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Estimation of chromium (VI) from industrial effluents- a solvent extraction study

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ABSTRACT

Out of the two most stable forms of Chromium hexa valent one considered as a serious health hazard and it has attracted attention as a pollutant in natural waters. The sources of contamination of chromium in natural waters and in the Environment are from electroplating, tanning industries and waste solution from oxidative dyeing and leaching from sanitary land – fills, In view of this the separation and determination of chromium has been receiving considerable attention. Solvent extraction of Chromium (VI) from phosphoric, acetic, oxalic and perchloric acid solutions with Tributyl amine (TBA) in chloroform has been studied. The optimum conditions for extraction were established from the study of the effect of several variables like concentration of extractant, metal ion, acidity, diluent etc. The extractions are nearly quantitative with acetic and oxalic acid & are partial from phosphoric and perchloric acid systems. The extracted species are identified. An attempt has been made to determine chromium in natural as well as electroplating wastets.

Key Words: Extraction, chromium (VI), Tributyl amine, mineral acid, Electroplating wastes.

INTRODUCTION

Chromium is an important non-ferrous metal with high corrosion resistance finding its application in electroplating, tannery, chloral kali industries etc. Several workers[1-7] reported the extraction of Chromium(VI) using tertiary amines. There are no reports appeared in literature on the extraction of chromium (VI) by tri butyl amine. The present communication describes our studies on the extraction of chromium (VI) by tri butyl amine (TBA) from phosphoric, acetic, oxalic and perchloric acid solutions.

EXPERIMENTAL SECTION

TBA Merck sample (Molecular wt. 185.35, B.P 216 ^{0}C, purity 99%) was used as such without any purification. A stock solution of TBA (0.35 M) in chloroform was prepared and diluted appropriately to get the required concentration. Chromic Acid (E. Merck grade) was used for the preparation of chromium (VI) stock solution.

All other chemicals used were of A.R. Grade or samples purified according to the standard methods.

Chromium (VI) Extraction :
An aqueous solution (10ml) of Chromium (VI) containing appropriate concentrations of chromic acid (1.0×10^{-3}M) and the acid has equilibrated with an equal volume of TBA (0.05 M) in chloroform pre equilibrated with 0.1 M mineral acid. The chromium (VI) concentration in the aqueous phase before and after extraction was estimated spectrophotometrically [8] by measuring the absorbance of Cr (VI) -DPC complex at 540 nm. The equilibrium chromium (VI) concentration in the organic phase was determined by taking the difference in the initial chromium concentration in the aqueous phase. The results obtained on the extraction of chromium (VI) as a function of aqueous phase concentration of various acid solutions are presented in Table–1.

RESULTS AND DISCUSSION

Effect of Acidity: The distribution ratio of chromium (VI) in the case of acetic and oxalic acid solution increases with increasing acidity up to 0.5 M (Maximum extraction) followed by decreasing in efficiency. On the other hand Kd decreases gradually with increasing acidity in the case of phosphoric acid solutions and perchloric acid under the experimental conditions (Table.1).

Table.-1: Percentage Extraction of Cr(VI) with TBA

[Cr(VI)] = 1.0×10^{-3} M *[TBA] = 5.0×10^{-2} M*

Molarity (M)	H_3PO_4 %Extn	ACOH %Extn	OXALIC %Extn	$HClO_4$ %Extn
0.1	85.25	87.50	99.98	82.12
0.25	84.20	95.72	99.96	80.54
0.5	82.41	99.90	99.94	79.32
0.75	82.02	99.90	99.94	75.12
1.0	80.52	99.90	99.94	67.32
1.25	80.32	88.10	99.32	67.10
1.5	79.22	84.43	99.20	65.08
1.75	79.08	80.71	99.12	65.16
2.0	75.60	99.93	98.25	62.42
2.5	72.22	73.50	98.32.	59.25
3.0	71.05	72.40	95.72	58.44

To determine the loading capacity of TBA for the extraction of Cr(VI) the metal ion solutions of different concentrations were subjected to extraction [9]. The molar ratio of extractant to chromium (VI) of unity was noticed in the extraction isotherm method with all the mineral acid systems (Fig-1). Further the log-log plots of equilibrium chromium (VI) concentration in the aqueous phase Vs. organic phase in the distribution studies[10] with variation of aqueous chromium (VI) concentration at initial aqueous phase acidity of 1.0 M gave straight lines of unit slope indicating the extracted chromium (VI) species as monomeric in nature. The log-log plots of K_d Vs (TBA) from different acid solutions gave straight lines with slope two (Fig – 2).

