Extraction-Spectrophotometric Determination of Chromium(VI) with Hydroxyamidine and Amides

C. Agarwal[a]; K. S. Patel[a]; R. K. Mishra[a]

[a] Department of Chemistry, Ravishankar University, Raipur, M.P., India

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EXTRACTION-SPECTROPHOTOMETRIC DETERMINATION OF CHROMIUM(VI) WITH HYDROXYAMIDINE AND AMIDES

C. AGARWAL, K. S. PATEL and R. K. MISHRA

Department of Chemistry, Ravishankar University, Raipur, 492 010, M.P., India

A new method for selective extraction and spectrophotometric determination of micro-gram amount of chromium(VI) with N-hydroxy-N,N'-diphenylbenzamidine (HOA) and N-aryl-acetamides (HL) in coal dust, coal ash, cement dust and industrial waste water is described. It is based on chloroform extraction of $[CrO_2.(OA)_2]$ 2HL complex from 0.3–0.6 M hydrochloric acid solution. The molar absorptivity of $[CrO_2.(OA)_2]$ complex, with three different amides in chloroform, lies in the range of $(1.1–1.3) \times 10^4$ $l.mole^{-1}cm^{-1}$ at λ_{max}, and of these, the simplest amide, N-phenylacetamide (PAA) has been selected for the detailed studies. The detection limit of the method is 0.01 μg Cr/ml. The relative standard deviation of the method for the recovery of the metal in the environmental samples is found to be in the range of ± 0.8 to 1.3%. The effect of diverse ions on the determination of the metal were examined. Most of the common metals except Mn(VII) were not found to interfere.

KEY WORDS: Spectrophophotometry, extraction, chromium(VI), coal ash, coal dust, cement dust, industrial waste water.

INTRODUCTION

Chromium(VI) is a toxic metal and its determination in a variety of environmental samples is of great importance. Several spectrophotometric methods for determination of the metal have been reported.[1–8] Of these, chromate and diphenylcarbazide methods are widely applicable for the routine analysis. The chromate method suffers from serious interference of coloured ions, i.e. Fe, Cu, U, etc. and its sensitivity is poor.[1] Diphenylcarbazide is a sensitive reagent, however it involves the interference of Fe(III), V(V), Mo(VI), Cu(II), etc. and the coloured ions that absorb at λ_{max} of the complex.[1–3] Pentamethylenebis (triphenyl-phosphonium) cation and cyclohexane-1,3-dione-bithiosemicarbazone monohydro-chloride were claimed for the extraction-spectrophotometric determination of Cr(VI) in the UV region but it also suffers from interference of some metal ions.[4, 5] Phenylflurone was also used for spectrophotometric determination of Cr(VI) through ion-pair formation but the sensitivity is not good.[6] 3-4-(5-Bromo-2-pyridylazo)-3-hydroxy-N-propylanilino propanesulphonic acid is a sensitive reagent for the determination of Cr but the pH range is critical and the metal ions, i.e. Co, Ni, V and U interfere.[7] PAR with xylometazolonium cation was reported for microdetermination of the metal at high temperature and involved the interference of many metal ions.[8] Therefore, in this communication we report a

new, simple and rapid method for selective extraction and spectrophotometric determination of Cr(VI) in micro-gram amounts with N-hydroxy-N,N'-diphenyl-benzamidine (HOA) in the presence of three N-arylacetamides (HL) from hydrochloric acid solutions. This method is highly reproducible and free from interference of most of the metal ions that cause interference in the established methods cited above.

EXPERIMENTAL

Apparatus

A Varian DMS 100 UV-VIS (double beam) spectrophotometer equipped with 1-cm quartz cuvettes were used for absorbance measurements.

Chemicals

The stock solution of Cr(VI) was prepared by dissolving 0.7070 g potassium dichromate in de-ionized water and made up to 250 ml. The hydroxyamidine was prepared as described in the literature.[9] A chloroform solution of the reagents containing 0.14%, w/v (0.005 M) hydroxyamidine and 0.5%, w/v N-arylacetamide was used for the extraction work. All chemicals used were of analytical grade reagents (BDH/E. Merck).

Procedure

Add 1.5 ml of 5 M HCl to a solution containing 50 μg of Cr(VI) and dilute to 15 ml with de-ionized water in a 150-ml separatory funnel. Extract the aqueous phase with 15 ml chloroform solution of the reagents for 2 min. Dry the extract over anhydrous sodium sulphate (2 g) in a 25-ml beaker. Wash the aqueous layer with 3×2 ml fresh portion of chloroform. Transfer all the extract to a 25-ml volumetric flask and dilute to the mark with chloroform. Measure the absorbance of the complex at λ_{max} against the reagent blank.

