# Solvent Extraction of Iron(III) by Tri-n-Octyl Phosphine Oxide

## A. V. L. N. S. H. Hariharan*, Ch. Sudhakar and A. Srinivasanaidu

*Department of Chemistry, GIT, GITAM University, Visakhapatnam, India*

**ABSTRACT**

*The extraction of Iron (III) from Sulphuric nitric, perchloric and acetic acid solutions with Tri-n-Octyl Phosphine Oxide (TOPO) in benzene has been studied. The extractions from sulphuric and acetic acid solutions are nearly quantitative and are partial from nitric and perchloric acid solutions. The optimum conditions for extraction were established from the study of the effect of several variables like– concentration of the extractant, metal ion, acidity, foreign ions etc. Based on the results obtained, the probable extracted species are also suggested. The method has been applied for the determination of iron in natural food as well as pharmaceutical samples.*

**Key words:** Extraction -iron (III) - Tri-n-Octyl Phosphine Oxide (TOPO) – pharmaceutical samples.

## INTRODUCTION

The solvent extraction of iron (III) has been studied with neutral extractants, such as ethers, ketones, amines[1] and tributylphosphate[2,3] and also with cationic reagents, such as quaternary ammonium ions[4]. Studies appeared in literature on the determination of different metals[5-9] along with the extraction of iron (III)from chloride solutions by phosphine oxides (TOPO)[10-13]. All these studies concern with extraction of iron with one acid system only. Therefore, in this present communication it is proposed to carry out detailed study on the extraction of iron (III) by Tri n-Octyl phosphine oxide (TOPO) from sulphuric, nitric, acetic and perchloric acid solutions.

## EXPERIMENTAL SECTION

A stock solution of 0.35 M TOPO ( Mol. wt. 386.65) in benzene was prepared and diluted appropriately to get the required concentration. Ferric ammonium sulphate (E.Merck) was used

for preparing iron(III)  solution (0.45M) and was standardized using standard potassium dichromate solution  volumetrically. All other chemicals used were of AnalaR grade . Double distilled water was used through out.

IRON(III) EXTRACTION**:**
Iron (III) distribution studies were made using appropriate concentrations of the iron salt and mineral acid by equilibrating with an equal volume (20ml) of TOPO in chloroform (0.025M) pre-equilibrated with 0.1M mineral acid. The solution was shaken for 5 minutes. The two phases were allowed to settle and separate .Iron(III)from the  organic  phase was stripped with 20ml of 0.1M  $H_2SO_4$  and was   estimated spectrophotometrically [14] by measuring the absorption of Fe(III) – thiocyanate complex at 480nm, using Shimadzu UV-Visible Spectrophotometer type UV-260. The equilibrium iron (III) concentration in the organic phase was determined by taking the difference in the initial  iron (III) concentration and the equilibrium iron (III) concentration in the aqueous phase.

## RESULTS AND DISCUSSION

The variation of distribution ratio  as a function of aqueous phase concentration of the acid ($H_2SO_4$, $HNO_3$, $CH_3COOH$ and $HClO_4$ ) are presented in Fig-1.  From sulphuric acid solutions the distribution ratio ($K_d$) increased sharply   with increasing  concentration of the acid up to 8.0 M acidity  and remained constant between 8.0-9.0M  beyond  which by a decrease in extraction is noticed.  In acetic acid media,  the distribution ratio found to be decreased above 2.0M acidity. The extractions fall off rapidly in case of nitric and perchloric acid solutions.

*COMPOSITION OF THE EXTRACTED SPECIES:*
The extraction isotherm method[15] and   distribution ratio method[16]   were employed to determine the composition of the extracted species. In the  extraction isotherm method the limiting ratio of the metal to  TOPO was found   unity with all the acid systems (Fig-2).
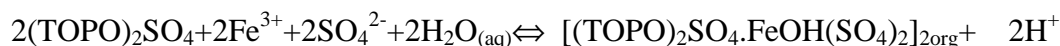
The log-log plots of $K_d$ Vs. TOPO from various acid solutions  gave straight lines. (Fig-3).The slope analysis of the distribution data in sulphuric acid  solutions indicates that the solvation number  is two  where as in other acid  solutions the log-log plots gave straight lines of unit slope.

