

## Solvent Extraction of Chromium(VI) from Orthophosphoric and Perchloric Acid Solutions by Triphenylphosphine Oxide

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The extraction of chromium(VI) from orthophosphoric and perchloric acid solutions with triphenylphosphine oxide has been studied. The optimum conditions for extraction were established from the study of the effect of several variables like-concentration of phosphine oxide, metal ion, acidity, foreign ions etc. The extractions are nearly quantitative from orthophosphoric acid and are partial from perchloric acid solutions. The extracted species are identified. Estimation of chromium content in industrial effluents and synthetic samples has been attempted.

**Key Words:** Extraction, Distribution ratio, Triphenylphosphine oxide, Chromium(IV), Absorption spectra.

### INTRODUCTION

The extraction of metals by phosphorus containing oxygen donor extractants has been studied by several workers<sup>1-5</sup>. Except a few studies<sup>6,7</sup> there are no reports appeared in literature on the extraction of chromium by these extractants. The present communication describes the extraction of chromium(VI) by triphenylphosphine oxide (TPPO) from orthophosphoric and perchloric acid solutions.

### EXPERIMENTAL

Chromic acid (E. Merck) was used for preparing chromium(VI) stock solution (0.5 M). TPPO was used as such without any further purification. A 0.2 M of TPPO (Fluka AG) solution in benzene was prepared and diluted appropriately to get the required concentration. All other chemicals used were of Anala R grade or samples purified according to the standard methods. The radioisotopes used in this study were obtained from Broad of Radiation and Isotope Technology, Department of Atomic Energy, Government of India, Mumbai, India.

### Chromium(VI) extraction

Chromium(VI) distribution studies were carried out using appropriate concentrations of chromic acid and mineral acid by equilibrating with an equal volume of TPPO in benzene (0.025 M) per-equilibrated with 0.1 M corresponding acid. The chromium (VI) concentrations in the aqueous phase before and after extraction were estimated spectrophotometrically<sup>8</sup> by measuring the absorption of Cr(VI)-DPC complex at 540 nm using Shimadzu UV-visible Spectrophotometer type UV-260. The equilibrium chromium(VI) concentration in the organic phase was determined by taking the difference in the initial chromium(VI) concentration and the equilibrium chromium(VI) concentration in the aqueous phase.

## RESULTS AND DISCUSSION

### Effect of acidity

In order to find out the effect of acidity on the extraction of chromium(VI), extractions were carried out at various acid concentrations using appropriate concentrations of TPPO in benzene. The results obtained on the extraction of chromium(VI) as a function of aqueous phase concentrations of orthophosphoric acid and perchloric acid (Fig. 1).

In the case of orthophosphoric acid solutions it is notified that the distribution of chromium(VI) is independent of acidity in the concentration range 1.0-2.0 M. On the other hand at acid concentration  $\leq 1.0$  M the distribution ratio increased with increase in acid concentration. In the case of perchloric acid solutions the extraction of chromium(VI) were found to decrease with increase in acid concentration. The extractions are nearly quantitative from orthophosphoric acid solutions (90.2 %) and are partial from perchloric acid solutions with maximum extraction (83.7 %) at 0.5 M acidity (Fig. 1). Addition of  $\text{NaHPO}_4$  and  $\text{NaClO}_4$  to aqueous phase in respective acid media resulted in significant decrease in extraction efficiency. These studies were continued upto 3 M acidity beyond which chromium(VI) undergoes reduction to chromium(III).

### Composition of the extracted species

The composition of the extracted species was determined by the extraction isotherm method and the distribution ratio method<sup>9,10</sup>. The maximum loading of  $1.0 \times 10^{-2}$  M TPPO with chromium(VI) at 1.0 M aqueous acidity, yielded a mole ratio of the [extractant] to [chromium(VI)]<sub>org</sub> unity (Fig. 2).

The log-log plots of  $K_d$  vs. TPPO from invariable concentrations of the acid solutions (0.1, 1.0 and 1.5 M) gave straight lines (Fig. 3). The slope analysis of the distribution data indicates that the solvation number depends on concentration of the acid. At low acid concentrations ( $< 1.0$  M) the slope of the log  $K_d$  vs. log [TPPO] plots show that the solvation number

is close to unity (1.01 at 0.1 M  $\text{H}_3\text{PO}_4$ ). As the concentration of the acid in the aqueous phase is increased, the stoichiometric ratio of the components of the organic phase increases gradually indicating that different extraction mechanisms are operating probably due to the formation of a mixture of chromium(VI) species.

