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Extraction-Spectrophotometric Determination of Chromium(VI) with Hydroxyamidines

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A new, simple, rapid, and selective spectrophotometric method for determining Cr(VI) by extraction with hydroxyamidines in chloroform over 0.2—0.8 M HCl is described. The molar extinction coefficient of the complexes of Cr(VI) with 10 different hydroxyamidines lie in the range of $(1.30—1.52)\times10^4$ l mol^{-1} cm^{-1} at λ_{max} 390—400 nm. Of these, the simplest compound, *N*-hydroxy-*N*,*N*′-diphenylbenzamidine (HDPBA) has been chosen for the detailed studies. The limit for detection is 0.1 μg Cr/cm^3. The composition of the complex, and the effect of solvents, acids and diverse ions on the extraction of the metal are discussed. The method is free from interference of most of the metal ions except Mn(VII) which is removed by reducing with sodium nitrite. The method has been applied for determination of chromium(VI) to water samples containing the metal at ppb levels.

Chromium exists in two stable oxidation states Cr(III) and Cr(VI). Trivalent Cr is not as toxic as hexavalent Cr and it is also considered essential for maintenance of the glucose tolerance factor of the body whereas hexavalent Cr is a serious health hazard.[1] Chromium(VI) causes skin irritation resulting in the dermatitis and ulcer formation, adverse effect in the lungs, and interference in the sulfur uptake of the cells.[2-4] Therefore, a number of spectrophotometric methods for the determination of Cr in a variety of complex materials are reported.[5-14] Of these, the chromate and 1,5-diphenylcarbonohy-drazide methods are frequently used for determination of the metal. The first method is not sensitive and suffers from interference of e.g., Fe, Cu, U, Ce, etc.[5] The selectivity and sensitivity of its extraction method with large cations is also poor.[6-8] The diphenylcarbazide method is highly sensitive but involves the serious interference of many metal ions e.g. Fe(III), Cu(II), V(V), Mo(VI), Ce(IV), Hg(II), Ag(I), etc.[9-10] Numerous other reagents i.e. 8-quinolinol, tributyl phosphate, tropolone, and 2-(5-bromo-2-pyridylazo)-5-(diethylamino)phenol are claimed for the determination of the metal but subjected to interference of common ions e.g. Cu, Hg, Fe, Bi, Pd, V, U, etc., and some experimental difficulties e.g. rigidity of pH or temperature.[11-14] Therefore, in this paper, hydroxyamidines (HOA) are proposed for extraction-spectrophotometric determination of Cr(VI) in industrial waste water. They quantitatively extract the metal over 0.2—0.8 mol dm^{-3} HCl. The method is reproducible and removes the most of the interference of established methods above. It enhances the sensitivity of the classical chromate method approximately three folds with improved selectivity.

Experimental

Apparatus. A Varian DMS-100 UV-VIS Spectrophotometer matched with 1-cm quartz cells was employed for the absorbance measurements.

Reagents. All reagents used were of analytical grade (E. Merck). A standard solution of Cr(VI) was prepared by dissolving 0.283 g $K_2Cr_2O_7$ in deionized water and diluted to 100 cm^3. Hydroxyamidines were synthesized as in the literature[15] and their 0.007 mol dm^{-3} solution in chloroform were used. A 5 mol dm^{-3} HCl acid was employed to maintain the acidity.

Procedure. An aliquot of the solution containing 5—90 μg Cr(VI) is taken in a 100-cm^3 separatory funnel and treated with 1 cm^3 HCl acid. The aqueous solution is diluted to 10 cm^3 with deionized water, and shaken with 10 cm^3 chloroform solution of hydroxyamidine for 2 min. The extract is separated and dried over anhydrous sodium sulfate. The aqueous phase is repeatedly washed with two fresh portions of 3 cm^3 chloroform. All extract is combined and transferred to a 25 cm^3 volumetric flask and the volume is made upto the mark with chloroform. A reagent blank is prepared similarly and used as reference to measure the absorbance of the complex.

