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Spectrophotometric Evaluation of Trace level Chromium in Alloy Steel

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A facile and highly responsive spectrophotometric method for the quantification of ultra-trace quantities of chromium(VI) is described. The proposed method is derived from the oxidation of iminodibenzyl (IDB) with chromium in strong acid medium to get a blue coloured product, having λ_{max} at 690 nm. Stability of the colour developed is found to be around 48 h at room temperature. Beer's law range is observed between 0.02-0.35 μg mL^{-1} of chromium concentration. The coefficients of molar absorptivity and Sandell's sensitivity are found to be 1.03×10^5 L mol^{-1} cm^{-1} and 0.000523 μg cm^{-2}, respectively where as the detection limit is 0.9 ng mL^{-1}. The method has been optimized for reaction conditions and optical parameters. Tolerance limits for various interfering ions were studied. The efficiency of the method was shown by successful determination of traces of chromium in alloy steel samples.

Keywords: Iminodibenzyl, Alloy steel, Chromium(VI), Spectrophotometry.

INTRODUCTION

Chromium finds application in metallurgical industry as alloying agent in steels to increase temper, hardness and resistance to corrosion [1]. Many techniques have been reported for estimating chromium at low concentration that includes titrimetry [2], complexometry [3], AAS [4], IR [5], amplification method [6], radiochemical method [7], NAA [8], ICP-MS [9], ICP-AES [10], electro-analytical methods such as potentiometry [11], amperometry [12], coulometry [13], polarography [14] and spectrophotometry.

Existing spectrophotometric methods that use oxidation of organic compounds [15,16] or development of ionic associates [17] suffer from elevated blank values. The most common reagent used in spectroscopy is diphenyl carbazide [18], but not without hindrances from interfering ions such as Fe^{3+}, Mo^{6+}, Cu^{2+} and Hg^{2+}. In addition, the developed complex becomes unstable beyond 30 min. The other coupling agents studied such as (2-pyridylazo)resorcinol, phenyl arsenazo, gallacetophenone oxime, citrazinic acid, *etc.* are undesirable as they are either carcinogens, less sensitive and/or tedious methods. In this article, a new heterocyclic organic compound iminodibenzyl has been proposed for the assaying of chromium in alloy steel samples.

EXPERIMENTAL

Systronics make Spectrophotometer (model No. 106) with 10 mm calibrated quartz cell was used for scanning. Cr(VI) stock solution (1000 μg mL^{-1}) was made by dissolving 0.2828 g potassium dichromate (Merck, Germany) in deionized distilled water and diluted to 100 mL. The working standard was made by suitable dilution.

Procedure: Aliquot containing 0.02-0.35 μg/mL equivalent of Cr(VI) was taken into a sequence of 10 mL volumetric flasks and 1 mL of iminodibenzyl (0.1 % w/v in ethanol) was added. The solution was left for about 5 min to complete the reaction and diluted to 10 mL using 10 M sulphuric acid. The highest colour intensity was observed after 5 min and the same was found to be stable up to 48 h. The absorbance was measured at 690 nm against the equivalent reagent blank and a calibration graph was plotted.

Sample preparation: About 1 g of sample alloy steel was weighed and dissolved in 10 mL of conc. HCl, followed by the drop wise addition of about 3 mL conc. nitric acid to assist the dissolution. When the vigorous reaction was completed, the solution was digested with gentle heating for about 15 min. The solution was then cooled and diluted to 100 mL, filtered through a Whatmann No. 541 filter paper, washed the residue on the filter paper with 1:20 hot HCl and washings were collected. 3-5 mL of 10 % (w/v) sodium hydroxide was added to precipitate Fe^{2+}, Cu^{2+}, Co^{2+} as their hydroxides and filtered the precipitate. This was then diluted to 250 mL and mixed thoroughly. 0.5 mL of the stock was then diluted to 100 mL in a calibration flask and 1 mL of the diluted stock was analyzed by the recommended procedure.

