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# Synergistic Extraction of Chromium (III) Using TPPO and TIOA.

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## ABSTRACT

Synergistic extraction (SX) of Cr (III) from sulphuric, nitric, hydrochloric and perchloric acid solutions containing .a mixture of Triphenylphosphine oxide (TPPO) and Triisooctylamine (TIOA) in chloroform has been studied. The investigations were first performed to select optimal conditions for the effective separation including pH of the aqueous phase as well as concentration of synergistic mixture. Stoichiometries of extracted species in both individual and mixed extraction were ascertained by slope ratio analysis. Thermodynamic parameters controlling the nature of the extraction were also evaluated from the distribution ratio values obtained at different temperatures in order to explain the extraction mechanism.

**Keywords:** Chromium (III) - Triphenylphosphine oxide (TPPO) and Triisooctylamine (TIOA) Synergistic extraction – chloroform.

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## INTRODUCTION

The formation of a more hydrophobic ternary adduct in synergistic systems (as a result of the replacement of water molecules co-ordinated to the central metal ion) is mostly responsible for enhanced transfer of metal complex into organic phase [1]. There are evidences that, lanthanides and actinides are favourable for the synergistic extraction because of their higher co-ordination number [2]. Attempts were made on similar studies with d-block elements [3]. Mixture of D2EHPA and TBP was used to extract Zn (II) [4] and D2EHPA was used to extract Fe (III) [5] and TIOA/TOPO for Separation of Co (II)/Ni (II) [6].Although wide number of chelating extractions of chromium (III) are reported in literature [7, 8, 9] but only a few examples are available on Cr (III) extraction by binary mixtures [10], [11]. The present communication describes the results obtained on the synergistic extraction of Cr (III) using TPPO and TIOA which were optimised by the study of effects of several parameters - temperature dependence as well as nature of extraction etc.

## MATERIALS AND METHODS

### Reagents and equipments

Chromium sulphate $[Cr_2 (SO_4)_3]$(E Merck grade) was used for preparing chromium stock solution (1M) and standardized titrametrically [12], with a standard solution of ferrous ammonium sulphate after oxidation of Cr(III) to Cr (VI) ( using ceric ammonium nitrate as oxidant ) with n-phenyl anthranilic acid (NPA) as indicator. 0.25M (stock solution) of each Triphenylphosphine oxide (TPPO) and Triisooctylamine (TIOA) in chloroform was prepared and diluted appropriately to get the required concentration. All other chemicals used were of AR grade and purified according to the standard methods and are used as such without any further purification.

A digital pH meter equipped with single electrode was used for pH measurements, A temperature controlled mechanical shaker, made by KEMI was used for the equilibration studies, Atomic Absorption Spectrophotometer type AAS-SVL Spectronics Model 205 was used for the determination of chromium content in the samples.

### General Extraction Procedure

An aliquot of chromium (III) [$1.0x10^{-3}$ M ] with corresponding mineral acid in a 250ml separating funnel was added to 10ml portions of each $2.5x10^{-2}$ M of TPPO+TIOA mixture in chloroform pre-equilibrated with 0.1M mineral acid. The solution was shaken thoroughly for five minutes and was allowed to settle for few min. The chromium (III) concentration in the aqueous phase before and after extraction was estimated using AAS. The equilibrium chromium (III) concentration in the organic phase was determined by taking the difference in the initial chromium (III) concentration and the equilibrium chromium (III) concentration in the aqueous phase. It was clearly noticed that chromium (VI) could not be extracted under the experimental conditions. In order to study the effect of temperature, equilibrations were carried out in a temperature controlled mechanical shaker, after which distribution ratio (D) was determined.

## RESULTS AND DISCUSSION

### Effect of equilibration time

Preliminary studies on the extraction of Cr (III) by TPPO in chloroform show that the two phase reaction is fairly rapid and the equilibrium is reached within 15 minutes. Further increase in the time of equilibration does not affect the extraction equilibrium (Figure 1).