RESULTS AND DISCUSSION

Absorption Spectra

The absorption spectra of the ternary complex formed among Cr(VI), HOA and PAA, and that of the reagent blank are shown in Figure 1. The complex exhibits the wavelength of maximum absorption at 408 nm in chloroform. The reagent blank has some absorption in this region and so it was employed as a reference for all measurements.
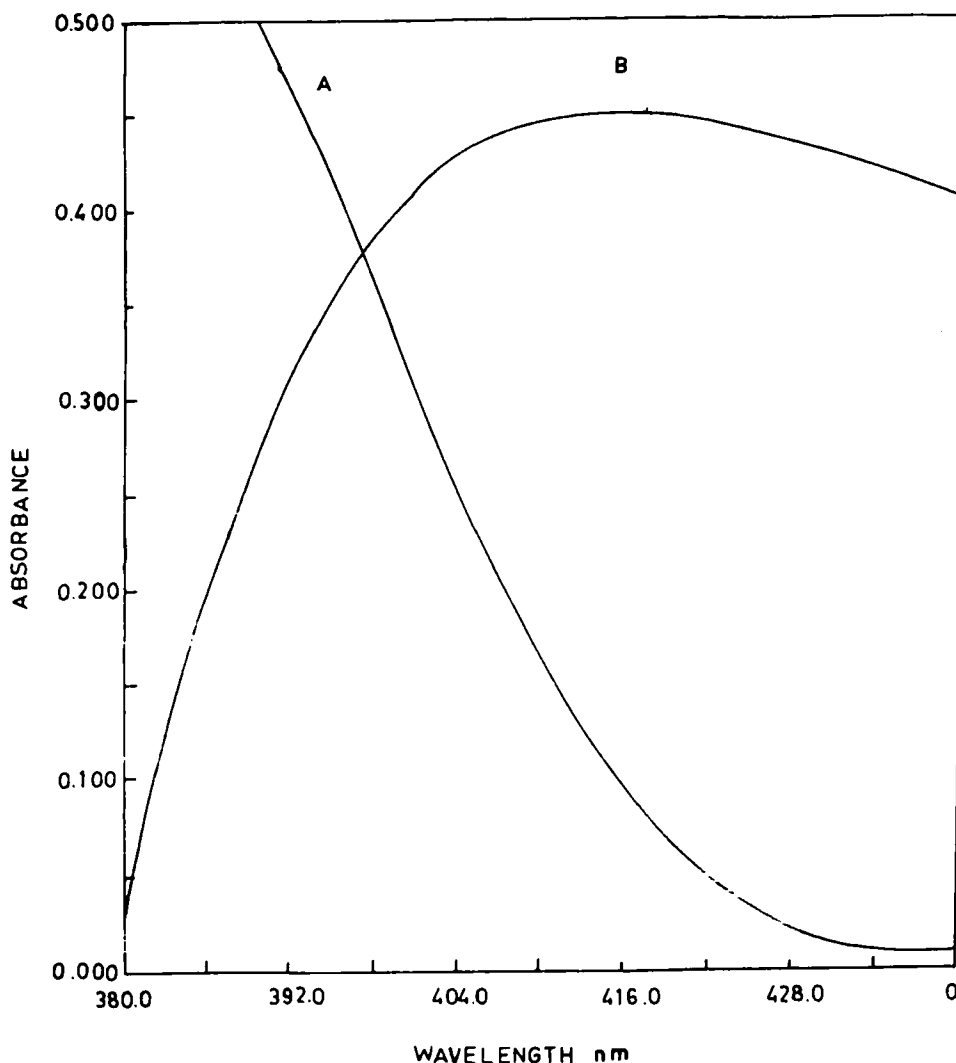
Figure 1 Absorption spectra of the reagent blank and its ternary complex in chloroform. $C_{HCl} = 0.5$ M; $C_{HOA_0} = 0.005$ M; $C_{PAA_0} = 0.037$ M. (A), The reagent blank; (B), Cr(VI)-HOA-PAA complex; $C_{Cr} = 2.51 \times 10^{-4}$ M.

Effect of Solvents

The effect of various solvents like carbon tetrachloride, chloroform, benzene, toluene, ethyl acetate, cyclohexanone and methylisobutyl ketone on the extraction of the ternary complex were tested. All of them quantitatively extract the complex with different values for the absorption maximum and molar absorptivity. Of these, chloroform gives the strongest hyper- and bathochromic shift of the complex and therefore, it was used for further extraction work.