RESULTS AND DISCUSSION

Preliminary experiments showed that iminodibenzyl do not form any coloured species in hydrochloric acid or in acetic acid medium. Though, iminodibenzyl was found to form blue coloured species with Cr(VI) in both sulphuric acid and phosphoric acid medium at ambient temperature, the colour sensitivity in the latter is very low. Therefore, sulphuric acid medium was selected for further studies. The common interfering ions such as Fe^{2+}, Cu^{2+}, Co^{2+}, Mn^{2+}, *etc*. can be removed as their respective hydroxides with sodium hydroxide. The blue colour was deemed to be due to a radical cation.

Spectral characteristics of coloured product: Blue coloured product is formed by the reaction between Cr(VI) and iminodibenzyl in sulphuric acid medium. The absorption spectrum was obtained by scanning between 400-800 nm with respect to reagent blank. The value of λ_{max} was found to be 690 nm as shown in Fig. 1. The optical properties and precision studies are given in Table-1.

TABLE-1
OPTICAL PROPERTIES OF THE COLOURED PRODUCT

Parameter	Iminodibenzyl system
Colour	Blue
λ_{max} (nm)	690
Stability (h)	48
Beer's law range (μg mL^{-1})	0.02-0.35
Molar absorptivity (L mol^{-1} cm^{-1})	1.03×10^5
Sandell's Sensitivity (μg cm^{-2})	0.000523
Regression equation (Y)[a]	
Slope (a)	1.988
Intercept (b)	0.0098
Correlation co-efficient	0.9999
Relative standard deviation*	0.1547
Range of error (95 % confidence level)	± 0.0029
Detection limit (ng mL^{-1})	0.9

Y = ax + b, where × is the concentration of Cr(VI) in μg mL^{-1}; Relative standard deviation (n = 5); Range of error (95 % confidential level).

The precision of the proposed method was verified by considering actual determination of λ_{max} of five replicate samples having same amount of Cr(VI). The percentage of relative standard deviation was calculated and is presented in Table-1. The extent of accuracy was evaluated by analyzing different quantities of chromium within the Beer's law range.

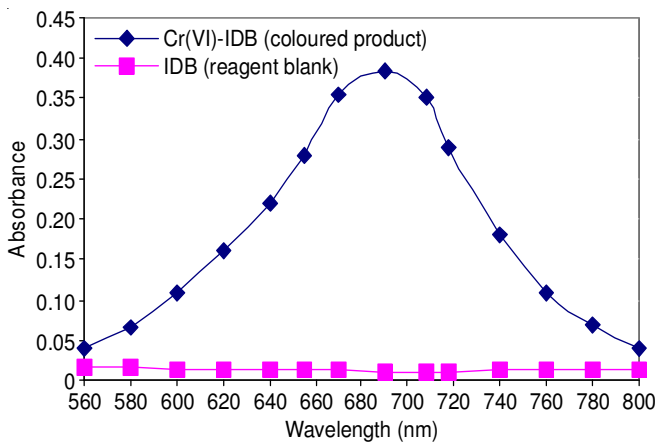

Fig. 1. Absorption spectrum: coloured product *vs.* reagent blank

Effect of iminodibenzyl concentration: This has been evaluated by adding different amounts of iminodibenzyl to 0.2 μg mL^{-1} chromium and then observing the absorbance. The optimal amount of iminodibenzyl for maximum was fixed at 1 mL at 690 nm. The addition of excess iminodibenzyl leads to the decrease in colour intensity, but higher concentration of iminodibenzyl above 0.01 % develops green colour in sulphuric acid medium probably due to reduction of Cr(VI) to Cr(III). Hence, 1 mL of 0.01 % iminodibenzyl was used in final volume of 10 mL for 0.2 μg mL^{-1} of Cr(VI).

Colour stability: No appreciable changes were noted in λ_{max} when the temperature is varied between 10 and 80 °C. As stated earlier, the colour was found to be steady for 48 h, however maximum and stable absorbance was achieved after 5 min.

Analytical characteristics: λ_{max} of the coloured product over varying concentration of chromium was tabulated. The calibration graph appears straight line between 0.02-0.35 μg mL^{-1} of chromium. These measurements were carried out with respect to corresponding reagent blank.