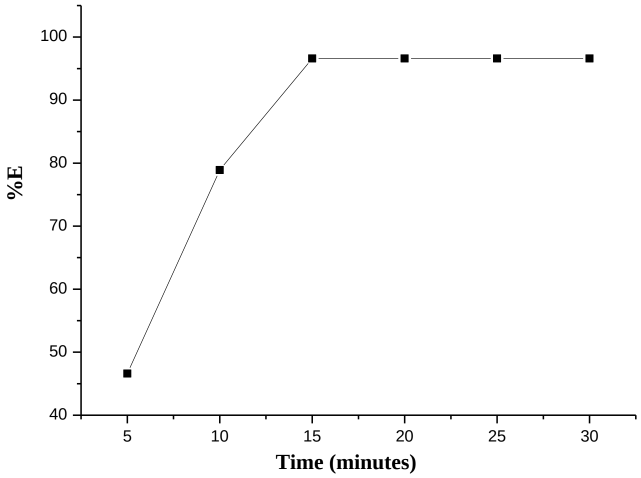

**Figure 1: Time Variation**

**Effect of pH in extraction process**

The pH is a very important parameter for extraction studies. Experiments were carried out with different pH of aqueous phase, extractant concentration 0.025M. At first, it was observed that the percentage of extraction increased with increasing pH from 1.0 to 5.0 in case of sulphuric and hydrochloric acid media and there is a gradual decrease in pH (1.0 -5.0) in case of nitric acid but in the case of perchloric acid solutions there is an increase in pH from 1.0 – 3.0 and above pH 3.0 the extent of extraction decreases perhaps due to hydrolysis of chromium (III) species. Extraction efficiency was maximum (88.88%) in the range 3.0 pH in perchloric acid solutions (Figure 2).

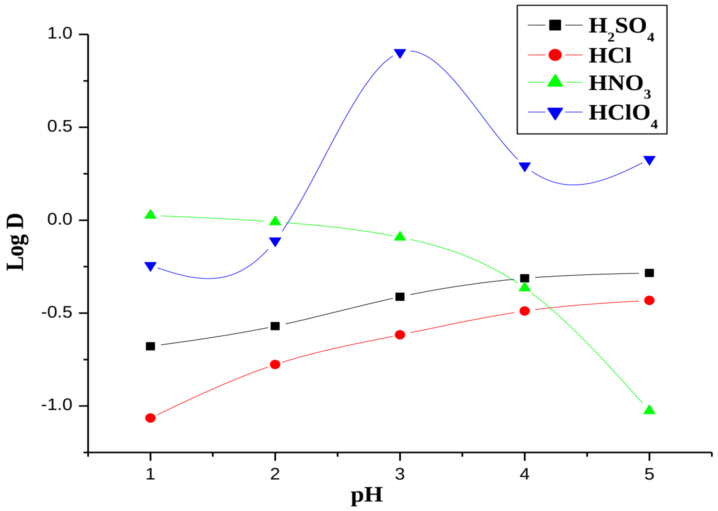

**Figure 2: pH Variation**

**Effect of diluents**

The effect of diluents on the extraction of TPPO with 0.025M was studied into different organic solvents and it was found that maximum extraction was obtained in case of chloroform. The order of extraction by different solvents is given below (Table 1).

**Table 1: Distribution ratio and %E at pH 3.0, $HClO_4$ medium in different solvents**

| Solvent | Distribution ratio (D) | %E |
|---|---|---|
| Chloroform | 0.875 | 46.6 |
| Toluene | 0.694 | 40.9 |
| Benzene | 0.678 | 40.4 |
| Cyclohexane | 0.615 | 38.0 |
| Nitrobenzene | 0.542 | 35.1 |
| Carbon tetrachloride | 0.397 | 28.4 |

### Variation of extraction of Cr (III) with TPPO

Extraction of Cr (III) by TPPO in chloroform in the concentration range (0.025 to 0.005 M) indicates that the distribution ratios were very poor (46.6%). The composition of extractable species was obtained from the plot of log D vs. log[TIOA] and the data are fitted to a straight line equation with an average slope of ~ 1 (Figure 3) , indicating one molecule of TPPO is involved in the extraction process.