An attempt is made to characterize the nature of the extracted chromium(VI) species using  $^{32}\text{P}$  as radiotracer. In these studies the extraction of the anion ( $\text{H}_2^{32}\text{PO}_4^-$ ) in phosphoric acid media as a function of aqueous chromium(VI) concentration reveal whether or not the involvement of the anion in the nature of the extracted species. It is seen that initially the concentration of orthophosphoric acid in the organic phase gradually increased with increasing chromium(VI) concentration, reaching a maximum value and remained constant, over the aqueous chromium(VI) concentration range, 0.175-0.400 M and then gradually decreased. Also it is evidenced that under saturation conditions the molar ratio, Cr: TPPO: ( $\text{H}_2\text{PO}_4^-$ ) varied from 1.0 : 1.0 : 0.22 to 1.0 : 1.0 : 0.38 in  $\text{H}_3\text{PO}_4$  system (Table 1). This indicates the involvement of anion of the acid in the extracted chromium (VI) species.

TABLE-1  
COMPOSITION OF THE ORGANIC PHASE UNDER SATURATION  
CONDITIONS WITH CHROMIUM(VI) -  $\text{H}_3^{32}\text{PO}_4$

Initial aqueous phase [Cr(VI)] (M)	Concentration of organic phase (M)		Molar ratio		
	Cr(VI)	$\text{H}_2\text{PO}_4^-$	Cr	TPPO	$\text{H}_2\text{PO}_4^-$
0.100	0.080	0.022	0.80	1.00	0.22
0.125	0.089	0.026	0.89	1.00	0.26
0.150	0.100	0.031	1.00	1.00	0.31
0.175	0.100	0.038	1.00	1.00	0.38
0.200	0.100	0.038	1.00	1.00	0.38
0.250	0.100	0.038	1.00	1.00	0.38
0.300	0.100	0.038	1.00	1.00	0.38
0.400	0.100	0.038	1.00	1.00	0.38
0.500	0.100	0.035	1.00	1.00	0.35

**Absorption spectra:** The above findings are further confirmed by measurement of absorption spectra of chromium(VI) in the organic phase. As benzene has cut off point at 280 nm, cyclohexane is used as solvent in these studies. The absorption spectra of chromium(VI) in the organic phases obtained by extraction from phosphoric acid media exhibit absorption bands at 245, 285 and 355 nm indicating the presence of ( $\text{HCrO}_3$ ,  $\text{H}_2\text{PO}_4^-$ )<sup>11</sup> in the extracted species. The ratio varied in the range with the change in the concentration of phosphoric acid solutions indicating the presence of a mixture of chromium (VI) species, predominantly ( $\text{H}_2\text{PO}_4^-$ ) (Fig. 4).

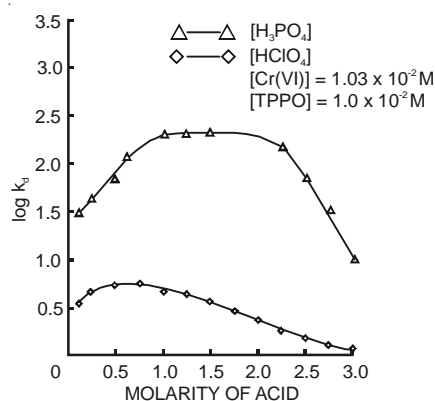


Fig. 1. Effect of acidity

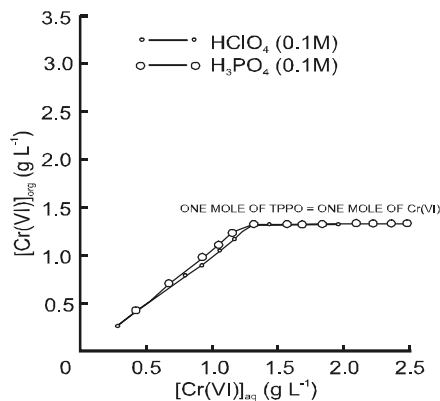


Fig. 2. Extraction isotherm with 0.025 M TPPO

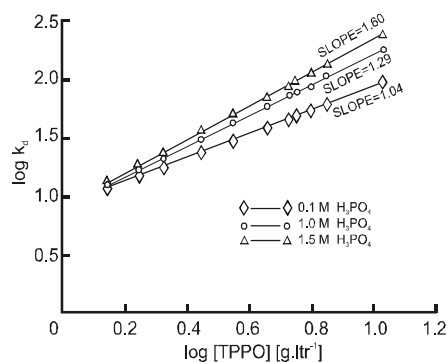


Fig. 3. Composition of the extracted species

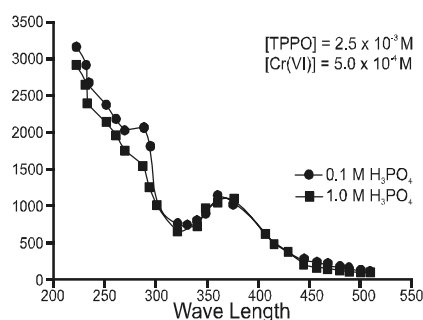


Fig. 4. Absorption Spectra of [TPPO] extracts of Chromium (VI) from Phosphoric acid media