*ABSORPTION SPECTRA:*
The individual Iron (III) extracted species with TOPO was studied in U.V. region[17,18].   The absorption spectra from sulphuric acid media exhibits absorption band at 295 and 355 nm . These two are the absorption characteristics of Fe(OH) and hydroxyl – group bridging species Fe(OH)$_2$ Fe respectively,   and the  appearance  of  new peak at 305 nm corresponds to the complexes $FeSO_4^+$ and $Fe(SO_4)^{-2}$.

The observed iron: TOPO molar ratio of unity and two from    different acid solutions (by distribution ratio method) could be explained as arising from the extraction of iron (III) by the following ion-exchange  mechanism.

From sulphuric acid   solutions:

$2(TOPO)_2SO_4 + 2Fe^{3+} + 2SO_4^{2-} + 2H_2O_{(aq)} \Leftrightarrow [(TOPO)_2SO_4.FeOH(SO_4)_2]_{2org} + 2H^+$

From Other acid solutions:

___

$TOPOHNO_3 + Fe^{3+} + 4 NO_3^- \Leftrightarrow [TOPOH^+ Fe(NO_3^-)_4]_{org} + NO_3^-$

$TOPOHClO_4 + Fe^{3+} + 4 ClO_4^- \Leftrightarrow [TOPOH^+Fe(ClO_4^-)_4]_{org} + ClO_4^-$

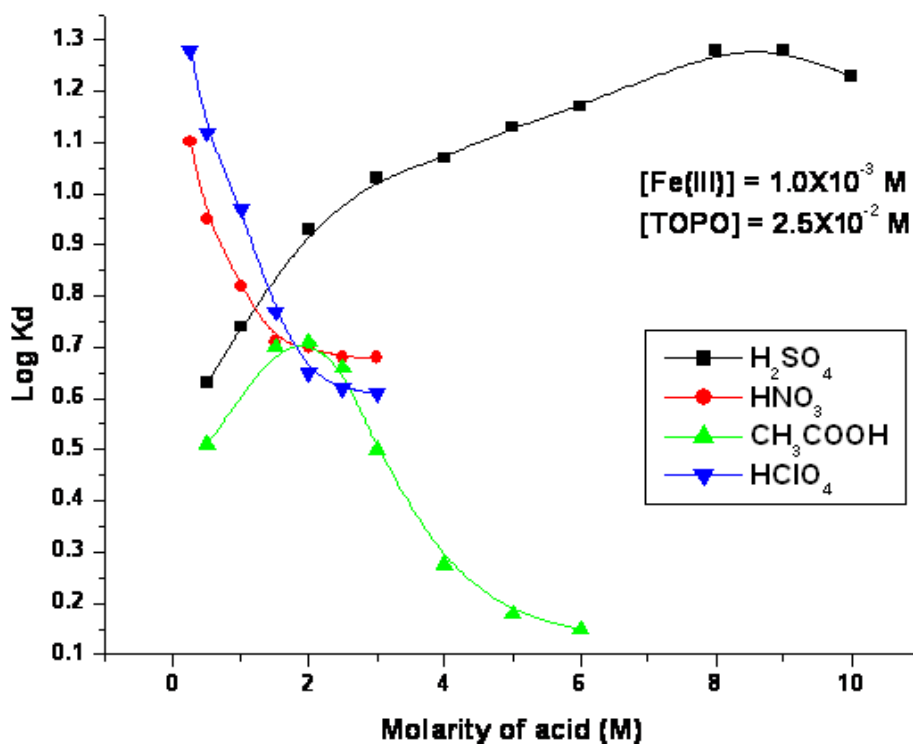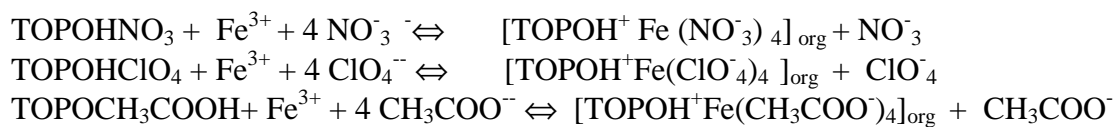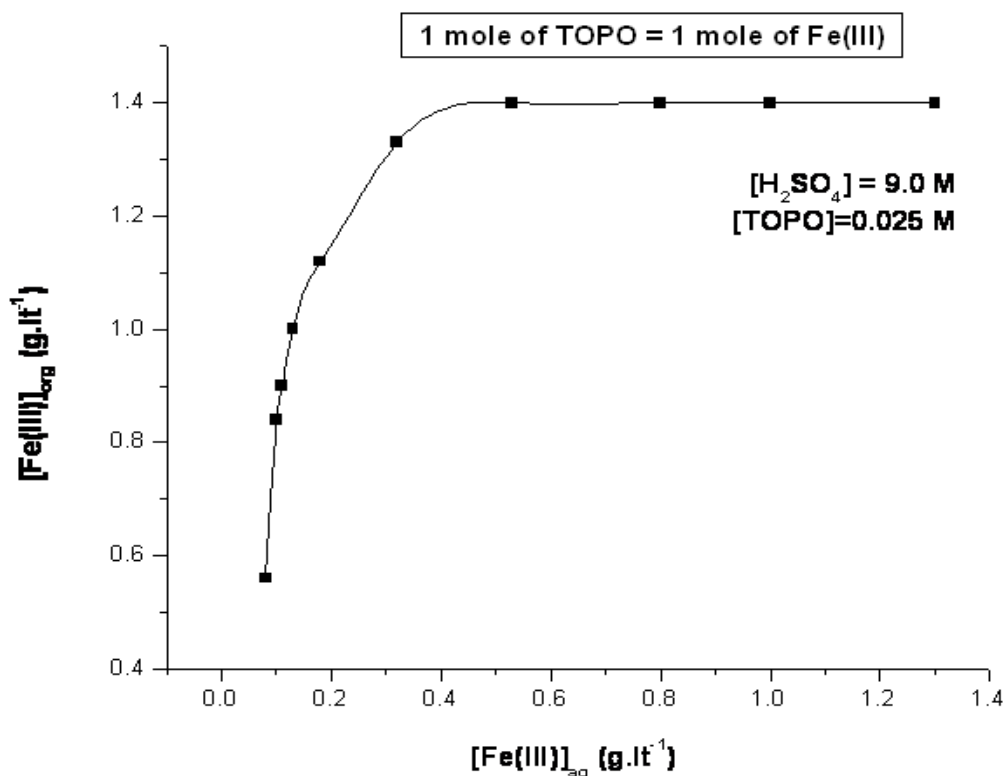$TOPOCH_3COOH + Fe^{3+} + 4 CH_3COO^- \Leftrightarrow [TOPOH^+Fe(CH_3COO^-)_4]_{org} + CH_3COO^-$