$$K\ [Cr^{+3}]aq + 3X^{-} + [TPPO]_{org} \leftrightarrow Cr\ X_3.TPPO_{org} \ .........(1)$$

$$k = \frac{[Cr\ X_3.TPPO]_{org}}{[Cr^{+3}]_{aq}\ [X]^{3-}\ [TPPO]} \ .........\ (2)$$

$$\text{and Distribution ratio, } D = \frac{[Cr\ X_3.TPPO]_{org}}{[Cr]^{+3}_{aq}}$$

Taking logarithm and putting the value of D in eq. (1) we have,

$$\log D = \log k + \log\ [TPPO]_{org} \ .........\ (3)$$

Stoichiometric co-efficients for the extraction reaction can be determined from the plot of log D against log $[TPPO]_{org.}$ , Slope of unity is observed from all the acids employed in the study (Figure 3) and hence individual extraction reaction of Cr (III) by TPPO is described as,

$$[Cr^{+3}]aq + 3X^{-} + [TPPO]_{org} \overset{K =}{\leftrightarrow} [CrX_3\ .TPPO]_{org} \ ......(4)$$

$$\text{Thus, } \log k = \log D - \log\ [TPPO]_{org} \ .......\ (5)$$

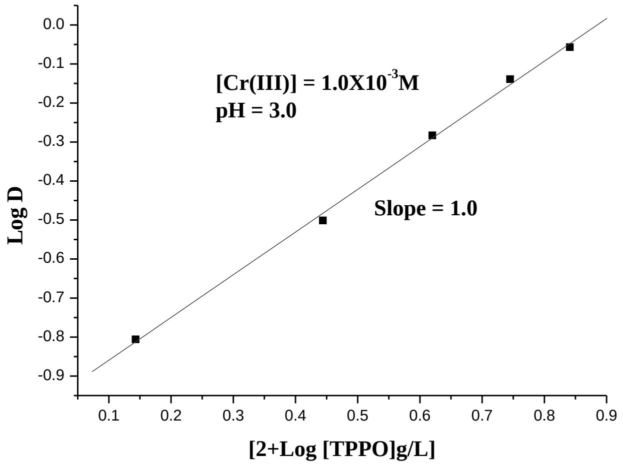

**Figure 3: Extractant Variation of Cr (III) with TPPO**

**Extraction of chromium (III) with TIOA**

Extraction of Cr (III) by TIOA in chloroform was also investigated in the concentration range as mentioned above. Plot of log D vs. log [TIOA] gave a straight line with an average slope of ~ 1 (Figure 4), indicating one molecule of TIOA is involved in the extraction process.