Absorption Spectra: The individual chromium (VI) species can be identified on the U.V. region [11-14]. The absorption spectra of chromium (VI) in the organic phase obtained by extraction from all the acid systems, exhibit absorption maxima at 285 and 355 nm. **(**Table-2). A comparison of the ratio of the molar extinctions (ε) at 285 nm and 355 nm as a function of acid molarity is taken as a criterion for identifying the species. The peak ratios are constant (~2) in all the acid systems – confirming the presence of a single species which is in conformity with the observation of Tuck and walters [15] .

Table-2: UV – Visible spectral Data of the organic extracts

[Cr(VI)] = 0.00045M *[TBA] = 0.035 M*

Acid (M)		**Molar Extinction (E) at**		**($\varepsilon_{285}/\ \varepsilon_{355}$)**
		285nm	**355nm**	
$H_2C_2O_4$	0.1	1980	935	2.11
	0.5	1920	975	1.97
	1.0	1885	990	1.90
H_3PO_4	0.1	1985	1010	1.96
	0.5	1965	990	1.98
	1.0	1950	955	2.04
ACOH	0.1	1870	990	1.89
	0.5	1905	965	1.97
	1.0	1895	940	2.01
$HClO_4$	0.1	1875	975	1.92
	1.0	1855	1015	1.83

Effect of Diluent :

Diluents with varying dielectric constants were used in the extraction studies. Maximum extraction efficiency was achieved with chloroform as diluent (Table-3) . Hence the same diluent was used in all these studies. With cyclohexane, dichloromethane and toluene low % extraction was found (70 to 80%).

Based on the result obtained, the observed chromium**:** TBA molar ratio of two from all the acid solutions (by distribution ratio method as well as absorption studies) could be explained as arising from the extraction of chromium (VI) by the following solvation mechanism.

$$2\,R_3NH^+org + Cr_2O_7^{2-} \quad \Leftrightarrow \quad (R_3NH)_2Cr_2O_{7\,org}$$

The decrease in the distribution ratio at higher acidities (>3.0M) can be explained as due to the greater extractability of the mineral acid over the chromium (VI) species.

Table-3: Effect of Diluent on Extraction

[Cr(VI)] = 1.0 x 10^{-3} M *[TBA] = 0.5 x 10^{-2} M*
(From oxalic acid medium)

Diluent	**Dielectric constant**	**% extn**
Benzene	2.28	95.72
$CHCl_3$	4.8	99.94
CCl_4	2.24	92.55
Cyclohexane	2.0	75.36
Dichloro methane	8.08	70.80
Hexane	1.9	87.20
Toluene	2.3	79.65.
Xylene	2.38	86.45

Choice of stripping agent:

Stripping of chromium (VI) after extraction was done with 10 ml reagents of various concentrations (0.01 – 1.0 M) of HCl, NaCl, $NaNO_3$, and NaOH solutions. It was found that 1.0 M NaOH alone is a good stripping agent. However in no case NaOH strips out all the chromium (VI) in a single extraction. It was observed that 99.9% chromium (VI) could be recovered from organic phase by making contact three times with equal volumes of 1.0 M NaOH.

Effect of diverse ions:

The effect of several diverse ions on the extraction of chromium (VI) was studied using the general extraction procedure. The tolerance limit was set at the amount of diverse ion required to cause ± 2% error in the recovery of chromium (VI) (13.5 µg/ 20 ml). The results show that the ions such as Al (III), Ba (II), Ce (IV), Cu (II), Mn (II), Co (II), Zn (II), Ascorbate, Chlorate, Tartarate, Tellurite are tolerated in the ratio 1:200 and the ions such as Bi (II), Pb (II), Pd (II), Ru (III), U (VI), Ca (II), VO_3^- , do not interfere even if present in the ratio 1:100. The ions showing small tolerance limit in the ratio 1:50 are Fe (III) and F^- .It is thus possible, to extract chromium (VI) in the presence of large number of cations and anions. The average recovery of chromium (VI) was 99.8 $\pm$ 0.2 %. The relative standard deviation and relative error calculated from ten repeated determinations with 13.5 µg of Cr (VI) were found to be ± 1.06% and ± 0.4% respectively.

