis of Reagent 2, 4-DIMETHYL -3H- 1,5 BENZODIAZEPINE (DBA)

Preparation of stock solution: A weighed quantity of chromium chloride was dissolved in double distilled water then diluted to desired volume by double distilled water.

Extraction as a function of pH: The extraction of Chromium was carried out at various pH conditions ranging from the pH 1to pH11 using various buffer solutions. The ratio of organic phase to aqueous phase was kept 1:1. The present extraction was observed to be quantitave at pH 8.8. Therefore pH 8.8 was selected for further studies and presented in Fig 2.

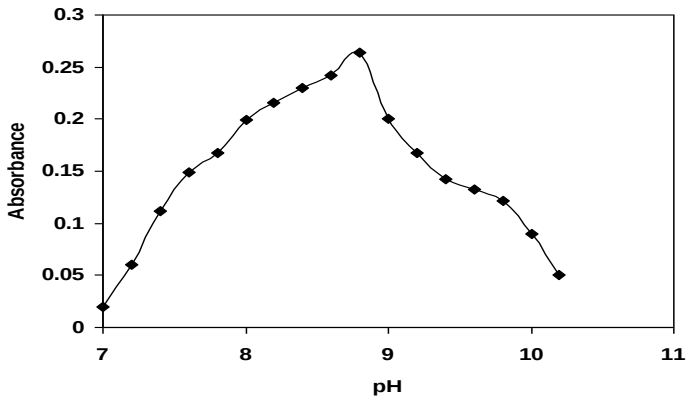

Fig 2. Extraction as a function of pH

Effect of solvent: The suitability of extraction was studied using various organic solvents such as n-butanol, toluene, cyclohexanone, cyclohexanol, chloroform, ethyl acetate, carbon tetrachloride, xylene, diethyl ether and hexane. The extraction of chromium was observed to be quantitave in the organic solvent n-butanol. Therefore n-butanol is used for extraction of chromium.Fig.3 indicate that n-butanol is observed to be an appropriate solvent.

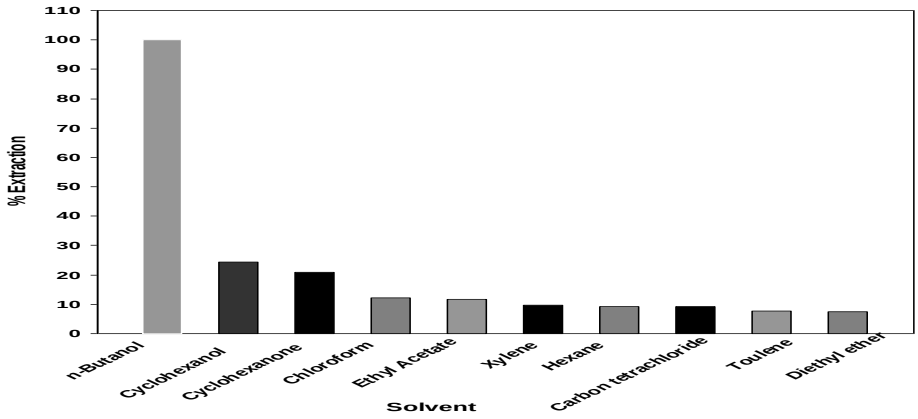

Fig 3. Effect of solvent

Absorption spectrum: Fig.4 depicted that the absorption spectrum in n-butanol observed to be maximum absorption at 500nm and the absorption due to reagent was found to be negligible at this wavelength. Hence 500nm was selected as wavelength for the absorbance measure in the spectrophotometric determination of chromium against reagent blank.

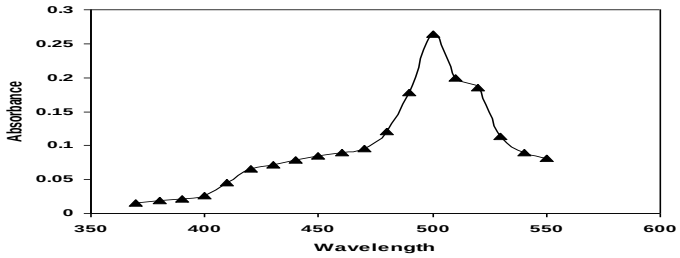

Fig 4. Wavelength of absorption

Recommended procedure: Mix 1 cm^3 aqueous solution containing 1-100mg of chromium and 1cm^3 of 0.05% methanolic solution of reagent in 25 cm^3 beaker. Adjust the pH of the solution to required value with buffer solution Make the final volume 10 cm^3. Transfer the solution into 125 cm^3 separating funnel and equilibrate for 1min with 10 cm^3 n- butanol. Allow the two phases to separate and measure the absorbance of organic phase containing the complex at 500 nm against reagent blank.

RESULTS AND DISCUSSION

Preparation of calibration plot: The calibration curve was prepared by taking known amount of Chromium which was treated as described in the procedure. A graph of absorbance against concentration was prepared (Fig.2). The concentration of the unknown Chromium solutions is determined from the calibration plot as presented in Fig.5.