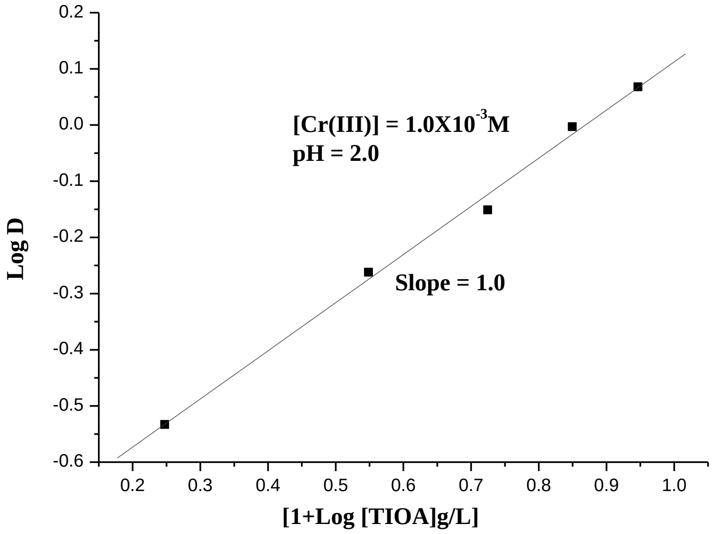

**Figure 4: Extractant Variation of Cr (III) with TIOA**

**Synergistic extraction of chromium (III) in presence of TPPO and TIOA**

Preliminary experiments show that the extent of extraction is poor in case of individual extractants ie., TPPO and TIOA, employed in the present study. However, when TPPO is mixed with TIOA, a marked enhancement in the extent of Cr (III) extraction takes place. As $D_{mix}$ is always greater than $D_{TPPO}$ and $D_{TIOA}$, mixed extraction definitely leads to synergism. If S.C & ΔD are positive then synergism occurs. ΔD and SC were defined to evaluate synergistic effect as mentioned below (Table 2).

$$\text{Synergistic Coefficient S.C} = \log \frac{D_{mix}}{(D_{TPPO} + D_{TIOA})}$$

$$\Delta D = D_{mix} - (D_{TPPO} + D_{TIOA})$$

Where, $D_{mix}$ = distribution coefficient in presence of binary extractants. $D_{TPPO}$ = distribution coefficient in presence of TPPO only. $D_{TIOA}$ = distribution coefficient in presence of TIOA only.

**Table 2: Results of synergistic extraction of Cr (III)**

| Solvent | [TIOA] (M) | $D_{TPPO}$ | $D_{mix}$ | %E | SC | ΔD |
|---|---|---|---|---|---|---|
| Chloroform | 0.025 | 0.875 | 7.999 | 88.88 | 0.59 | 5.95 |
| | 0.02 | | 1.926 | 85.22 | 0.05 | 0.20 |
| | 0.015 | | 1.543 | 60.67 | 0.10 | 0.31 |
| | 0.01 | | 1.259 | 55.73 | 0.16 | 0.39 |
| | 0.005 | | 1.109 | 52.58 | 0.39 | 0.66 |
| Cyclohexane | 0.025 | 0.615 | 2.013 | 66.81 | 0.37 | 1.15 |
| | 0.02 | | 1.962 | 66.23 | 0.42 | 1.21 |
| | 0.015 | | 1.759 | 63.75 | 0.46 | 1.15 |
| | 0.01 | | 1.406 | 58.43 | 0.47 | 0.93 |
| | 0.005 | | 0.093 | 8.50 | -0.44 | -0.16 |
| Nitrobenzene | 0.025 | 0.542 | 1.095 | 52.26 | 0.22 | 0.44 |
| | 0.02 | | 1.016 | 50.39 | 0.31 | 0.52 |
| | 0.015 | | 0.092 | 8.42 | -0.49 | -0.19 |
| | 0.01 | | 0.080 | 7.40 | -0.37 | -0.11 |
| | 0.005 | | 0.076 | 7.06 | -0.36 | -0.10 |
| Benzene | 0.025 | 0.678 | 1.309 | 56.69 | 0.17 | 0.42 |
| | 0.02 | | 1.168 | 53.87 | 0.16 | 0.36 |
| | 0.015 | | 0.099 | 9.00 | -0.74 | -0.44 |
| | 0.01 | | 0.086 | 7.91 | -0.67 | -0.32 |
| | 0.005 | | 0.081 | 7.49 | -0.32 | -0.09 |
| Carbon tetrachloride | 0.025 | 0.397 | 1.994 | 66.59 | 0.20 | 0.75 |
| | 0.02 | | 1.763 | 63.80 | 0.27 | 0.82 |
| | 0.015 | | 1.549 | 60.76 | 0.40 | 0.93 |
| | 0.01 | | 1.321 | 56.91 | 0.57 | 0.96 |
| | 0.005 | | 1.019 | 50.47 | 0.72 | 0.82 |
| Toluene | 0.025 | 0.694 | 3.451 | 77.53 | 0.40 | 2.09 |
| | 0.02 | | 2.969 | 74.80 | 0.46 | 1.94 |
| | 0.015 | | 2.437 | 70.90 | 0.51 | 1.68 |
| | 0.01 | | 1.665 | 62.47 | 0.51 | 1.16 |
| | 0.005 | | 1.013 | 50.32 | 0.50 | 0.69 |