Table 1   Spectral data of $[CrO_2(OA)_2]$ complex with various amides in chloroform at λ_{max} 408 nm

Amide	ε $l.mole^{-1}cm^{-1}$	Sandell's sensitivity, $\mu g\,Cr/cm^2$
$CH_3CO.NH.C_6H_5$	11,800	0.0044
$CH_3CO.NH.C_6H_4$-4-CH_3	13,000	0.0040
$CH_3CO.NH.C_6H_3$-2,5-$(CH_3)_2$	11,000	0.0047

Effect of Acids and Dilution

The effect of acids (e.g., HCl, H_2SO_4 and HNO_3) on the extraction of the metal were examined. Of these, hydrochloric acid was used for further extraction because of higher colour intensity of the extract. The optimum acidity range is found to be 0.3–0.6 M HCl. The effect of variation in the volume ratio of the organic to aqueous phase was studied and the full colour development was observed when the ratio of the organic to aqueous phase was from 3:1 to 3:4.

Effect of Amount of Reagents, Time and Temperature

The effect of reagent concentration on the extraction of the metal were examined. At least 0.0034 M HOA and 0.025 M PAA in chloroform were necessary for the full colour development and a further addition up to 0.007 M HOA and 0.06 M PAA had no adverse effect. The sequence in which reagents were added is not critical. A shaking time of 2 min is sufficient for full extraction of the metal and further extraction up to 10 min did not affect the spectral properties of the complex. The extract is stable for a least 1 hr at room temperature. The temperature variation on the extraction of the metal was investigated and a full extraction was marked over temperature range from 10 to 40 °C.

Effect of Amide

The effect of nature of amides, e.g. N-arylacetamides, N-arylbenzamides on the extraction of the metal was studied. Of these, only N-phenylacetamide, N-(4-methylphenyl)acetamide and N-(2,5-dimethylphenyl)acetamide are able to cause a bathochromic shift of the complex (Table 1). The nature of amides does not practically affect the position of λ_{max} of the complex that lies around 408 nm. However the value of molar absorptivity of the complex in chloroform is affected and found to be in the range of $(1.1–1.3) \times 10^4\,l.mole^{-1}cm^{-1}$. The addition of amide on the extraction of the metal has two advantages. First, it causes a

bathochromic shift of the complex ($\approx 13\,\text{nm}$) where the reagent blank has not much absorption and thereby the reproducibility of the system is enhanced. Secondly, it stabilises the complex against the variation in temperature, amount of reagents or dilution, diverse ions, etc.

Quantitative Extraction of the Metal

A 150, 500 and 1,000 μg Cr(VI) is extracted with 15 ml chloroform solution of the reagents as in the procedure. The extract is evaporated, destroyed with acids, oxidized by sodium persulphate in the presence of silver ions and the metal content is determined with diphenylcarbazide.[1] The recovery was 149, 496 and 993 μg Cr(VI) and these data show that the extraction is quantitative.

Detection Limit, Optimum Concentration Range and Precision of the Method

The detection limit of the method is 0.01 μg Cr/ml with HOA and PAA. The optimum concentration range on the basis of Beer's law is 0.3–4.0 μg Cr/ml. The precision of the method for ten replicate measurements at 2 ppm levels is found to be $\pm 1.0\%$.

Composition and Extraction Mechanism

The binary complex is prepared by taking a known amount of Cr(VI) in a 400-ml beaker and reacted with at least two-fold molar excess of HOA (in 20 ml of ethanol) at 0.4 M HCl in a total aqueous volume of 200 ml at room temperature. The complex is digested over water bath at 60 °C, and is filtered and washed out with dilute ethanol (5%, w/v) and de-ionized water. The colour of the complex is yellowish brown and its m.p. is 86 °C.

The ternary complex is prepared as above in the presence of 0.025 M PAA. It is a greenish yellow coloured compound with m.p. of 105 °C.

The molar absorptivity of the solid binary and ternary complexes in chloroform are 14,000 (at λ_{max} 395 nm) and 11,800 l.mole^{-1}cm^{-1} (at λ_{max} 408 nm) respectively and found to be the same as those of extracted complexes.