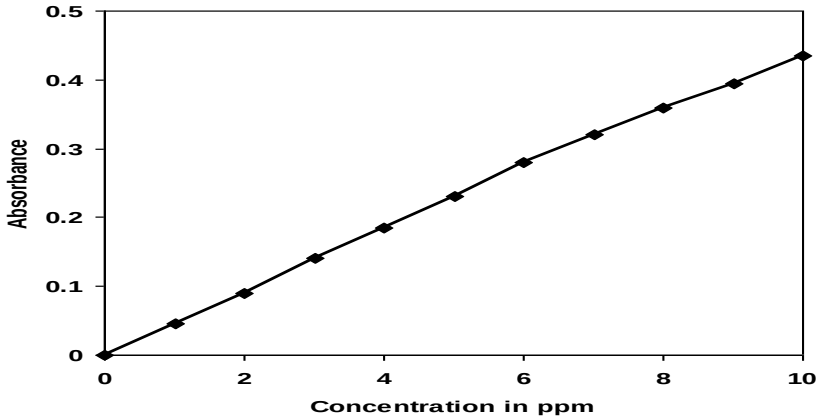

Fig 5. Calibration Plot of Cr (III) in mg/ml against Absorbance

Composition of the extracted species: The composition of the extracted species was determined by using the Job's continuous variation method and verified by mole ratio method and slope ratio method. These methods show that the composition of Cr (III): DBA regent is 1: 1 and above results are confirmed from Fig.6.

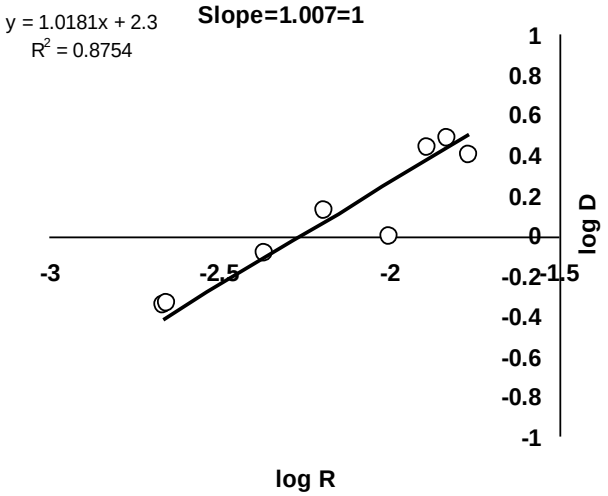

Fig 6. Slope Ratio method

Effect of foreign ions: The effect of diverse ions on the Chromium (III) determination was studied, in presence of a definite amount of a foreign ion. Various cations and anions were investigated in order to find the tolerance limit of these foreign ions in the extraction of Chromium (III) as presented in Table 2. The tolerance limit of the foreign ion was taken as the amount required causing an error of not more than 2% in recovery of Chromium (III). The ions which interfere in the spectrophotometric determination of Chromium were masked by using appropriate masking agents as presented in Table 3.

Table 2. Effect of foreign ions

S. No.	Interfering ions	Tolerance limit
1	Acetate, Oxlate, CN-, I-, Br-, NO3-, Cl-, BrO-3, ClO3-, IO3-, NO2-, SO4-,SO3-	18
2	Tartarate	16
3	phosphate	14
4	Mg(II), Zn(II), Mo(VI), Ce(IV), Bi(III), Ca(II), As(III), Pb(II), Al(III),	14
5	V((V), Cd(II)	10
6	Na+, Ag+	18
7	Fe(II), Ni(II), Mn(II), Zr(II), Co(II), Fe(II),Cu(II), EDTA	Interfiere strongly

Table 3. Masking agents

Interfering Ion	Masking agent added	Interfering Ion	Masking agent added
Cd (II)	Potassium Iodide	EDTA	Boiled with concentrated HNO_3
Fe (II)	Sodium fluoride	CN-	Boiled with concentrated HNO_3
Ce (IV)	Sodium fluoride	Ni (II)	Thiourea
Cr (VI)	Ammonium acetate	Zr (IV)	Sodium fluoride
Mn (II)	Sodium fluoride	Tartrate	Sodium molybdate
Ag +	Potassium Iodide	V (V)	Thiourea

Comparison between reagents: Various reagents were investigated by the earlier researchers for removal of Chromium (III). The proposed reagent 2, 4-dimethyl -3H- 1, 5 benzodiazepine (DBA) is found more superior as that of reported regents and are presented in Table 4.

Table 4. Comparison between regents

Name of the Reagent	Limitations
4-(2- thiazolylazo)-resorcinol (TAR)	Cu (II), Co (II), Ni (II), Zn (II) Ag (I), EDTA Interferes.
2-hydroxybezaldiminoglycine	Sandell's Sensitivity is poor.
Tetramethylammonium- Chromate	Unstable complex
Neotetrazolium Blue	Less pH range is required
5,11,17,23-Tetra [(2-ethyl acetoethoxy phenyl) (azo) phenyl] calyx[4] arene	CO3,Hg(II),Fe(II), Zn(II),Mn(II),Cr(VI) Interferes.

APPLICATIONS

The present method was applied for determination of amount of Chromium (III) in various samples of alloys, commercial mixtures; water samples etc. are in well agreement with standard methods as shown in Table 5. Every result is average of independent determinations.

Table 5. Applications

S. No.	Sample	Amount of Cr(III) in standard method	Amount of Cr(III) in present method
1	Ferrochrome	58%	56.8%
2	Nichrome	20%	!9.65%
3	Cr(III)(5) + Fe(III)(5)	4.97 ppm	4.96 ppm

4	Cr(III)(5) + Bi(III)(5)	4.98 ppm	4.98 ppm
5	Water sample (per Lit)	0.1 µg//gm	0.098 µg//gm

CONCLUSIONS

The results obtained show that the newly developed method in which the reagent 2,4-DIMETHYL -3H-1,5 BENZODIAZEPINE (DBA) was synthesized, can be used for quantitative estimation of Cr(III). The proposed novel reagent is found to be more effective over reported reagent from earlier investigators. The proposed method is simple, rapid and requires less volume of organic solvent. The method is also precise, less time consuming and easily employed anywhere as does not require sophisticated instruments.

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