The plot of log ($D_{mix}$) against both log [TPPO] and log [TIOA] shows straight lines of slope values ~1 (Figure 5) and ~1 (Figure 6) respectively. Thus one TPPO molecule and one TIOA molecule are present in ternary extracted species. Thus, mixed extraction could be shown as,

$$K\ [Cr^{+3}]_{aq} + [TPPO]_{org} + [TIOA]_{org} \leftrightarrow [Cr(TPPO).(TIOA)]_{org} \text{.......(6)}$$

Therefore,

$$K = \frac{[Cr.\ (TPPO).\ (TIOA)]_{org}}{[Cr^{+3}]_{aq} \times [TPPO]_{org} \times [TIOA]_{org}} \qquad \text{....... (7)}$$

$$D_{mix} = \frac{[Cr.\ (TPPO).\ (TIOA)]_{org}}{} \qquad \text{........ (8)}$$

$[Cr^{+3}]_{aq}$

Substituting values of D in $D_{mix}$ expression and taking log values both sides,

$$\text{Log } K = \log [D_{mix} - D]_{org} - \log [TPPO]_{org} - \log [TIOA]_{org} \quad \text{....... (9)}$$

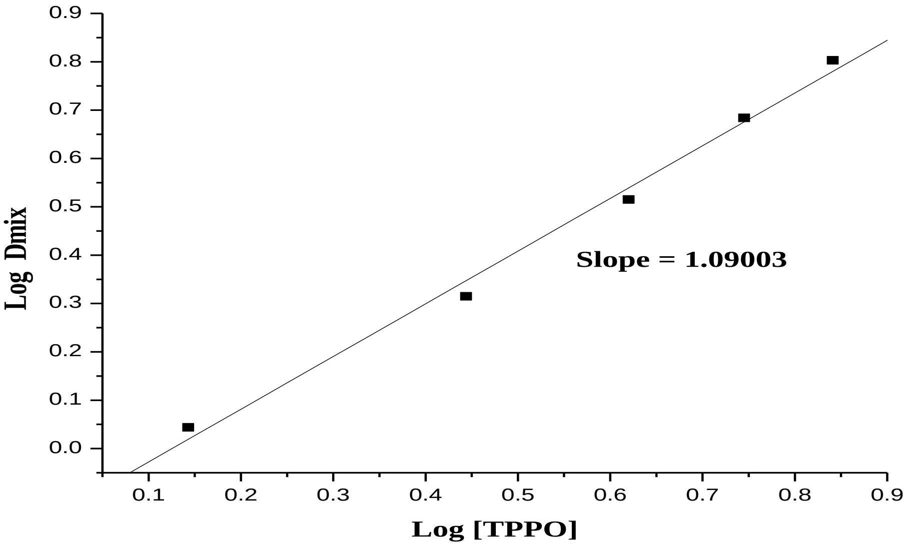

**Figure 5: Plot of Log Dmix vs. Log [TPPO] in synergistic extraction of Cr (III)**

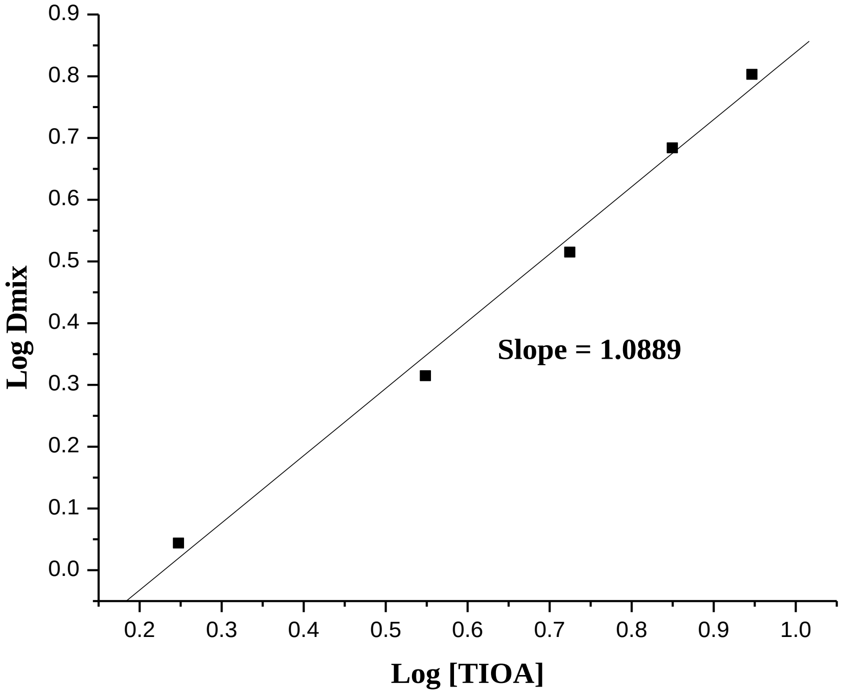

**Figure 6: Plot of Log D mix vs. Log [TIOA] in synergistic extraction of Cr (III)**

Thus, the adduct formation in the organic phase may be described as,