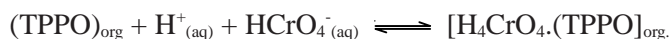
**Choice of stripping agent:** After the extraction of chromium(VI) by 0.025 M TPPO, it was stripped with 10 mL reagents of various concentrations (0.05 - 0.2 M) of HCl, HNO<sub>3</sub>, NaCl, NaNO<sub>3</sub> and NaOH solutions. It was observed that HCl, NaCl and NaNO<sub>3</sub> are extremely poor stripping agents for chromium(VI). On the other hand, 0.2 M HNO<sub>3</sub> alone is a good stripping agent. However in no case HNO<sub>3</sub> 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 0.2 M HNO<sub>3</sub>.

**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  $\pm 2\%$  error in the recovery of chromium(VI) (13.5  $\mu\text{g}/20\text{ mL}$ ). The results show that the ions such as Al<sup>3+</sup>, Ba<sup>2+</sup>, Th<sup>4+</sup>, Ce<sup>4+</sup>, Cu<sup>2+</sup>, Mn<sup>2+</sup>, Co<sup>2+</sup>, Zn<sup>2+</sup>, acetate, chlorate, tartarate, tellurite, oxalate and ascorbate are tolerated in the ratio 1 : 200 and the ions such as Pb<sup>2+</sup>, Bi<sup>3+</sup>, Pd<sup>2+</sup>, Ru<sup>3+</sup>, U<sup>6+</sup>,

$\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{VO}_3^-$  and malonate $^{2-}$ , do not interfere even if present in the ratio 1 : 100. The ions showing small tolerance limit in the ratio 1 : 50 are  $\text{Fe}^{3+}$  and  $\text{F}^-$ . 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  $13.5 \mu\text{g}$  of Cr(VI) were found to be  $\pm 1.03$  and  $\pm 0.7\%$ , respectively.

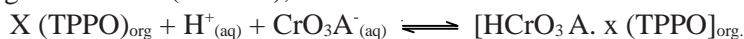
Based on the results obtained the following extraction mechanism from different acid media has been proposed.

**From perchloric acid solutions:**

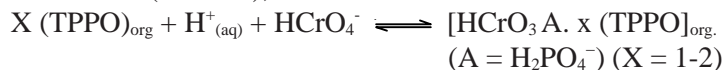


**From phosphoric acid acid solutions:**

At higher acidities ( $> 0.1 \text{ M}$ ),



At lower acidities ( $\leq 0.1 \text{ M}$ ),



**Determination of chromium in tannery and synthetic samples:** The method of extraction was extended for the analysis of chromium from tannery effluents and synthetic samples. The applicability of this method was first tested by extracting chromium from synthetic samples having composition ( $\text{Cr(III)} = 0.35-5.0 \text{ g/L}$ ,  $\text{Al} = 0.75 \text{ g/L}$ ,  $\text{Fe(III)} = 2.24 \text{ g/L}$ ,  $\text{PO}_4^{3-} = 35.5 \text{ g/L}$ ,  $\text{pH} = 0.9$ ). The chromium(III) content of the tannery samples is oxidized to chromium(VI) content of the tannery samples is oxidized to chromium(VI) using ammoniumhexanitratocerate(IV) as oxidizing agent. As iron(III) interferes in the process and it is separated by precipitation as  $\text{Fe(III)}$ -cupferron complex as suggested by Beccari *et al.*<sup>12</sup> prior to the extraction step. The results are presented in Table 2.

TABLE-2

ASSAY OF CHROMIUM IN THE SYNTHETIC SAMPLES AND TANNERY EFFLUENTS

Sample	Chromium(III) added (g/L)	Chromium found after recovery by extraction $\times 10^1$ (g/L)	S.D.
Synthetic Samples			
1.	0.35	3.47	0.47
2.	0.50	4.97	0.46
3.	1.00	9.96	0.49
4.	3.00	29.98	0.47
5.	5.00	49.95	0.46
Tannery Effluent Samples			
1. (Inlet of ETP)	---	3.68	0.49
2. (Outlet of ETP)	---	$4.63 \times 10^{-4}$	0.47

ETP = Effluent Treatment Plant

S.D. = Standard Deviation (Average of five determinations).

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

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