



SOLVENT EXTRACTION OF CHROMIUM (VI) FROM MINERAL ACID SOLUTIONS BY TRIBUTYL AMINE

A.V.L.N.S.H. HARI HARAN * AND D.MURALI KRISHNA

*** Department of Chemistry
Gitam Institute of Technology, GITAM UNIVERSITY
VISA KHAPATNAM-530 045. INDIA**

Corresponding author ahharan@rediffmail.com

ABSTRACT

Chromium (VI) 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.

The extraction of Chromium (VI) from hydrochloric, sulphuric and nitric 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 etc. The extractions are nearly quantitative with all the acid systems. The extracted species are identified. The method has been applied for the recovery and determination of chromium in natural as well as industrial effluents.

KEY WORDS

Chromium (VI)--Tributyl amine -- mineral acid -- industrial effluents

INTRODUCTION

Extraction of metals including chromium (VI) has been carried out by several workers¹⁻⁷ using high molecular weight 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 hydrochloric, sulphuric and nitric acid solutions.

MATERIALS AND METHODS

Chromic Acid (E. Merck) was used for preparing chromium (VI) stock solution. TBA Merck sample (Molecular wt. 185.35, B.P 216C, 99% pure) was used as such without any purification. A stock solution of TBA (0.5 M) in chloroform was prepared and diluted appropriately to get the required concentration. Estimation of chromium has been carried out using Shimadzu UV visible recording spectrophotometer type UV – 260.



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All other chemicals used were AnalaR Grade or samples purified according to the standard methods.

Chromium (VI) Extraction

Chromium (VI) distribution studies were made using appropriate concentrations of chromic acid ($1.0 \times 10^{-3} \text{ M}$) and mineral acid by equilibrating 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 spectrophotometrically⁸ 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 mineral (hydrochloric, sulphuric and nitric) acid solutions are presented in Table-1.

RESULTS AND DISCUSSION

Effect of Acidity

The distribution ratio of chromium (VI) in the case of hydrochloric acid solution is maximum at 0.25 M with a gradual fall there after. It increases with increase in acidity up to 0.75M and is independent of acidity in the concentration range 0.75.-1.75 M and 0.1- 1.0 M in the case of sulphuric and nitric acid solutions respectively with a gradual fall there after (Table.1).

Table -1
Extraction of Chromium (VI) by TBA from various Acid Solutions
[Cr(VI)] = $1.0 \times 10^{-3} \text{ M}$ [TBA] = $5.0 \times 10^{-2} \text{ M}$

Molarity (M)	HCl %Extn	H ₂ SO ₄ %Extn	HNO ₃ %Extn
0.1	99.92	89.15	99.91
0.25	99.97	89.38	99.91
0.5	99.93	89.85	99.91
0.75	99.89	99.92	99.91
1.0	99.80	99.92	99.91
1.25	98.68	99.92	96.52
1.5	97.72	99.92	95.32
1.75	97.05	96.52	89.0
2.0	96.71	96.38	89.22
2.5	96.6	95.65	85.65.
3.0	95.49	95.28	82.79

The dissimilar extraction trends from various acid systems observed point to the possibility of the association of the anion of the acid resulting in the variation of the composition of the extracted chromium (VI) species.



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Absorption Spectra

The above findings are further confirmed by measurement of absorption spectra of the extracted species. The individual chromium (VI) species can be identified on the U.V. region⁹⁻¹¹. The absorption spectra of chromium (VI) in the organic phase obtained by extraction from hydrochloric acid media exhibit absorption bands at 245, 285 and 355 nm in the extracted species and the spectra from other acid systems, exhibit absorption maxima at 285 and 355 nm. (Table-2).

Table-2
UV-Visible spectral data on the organic extracts of TBA

[Cr(VI)] = 0.00045M

[TBA] = 0.035 M

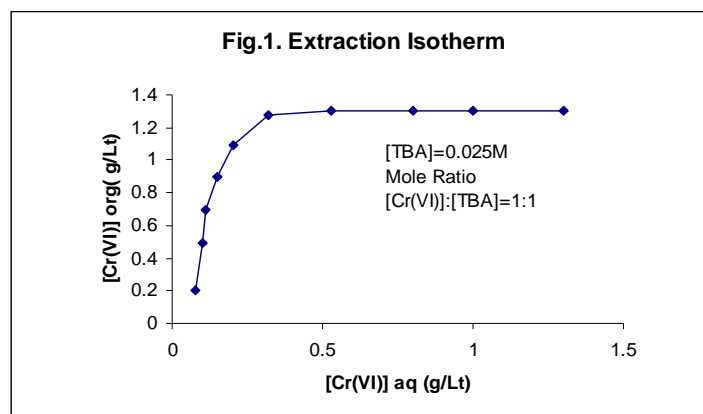
Acid (M)	Molar Extinction (E) at		$(\epsilon_{285} / \epsilon_{355})$
	285nm	355nm	
HCl	0.1	1180	1.09
	0.5	1120	1.03
	1.0	1250	1.05
H ₂ SO ₄	0.1	1980	1.96
	0.5	1965	1.98
HNO ₃	0.1	1950	2.04
	0.5	1870	1.89
	1.0	1905	1.97

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. These ratios varied with the change in the concentration of all the acid solutions indicating the presence of a mixture of species