$[CrX_3 (TPPO) (H_2O)_2] + TIOAH^+ \rightarrow [CrX_3 (TPPO) (H_2O) TIOAH^+]_{org} + H_2O$

**Effect of temperature**

Temperature effects on the extraction of chromium (III) by individual and mixture of extractants have also been studied. In the case of binary and ternary extraction systems, the higher temperature leads to increase in the chromium (III) extraction at this aqueous phase acidity. Equations (5) and (9) are used for the calculation of equilibrium extraction constant logK for the complexes studied.

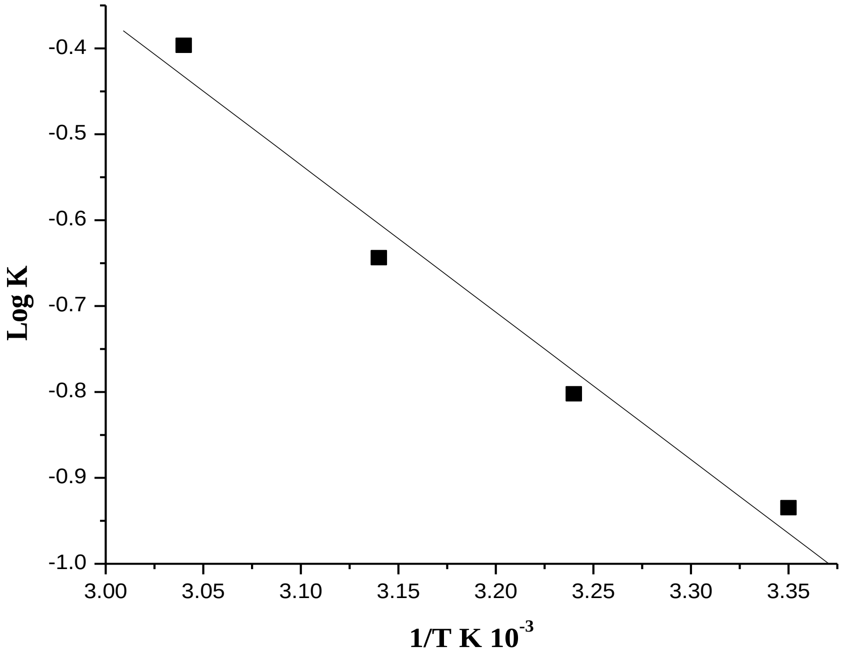

**Figure 7: Temperature Variation**

From the values of equilibrium extraction constant at the temperature range investigated, the Vant Hoff equation was used to calculate the enthalpy change.

$$\log K = -\Delta H/2.303RT + \Delta S/2.303R \quad \ldots\ldots\ldots\ldots\ldots(10)$$

The plot of log K against 1/T is a straight line (Figure 7) where the slope gives the enthalpy of reaction (ΔH°) and the intercepts correspond to entropy (Δ S°) value. The values of Δ G°, ΔH°, Δ S° are shown in (Table 3).