Determination of Chromium in industrial effluents:

In order to test the applicability of the proposed method, it was applied to analyze real samples for chromium content in chrome alloys and from a local chrome plating industry (Macro powder coatings, Industrial estate, Visakhapatnam).

About 0.5 gm of a chrome alloy was dissolved in 10 ml of aquaregia. The solution was evaporated to dryness and extracted with 10 ml of dilute oxalic acid solution. The resulting solution was made up to 100 ml.

An aliquot (10 ml) of the filtered effluent sample or the plating effluent sample solution was heated to 1/5th of the initial volume. The interference due to Ni(II) and ,Mn(II) were removed by precipitating them as complex.

Fig.1. Extraction Isotherm

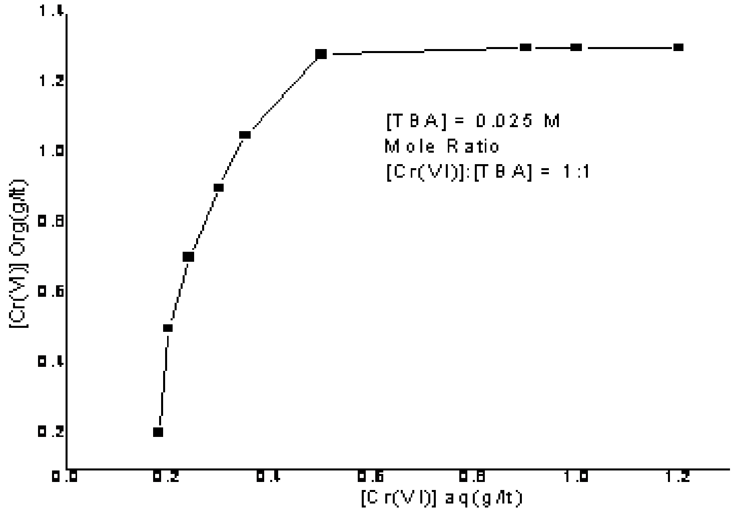

Fig.2: COMPOSITION OF THE EXTRACTED SPECIES

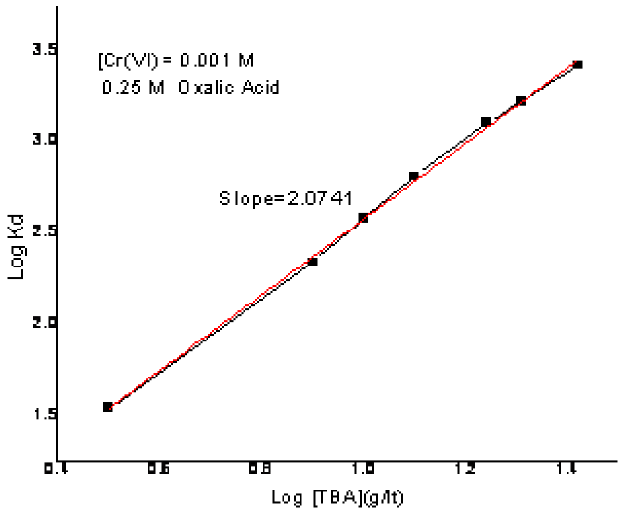

Table – 4: Analysis of chromium in Alloys and Chrome plating Effluents

Chrome alloy steel				**Chrome plating Effluents**		
% Chromium						
present		**found**	**% recovery**	**Sample**	**Chromium (VI) added (g/l)**	*** Chromium found after recovery extraction (g/l)**
Type 302	18	17.82	99.00	Synthetic sample 1	0.20	0.197
	18	17.90	99.44			
Type 303	20	19.84	99.11	2	0.25	0.248
	20	19.94	99.66	3	0.30	0.296
	20	19.78	98.77	4	0.35	0.348
				5	0.40	0.392
				Effluent sample : **1.(Before recycling)** **2.(After recycling)**	---- ----	**0.373 g/l** **6.60×10^{-4} g/l**

** Average of three determinations*

The precipitate was filtered and quantitatively washed for complete recovery of Chromium. It was then made up to 100 ml. 10ml of this solution was extracted with an equal volume of 0.05M TBA in benzene followed by stripping with 1.0M NaOH and estimated the Chromium content as Cr (VI) – DPC complex as per the procedure described earlier. The results are presented in Table-4.

CONCLUSION

The method was very selective and permits the separation and determination of chromium in minimum amount time with accuracy.

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