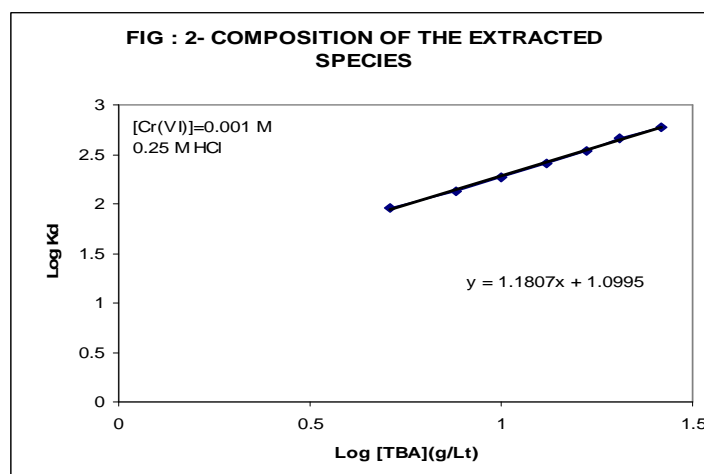
On the other hand the peak ratios are constant (~ 2) in other acid systems – confirming the presence of a single species. This is in conformity with the observation of Deptula¹⁰ using tri-octylamine as extractant.

The Composition of the extracted species was determined by the maximum loading experiments and also by distribution ratio method^{12,13}. 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 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.

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The log-log plots of K_d Vs (TBA) from different acid solutions gave straight lines. The plots obtained from hydrochloric acid medium show that the solvation number is close to unity (Fig - 2). Plots from other acid media gave straight lines with slope two.



Effect of Diluent

Diluents with varying dielectric constants were used in the extraction studies. It was observed that maximum extractability is obtained from chloroform solutions (Table-3).



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Table-3

Effect of Diluent on Extraction

[Cr(VI)] = 1.0×10^{-3} M

[TBA] = 5.0×10^{-2} M

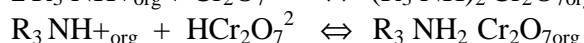
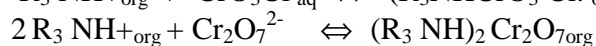
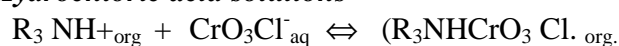
(From HCl medium)

Diluent	Dielectric constant	HCl % ext.
Benzene	2.28	95.72
CHCl ₃	4.8	99.92
CCl ₄	2.24	91.48
Toulene	2.3	90.38
Hexane	1.9	86.25
Cyclo hexane	2.0	81.53
Dichloro methane	8.08	69.12
Xylene	2.38	88.65

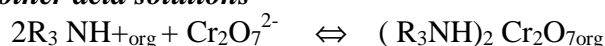
It is concluded that a mixture of species appear to be predominantly HCrO_3Cl , HCr_2O_7 and $\text{Cr}_2\text{O}_7^{2-}$ from hydrochloric and $\text{Cr}_2\text{O}_7^{2-}$ from other acid solutions respectively. The extraction of protonated chromium (VI) species from mineral acid solutions by Oxygen donor solvent TBP was earlier reported¹⁴.

The observed chromium: Extractant molar ratio of unity from the acid solutions (by distribution ratio method) could be explained as arising from the extraction of chromium (VI) by the following solvation mechanism.

From Hydrochloric acid solutions



From other acid solutions



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

Choice of stripping agent

After the extraction of chromium (VI) by 0.05 M TBA, it was stripped with 10 ml reagents of various concentrations (0.01 – 0.1 M) of HCl, NaCl, NaNO_3 , and NaOH solutions. It was observed that HCl, NaCl, and NaNO_3 , are extremely poor stripping agents for chromium (VI). On the other hand, 1.0 M NaOH lone is a good stripping agent. However in no case NaOH strips out all the chromium (VI) in a single extraction. It was



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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 $\pm 3\%$ error in the recovery of chromium (VI) (13.5 $\mu\text{g}/20\text{ ml}$). The results show that the ions such as Al (III), Ba (II), Ce (IV), Cu (II), Mn (II), Co (II), Th (IV), Zn (II), Acetate, Ascorbate, Chlorate, Tartarate, and 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^- , WO_4^{2-} and malonate²⁻ 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 $99.7 \pm 0.3\%$. The relative standard deviation and relative error calculated from ten repeated determinations with 13.5 μg of Cr (VI) were found to be $\pm 1.04\%$ and $\pm 0.6\%$ respectively.

Determination of Chromium in samples

The precision and accuracy of the method of extraction for recovery of chromium has been tested by analyzing real samples from chrome alloys and from a local chrome tanning industry (A.P. Tanneries, Nellimarla, Vizianagaram Dt.).

About 0.5 gm of a chrome alloy (Type 416) was dissolved in 10 ml of aquaregia. The solution was evaporated to dryness and extracted with 10 ml of dilute hydrochloric acid solution. The resulting solution was made up to 100 ml.

25 ml of the filtered effluent sample was acidified and diluted to 250ml. An aliquot (10.0ml) of the effluent or chrome alloy sample solution was extracted with an equal volume of 0.05M TBA in benzene followed by stripping with 2.0 M HNO_3 and estimated the Chromium content as Cr (VI) – DPC complex as per the procedure described earlier. The results are presented in Table-4.

Table-4
Analysis of chromium in Alloys and Industrial Effluents

Chrome alloy type 416 steel		Tannery Effluents		
% Chromium found	% recovery	Sample	Chromium (VI) added (g/l)	* Chromium found after recovery extraction



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			(g/l)	
13.80	98.85	Synthetic sample 1		
13.91	99.35		0.25	0.246
13.86	99.00	2	0.30	0.295
13.82	99.71	3	0.35	0.348
13.76	98.29	4	0.40	0.392
		5	0.45	0.446
Effluent sample :				
1.(Before recycling)			----	0.352 g/l
2.(After recycling)			----	6.45×10^{-4} g/l

* Average of three determinations

CONCLUSIONS

The proposed method is very simple and selective .It requires less time for extraction and determination of chromium in various samples with accuracy.

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