**Table 3: Thermodynamic Parameters**

| System | Solvent | ΔH° (kJK$^{-1}$. mol$^{-1}$) | ΔS° (JK$^{-1}$. mol$^{-1}$ ) | ΔG° (kJK$^{-1}$. mol$^{-1}$) |
|---|---|---|---|---|
| Cr(III)- TPPO-TIOA | Chloroform | 14.26 | 39.76 | -11.86 |
| | Cyclohexane | 18.56 | 48.36 | -14.43 |
| | Nitrobenzene | 26.93 | 72.90 | -21.76 |
| | Benzene | 22.88 | 59.59 | -17.79 |
| | Carbon tetrachloride | 17.24 | 44.28 | -13.21 |
| | Toluene | 13.80 | 34.90 | -10.42 |

Data shows that extractions are entropy favoured but enthalpy disfavoured. Although the values of $\Delta H^0$ are low but positive values indicate bond breaking takes place during extraction. Again, release of water molecules in mixed extraction has been reflected by positive values of entropy. During adduct formation it is highly favourable that extensive disruption of hydration sphere of metal leads to the release of such water molecules.

**Effect of stripping agent**

The stripping investigations were carried out to bring back chromium (III) into the aqueous phase. A 10 ml portion of reagents of various concentrations (0.01 – 1.0 M) of HCl, $H_2SO_4$, $HNO_3$ and NaOH solutions. It was observed that HCl, $H_2SO_4$ and NaOH are extremely poor stripping agents whereas 1.0 M $HNO_3$ was found to be more efficient for chromium (III) and can strip back in three attempts. After shaking, organic and aqueous phases were separated and metal concentrations in aqueous phases were determined by AAS in order to calculate stripping percent.

The results obtained on stripping of Cr (III) revealed that it is highly selective. Maximum stripping of Cr (III) was obtained with 1.0 M $HNO_3$ (Figure 8). This solution can be considered as a promising stripping agent since it leads to effective stripping (93%). Further increase in acid concentration has no significant effect on Cr (III) stripping.