The molar absorptivity at 690 nm was 1.03×10^5 L mol^{-1} cm^{-1}. Beer's law range, Sandell's sensitivity and other analytical properties were evaluated. The ideal concentration range for optimal spectrophotometric measurement, as evaluated by Ringbom plot was 0.03-0.3 μg mL^{-1} of Cr(VI). Ionic nature of Cr(VI)-iminodibenzyl species in sulphuric aid medium was determined by ion exchange experiment. When 10 mL of solution of blue Cr(VI)-iminodibenzyl species in sulphuric acid medium was passed through DOWEX 50 W-X8 anion exchange column (26 × 11.5 cm), the blue colour was completely absorbed and the evaluate was colourless, indicating the Cr(VI)-iminodibenzyl coloured species in sulphuric acid medium is cationic in nature.

Effect of foreign ions: The interference from common excipient ions in stainless steel was evaluated to study their impact in the proposed method. This was done by introducing definite amounts of each ion to a fixed chromium concentration and analyzing spectrophotometrically. The tolerance limit is ideally considered as the amount of foreign substances which can cause an error of 2 % in optical density (Table-2). Interestingly, metal ions such as Fe^{2+}, Fe^{3+}, Mn^{2+}, Cu^{2+}, *etc*. which interfered strongly with most of the other reported methods showed no interference.

Conclusion

The reported method has been validated by applying the same on stainless steel variants for evaluating concentration

TABLE-2
EFFECT OF EXCIPENTS

Foreign ion	Tolerance limit (μg mL^{-1})
EDTA	2000
[a]Mn^{2+}	800
Cd^{2+}, Mg^{2+}, Cl^-, [a]Cu^{2+}, [a]Co^{2+}, [a]Fe^{2+}, Sulphamic acid	400
Na^+, K^+, Hg^{2+}, Zn^{2+}, perchlorate	250
Al^{3+}, CO_3^{2-}, Acetate, Tartarate	200
[b]Ca^{2+}	100
NO_2^-, Ni^{2+}	50

[a]Metals are precipitated and filtered as their hydroxides by the addition of sodium hydroxide, prior to the addition of reagents.
[b]Precipitate formed, filtered and recorded the absorbance

TABLE-4
COMPARATIVE STUDY WITH REPORTED METHODS

Reagent	λ_{max} (nm)	Range (μg mL^{-1})	Molar absorptivity (L mol^{-1} cm^{-1})	Remarks	Ref.
3-(2-Pyridyl)-5,6-*bis*(5-(2-furyl disulfonic acid)-1,2,4-triazine disodium salt	593	1-40	3.5×10^4	Less sensitive, Interference from CN^-, NO_2, EDTA and citrates	[19]
Sulphanilamide–Saccharin	390	-	2.63×10^4	Complicated reaction involving	[20]
p-Nitroaniline–Saccharin	372	-	5.40×10^4	diazotization at 4 °C	[20]
4-(2-Thiazolylazo)resocinol	545	-	2.73×10^4	Microwave conditions required	[21]
Cyclam	379	-	1.60×10^4	pH dependent	[22]
Variamine blue	556	2-12	9.11×10^3	Less sensitive, pH dependent	[23]
Iminodibenzyl	690	0.02-0.35	1.03×10^5	Simple & sensitive	Proposed method

of chromium and the results are tabulated in Table-3. Iminodibenzyl appears to be a better choice as coupling agent for spectrophotometric study as evidenced by the comparative study given in Table-4. Further, recovery studies testify that the proposed method can be used successfully for the determination of chromium in steel alloys.

TABLE-3
DETERMINATION OF CHROMIUM IN STAINLESS STEEL

Samples	Cr (%)	Amount	Recovery (%)
GKW Steel, India (0.05 g/100 mL); C 0.54, Mn 0.89, S 0.008, P 0.034, Si 0.033, V 0.13[a]	1.02	1.018	99.7
Stainless steel no. 394 (0.05 g/100 mL); Ni 8.12, Fe 70-71[b]	18.0	18.08	101.2
Ferrochrome Cr 65, Fe 35	65.0	64.89	99.8

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