Results and Discussion

Absorption Spectra. The absorption spectra of Cr(VI)-HDPBA complex against the reagent blank and that of the reagent blank in chloroform are shown in Fig. 1. The complex exhibits the absorption maximum around 390 nm. The reagent blank has high absorption at this region, hence it was used as a reference for all further measurements.

Effects of Acids. The effect of various acids e.g. HCl and H_2SO_4 on the extraction of the metal with HDPBA into chloroform were examined. The extraction of the metal is quantitative with these two acids but the absorbance of the extract was relatively higher with HCl, hence it was selected for the detailed studies. The optimum acidity range is found to be 0.2—0.8 mol dm^{-3} HCl, and all experimental work was carried out at 0.5 mol dm^{-3}.

Effect of Solvents. The effect of various solvents on the extraction of the metal with HDPBA was examined. The complex could be quantitatively extracted in solvents 1-pentanol (PN), (ε, 900; λ_{max} 380 nm); ethyl acetate (EA) (ε, 800; λ_{max} 390 nm); isobutyl-

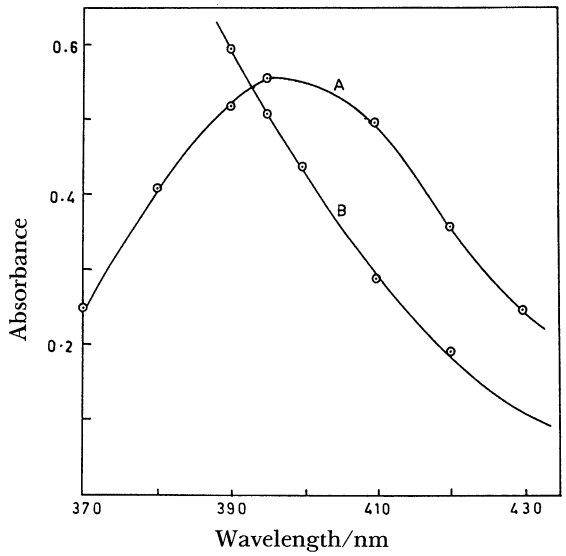

Fig. 1. Absorption spectra of the complex and the reagent blank in chloroform. (A), Cr(VI)-HDPBA complex, $C_{Cr(VI)}=3.8\times10^{-5}$ mol dm^{-3}. (B), the reagent blank, $C_{HDPBA}=2.7\times10^{-3}$ mol dm^{-3}.

methylketone (IBMK) (ε, 1200; λ_{max} 380 nm); diethyl ether (DEE) (ε, 9500; λ_{max} 380 nm); cyclohexane (CH) (ε, 5300; λ_{max} 375 nm); carbon tetrachloride (CTC) (ε, 6300; λ_{max} 370 nm); chloroform (C) (ε, 14500; λ_{max} 395 nm); benzene (B) (ε, 9700; λ_{max} 390 nm); and toluene (T) (ε, 11100; λ_{max} 380 nm). Of these, chloroform was chosen as diluent due to easy handling, high color intensity of the complex, high distribution of the reagent (B, T, CT) and selective extraction of the metal (PN, EA, IBMK, DEE, CH).

Percentage Extraction. A known amount of Cr(VI) (20, 50, and 80 μg) is extracted separately as in the procedure. The extract is separated out and the metal left in the aqueous phase is determined by spike method with 1,5-diphenylcarbonohydrazide.[5] The percentage extraction of the metal with HDPBA in chloroform is found to be 99.2% in a single extraction.

Effect of Reagent, Dilution, Electrolyte, and Standing Time. In order to get the maximum extraction of the metal at least 0.005 mol dm^{-3} HDPBA in chloroform is necessary. The color intensity of the complex remains unaffected upto 0.009 mol dm^{-3}. Hence, all extraction was carried out with 0.007 mol dm^{-3} HDPBA. The order of addition of reagents is not critical. The color intensity of the complex remains constant over a volume ratio of the organic to the aqueous phase 1 : 0.5 to 1 : 3.5. No adverse effect on the extraction of the metal upto 1 mol dm^{-3} of KCl or NH_4Cl was noticed. The extract is stable for at least 3 h at room temperature (27±2 °C). An equilibration time of 1 min is sufficient for complete extraction of the metal and prolonged extraction upto 10 min causes no adverse effect.