A known amount of the complexes are destroyed with acids, oxidized with potassium persulphate and the metal content is determined with diphenylcarbazide as in the literature.[1] The results obtained correspond to the empirical formulae [CrO$_2$.(OA)$_2$] and [CrO$_2$.(OA)$_2$] 2 PAA for binary and ternary complex respectively. The ratio of Cr to HOA in the ternary complex has also been determined by plotting log D vs log [HOA] (Figure 2). However, the ratio of Cr to PAA could not be determined by conventional methods. The probable overall extraction mechanism can be written as:
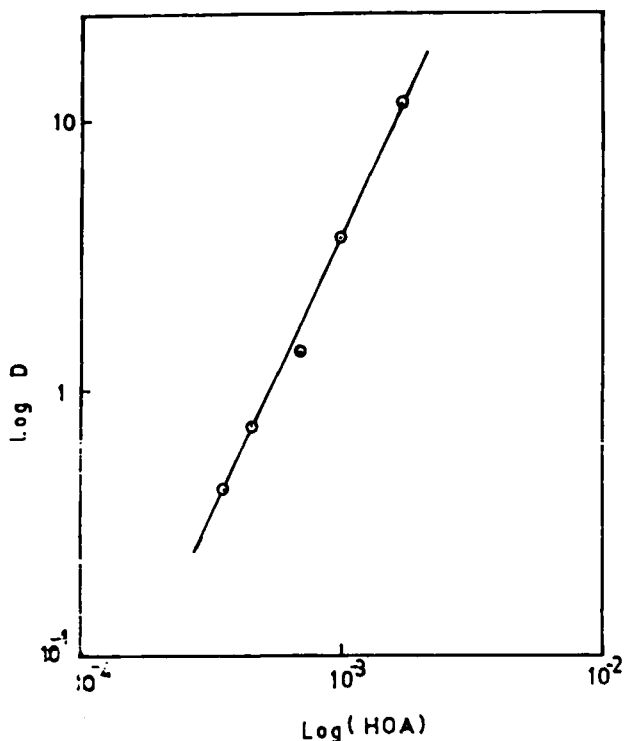
$$Cr_2O_7^{2-} + 4\,HOA_0 + 4\,PAA_0 + 2\,H^+ \rightleftharpoons 2\,[CrO_2.(OA)_2]\,2PAA_0 + 3\,H_2O$$
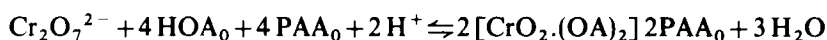
Figure 2 Determination of ratio of Cr to HOA in the complex. $C_{HCl} = 0.5$ M; $C_{Cr} = 4.37 \times 10^{-4}$ M; $C_{PAA_0} = 0.037$ M; $\log D$ vs $\log[HOA]_0$.

where subscripts 0, HOA and PAA denote the organic phase hydroxyamidine and amide respectively.

Effect of Diverse Ions

The effect of diverse ions in the determination of 50 μg of Cr(VI) were examined. Of various ions tested, only Mn(VII) and Ce(IV) are found to interfere seriously. The tolerance limit of other ions in ppm causing error less than 2% are shown in parenthesis as: Be^{2+} (200); Fe^{3+}, W^{6+}; V^{5+}, Cu^{2+}, Pb^{2+} (20); Ni^{2+} (800); Co^{2+} (80); Zn^{2+} (1,200); Zr^{4+} (220); Mo^{6+} (3); Cd^{2+} (50); Sb^{3+} (55); La^{3+} (60); Hg^{2+} (10); Bi^{3+} (15); U^{6+} (17); F^- (400); NO_3^- (40); Br^- (120); oxalate (180); phosphate (160); EDTA (400).

Application of the Method

The method has been applied for the recovery of Cr(VI) to the environmental samples, i.e. coal dust, coal ash, cement dust and industrial waste water as shown in Table 2. The coal and cement samples are digested with aqua regia and the

Table 2 Application of the method for the determination of the metal

Sample	Cr(VI) added μg	Found by this method		Found by diphenyl-carbazide method		Rel[a] Std. dev. ±%
		μg	ppb	μg	ppb	
a	50	67.11	212.68	65.23	206.72	1.2
b	40	43.88	177.78	41.69	173.90	1.3
c	40	46.66	162.45	45.82	159.52	1.2
d_1	25	42.00	528.64	41.37	520.71	1.0
d_2	25	44.44	604.42	43.20	587.55	0.8

[a]Five estimations are made.

a, b and c are cement dust, coal dust and coal ash obtained from Mandhar Cement Plant, CCI, Raipur, India.

d_1 and d_2 are industrial waste water obtained from Singhania Steels and Adwani Oerlikon, Raipur, respectively.

excess of nitric acid is removed by concentrated hydrochloric acid. Then the dry sample is dissolved in de-ionized water and the metal content is determined by standard addition method as described in the procedure. In the case of water sample, known volume (20 ml) is taken and evaporated to about 10 ml and the metal content is determined as above. For comparison of the data, the metal in these samples is also determined by diphenylcarbazide after prior separation with HOA as in the procedure. The extract is evaporated to dryness, destroyed with acids, oxidized by potassium persulphate in the presence of silver ions and determined.

Acknowledgement

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