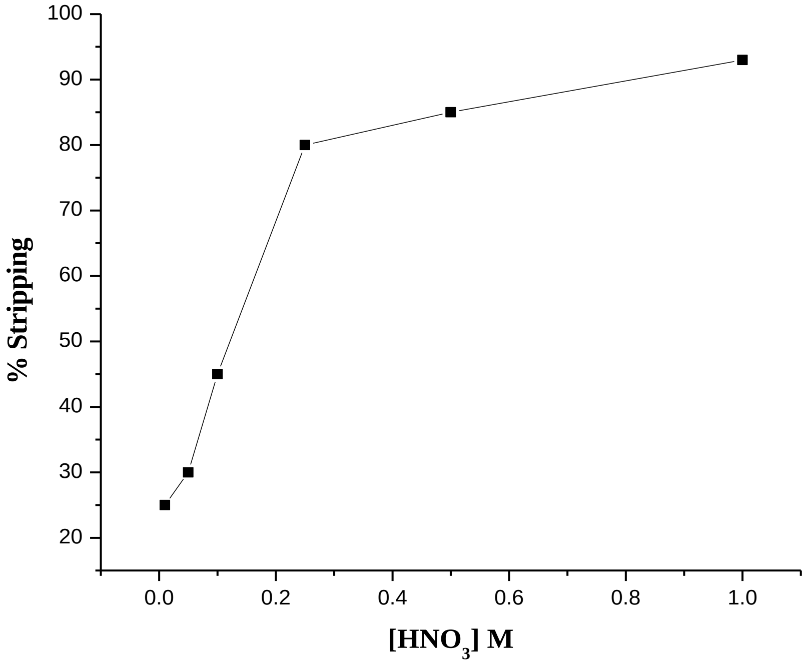

**Figure 8: Stripping of Cr (III)**

**Effect of Diverse ions**

Extraction of Cr (III) was studied in presence of several foreign ions using the general extraction procedure. The tolerance limit was set for the recovery of Cr (III) within ± 2% error chromium (III) (13.5 µg/20ml). The results (Table 4) show that the ions such as Al(III), Ce(IV), Cu(II), Sb(III), Sn(II), Mn(II), Co(II), Zn(II), Acetate, Chlorate, Oxalate Phosphate, Tartarate, Selenite and Telluride are tolerated in the ration 1:200 and the ions such as Bi(II), Ca(II), Pd(II), Ru(III), U(VI), Pb(II), Sr(II), $VO_3^-$ and $WO_4^{2-}$ 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 (III) in the presence of large number of cations and anions. The average recovery of chromium (III) was 99.6 ± 0.4%. The relative standard deviation and relative error ± 1.04% and ± 0.6% respectively.

**Table 4: Effect of Diverse ions**

**[Cr (III] =13.5 μg; [TPPO+ TIOA] =0.025 M**

| Foreign ion | Tolerance limit | Foreign ion | Tolerance limit |
|---|---|---|---|
| $Al^{3+}$ | 393 | $Ascorbate^{2-}$ | 842 |
| $Bi^{2+}$ | 702 | $Malonate^{2-}$ | 867 |
| $Cd^{2+}$ | 430 | $PO_4^{3-}$ | 902 |
| $Ce^{4+}$ | 708 | $Seo_2^{3-}$ | 708 |
| $Fe^{3+}$ | - | $S_2O_3^{2-}$ | 618 |
| $Mn^{2+}$ | 168 | $ClO_3^-$ | 851 |
| $Ni^{2+}$ | 261 | $VO_3^-$ | 209 |
| $Pd^{2+}$ | 904 | Tartarate2- | 650 |
| $Sb^{3+}$ | 904 | $Ru^{3+}$ | 702 |
| $Sn^{2+}$ | 181 | $UO_2^{2+}$ | 765 |
| $Sr^{2+}$ | 182 | $Zn^{2+}$ | 754 |
| $Th^{4+}$ | 862 | $EDTA^{4-}$ | 438 |

**Determination of chromium in synthetic samples and chrome alloys**

The applicability of the proposed method has been tested to analyze real samples for chromium content in chrome alloys. A known weight of chrome alloy (stainless steel sample) was dissolved in 10 ml of aquaregia. The solution was evaporated to dryness and extracted with 10 ml of hydrochloric acid solution. The precipitate was filtered and quantitatively washed for complete recovery of Chromium. 10ml of this solution was extracted with an equal volume of 0.025 M TPPO+TIOA in chloroform followed by stripping with 1.0M $HNO_3$ and estimated the chromium content as per the procedure described earlier. The results are presented in (Table 5).

**Table 5: Estimation of chromium in Synthetic samples and chrome alloys**

| **Sample** | **Chromium(III) present** | **Chromium found after recovery by extraction** | **Recovery** |
|---|---|---|---|
| Synthetic sample | (g/lit) | (g/lit)* | % |
| 1 | 0.20 | 0.198 | 99.22 |
| 2 | 0.30 | 0.294 | 98.46 |
| 3 | 0.40 | 0.396 | 97.68 |
| Stainless steel alloy type | % | % | % |
| 1 | 11.5 | 11.30 | 98.26 |
| 2 | 14.0 | 13.82 | 98.71 |

*(Average of Four determinations)

## CONCLUSIONS

Thermodynamic parameters obtained from the distribution ratio values of the extraction revealed that it is entropy favoured (endothermic in nature) indicated by release of water molecules in synergistic extraction.

## ACKNOWLEDGEMENTS

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