Hydroxyamidines as Extractants. The potentiality of 10 different hydroxyamidines towards the extraction of Cr(VI) in chloroform was examined. The introduction of the substituents e.g. Cl, CH_3 in the phenyl rings of *N*-hydroxy-*N*,*N*′-diphenylbenzamidine (HDPBA) does not much affect the spectral properties of the extracted complexes as shown in Table 1. The value of molar extinction coefficient with these hydroxyamidines lie in the range of (1.30—1.52)×10^4 l mol^{-1} cm^{-1} at λ_{max} 390—400 nm. Of these, the simplest compound, *N*-hydroxy-*N*,*N*′-diphenylbenzamidine (HDPBA) has been chosen for the detailed studies. The detection limit of the method is 0.1 μg Cr/cm^3 with HDPBA. The system

Table 1. Spectral Data of Cr(VI) with Various Hydroxyamidines

S.No.	Compound	λ_{max}	ε
		nm	L·mol^{-1}cm^{-1}
1.	*N*-Hydroxy-*N*,*N*′-diphenylbenzamidine	395	14500
2.	*N*-Hydroxy-*N*-(4-tolyl)-*N*′-(2,4-xylyl)-2-chlorobenzamidine	395	14500
3.	*N*-Hydroxy-*N*-(2-chlorophenyl)-*N*′-(2,5-xylyl)benzamidine	390	13000
4.	*N*-Hydroxy-*N*-(4-chlorophenyl)-*N*′-(3-chloro-4-methylphenyl)benzamidine	400	13000
5.	*N*-Hydroxy-*N*-(4-chlorophenyl)-*N*′-(2,3-xylyl)benzamidine	390	13500
6.	*N*-Hydroxy-*N*-(4-chlorophenyl)-*N*′-(4-tolyl)-2-chlorobenzamidine	400	15200
7.	*N*-Hydroxy-*N*-(3-tolyl)-*N*′-(2,3-xylyl)-2-chlorobenzamidine	390	14400
8.	*N*-Hydroxy-*N*-(4-chlorophenyl)-*N*′-(4-chloro-6-methylphenyl)-4-methylbenzamidine	395	13200
9.	*N*-Hydroxy-*N*-(4-tolyl)-*N*′-phenyl-2-chlorobenzamidine	400	13300
10.	*N*-Hydroxy-*N*-(4-tolyl)-*N*′-phenyl-4-methylbenzamidine	395	13200

obeys Beer's law over the range of 0.2—3.6 ppm Cr. The precision of the method was evaluated by taking 10 replicate measurements at level of 2 ppm Cr in chloroform and the rel. std. dev. was found to be ±1.2%.

Extraction Mechanism of the Complex. The solid complex was synthesized by mixing Cr(VI) and the ethanolic solution of HDPBA in 1 : 2 molar ratio at 0.5 mol dm^{-3} HCl. The complex formed was filtered and dried. The complex was analyzed by the acid digestion and elemental analysis techniques. The results obtained correspond to the empirical formulae, $[CrO_2(OA)_2]$. The composition of the complex was further verified by curve fitting method by plotting $\log D$ (distribution ratio of the metal) vs. log concentration of HDPBA in chloroform, Fig. 2. This curve shows a slope of 1.9, very close to integer 2 and supports the formation of above complex in chloroform. It is assumed that -OH groups of H_2CrO_4 are substituted by OA^- (where HOA denotes the monobasic, bidentate chelating agent: hydroxyamidine) in the fashion similar to replacement of -OH by Cl^-, Br^-, HSO_4^-, $H_2PO_4^-$, etc.[16] The probable reaction mechanism may be expressed as:

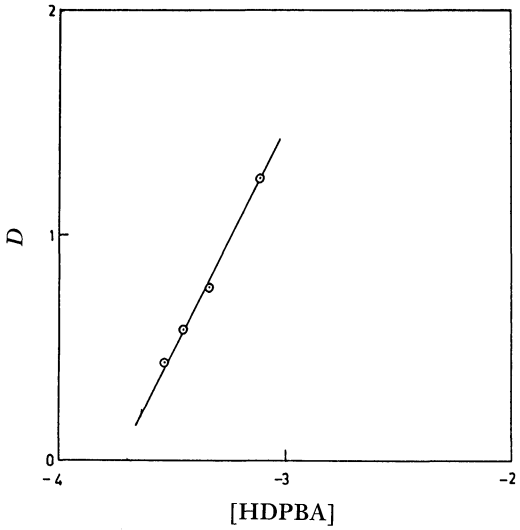

Fig. 2. Determination of ratio of the metal to the reagent in the extracted complex.
C_{HCl}=0.5 mol dm^{-3}, $C_{Cr(VI)}$=9.61×10^{-5} mol dm^{-3}, $\log D$ versus log C_{HDPBAo}.

$$H_2Cr_2O_7 + 4HOA_o \rightleftarrows 2[CrO_2\cdot(OA)_2]_o + 3H_2O$$

The relation between D and K is

$$K=\frac{D[CrO_2(OA)_2]_o}{[HOA]_o^4}=\frac{D[CrO_2\cdot(OA)_2]_o}{\left[\frac{Kd(HOA)_T}{1+kd}\right]^4}$$

where subscripts o, $[HOA]_o$, $[HOA]_T$, kd, D, and K denote to the organic phase, concentration of hydroxyamidine in chloroform, total analytical concentration of hydroxyamidine taken, distribution ratio of the reagent, distribution ratio of the metal, and conditional extraction constant, respectively. The value of Kd, D, and K are found to be 20.33, 124, and 1.16×10^{13} respectively at temperature 23±2 °C.

Effect of Diverse Ions. The effect of various diverse ions on the extraction of the metal was studied as described in the procedure. The results show that a number of common metal ions do not interfere in determination of the metal. Manganese(VII) seriously interferes in the determination of Cr(VI). The tolerance limit of various diverse ions causing an error less than 2% in the determination of 50 μg Cr(VI) are summarized in Table 2.

Application of the Method. The method has been applied for the determination of Cr(VI) in industrial waste water obtained from Electrode Adwani Orelikan

Table 2. Effect of Diverse Ions on the Determination of 50μg Chromium(VI)

Ion added	Tolerance limit /ppm
Zn(II), Ni(II)	800
F^-, EDTA, $S_2O_7^{2-}$, citrate	400
Be(II), La(III), Zr(IV), NO_2^-	200
Oxalate	160
Br^-, PO_4^{3-}	120
Co(II)	80
Al(III), Sb(III), NO_3^-	20
W(VI)	5 (28)[a]
Cu(II), Pb(II), Hg(II), Bi(III), Fe(III), U(VI)	20
Re(VII)	16
Mn(VII)	10[b]
Tl(I), Sb(III)	10
Cd(II)	5
Mo(VI)	(4)[c]

a) Masked with NaF (4 mg). b) reduced with $NaNO_2$ (1 mg). c) masked with citrate (4 mg).

Table 3. Determination of Chromium(VI) in Water Samples

Sample[a]	Volume of sample taken	Cr(VI) added	1,5-Diphenylcarbonohydrazide method		Present method		
			Cr(VI) found	Cr(VI) content present	Cr(VI) found	Cr(VI) content present	Rel. std. dev.
	ml	ppb	ppb	ppb	ppb	ppb	∓%
PWW	500	500	526	26	525	25	1.2
TWW	500	500	515	15	514	14	1.3

a) PWW=plant waste water; TWW=total waste water. b) Five determinations were made.

plant, Raipur. A known volume of the sample is taken, its volume is reduced to about 10 ml and the amount of Cr(VI) is determined by standard spike method as in the procedure. The results of analyses are compared with 1,5-diphenylcarbonohy-drazide method[5] and results are shown in Table 3.

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