Fig.1. Effect of acidity on Extraction



Fig.2. Extraction Isotherm method (H₂SO₄ medium)

*EFFECT OF STRIPPING AGENTS:*

After extraction, iron(III) was stripped with 20ml reagents of various concentrations (0.1 – 2.0 M) of ACOH, $H_2SO_4$ and NaOH solutions.. It was observed that 1.0 M $H_2SO_4$ alone is a good stripping agent. However in no case the acid strips out all the iron (III) in a single extraction. 99.7% iron (III) could be recovered from organic phase by making contact three times with equal volumes of 1.0 M $H_2SO_4$.
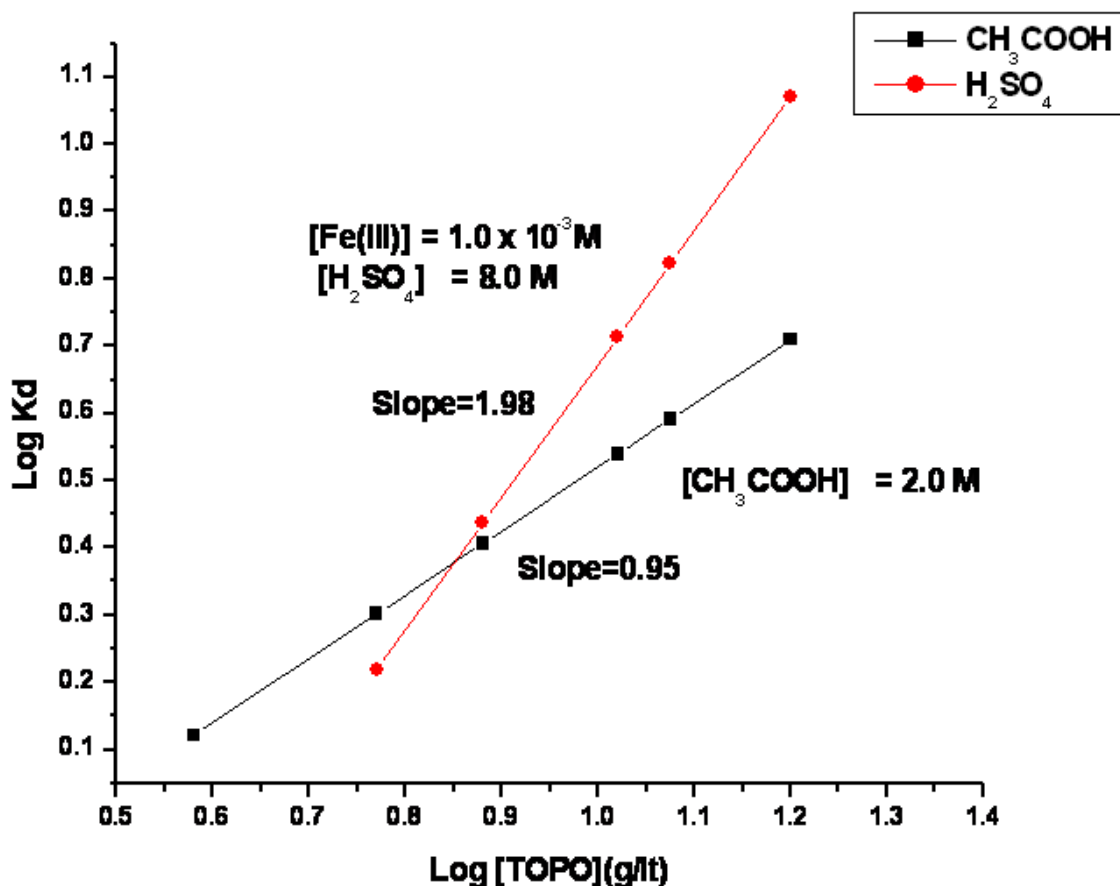


Fig.3. Extractant Variation

*VARIATION OF DILUENTS*

Besides chloroform various diluents used in the present study are benzene, xylene, toluene, carbon tetra chloride, n-hexane, n-heptane cyclo hexane, nitrobenzene, dichloro methane which are of wide verities in their chemical nature and dielectric constant. Maximum extraction efficiency was achieved with chloroform as diluent (Table-1). Hence the same diluent was used in all these studies. With, n-hexane, n-heptane, dichloromethane and nitrobenzene low % extraction was noticed (67 to 82%).

**Analysis of iron in various samples**

The precision and accuracy of the method of extraction for recovery of iron has been tested by analyzing food and pharmaceutical samples. Ten tablets were weighed accurately and finely powdered in a mortar. An amount of the powder equivalent to one tablet was transferred quantitatively to 100-ml volumetric flask and then 60 ml of 0.01 M $H_2SO_4$ was added. The mixture was shaken well for about 15 min. Then the mixture was diluted by 0.01 M $H_2SO_4$ solution to the mark and then filtered by Whatman filter paper No. 40. The first portion of filtrate was discarded. The clear solution obtained was used as a stock sample solution and different

aliquots of prepared solutions were diluted with 0.01 M $H_2SO_4$ to produce different concentrations.

**TABLE-1 :  Effect of Diluents  on  Extraction**

*[Fe (III)] = 1.0 x $10^{-3}$ M   ; [$H_2SO_4$] = 9.0M ;  [TOPO] = 2.5 x $10^{-2}$ M*

| Diluent | Dielectric constant | % extraction |
|---|---|---|
| Benzene | 2.28 | 90.9 |
| Chloroform | 4.81 | 97.2 |
| $CCl_4$ | 2.23 | 96.0 |
| Xylene | 2.56 | 82.3 |
| n-Hexane | 1.89 | 76.5 |
| Cyclo hexane | 2.0 | 80.3 |
| Dichloro methane | 8.08 | 78.5 |
| Toluene | 2.43 | 88.2 |
| n-heptane | 1.92 | 81.7 |
| Nitrobenzene | 34.82 | 67.8 |

**TABLE – 2: Estimation of iron in   food and pharmaceutical samples**

| Sample | Iron present (%) | Iron found by extraction | % recovery |
|---|---|---|---|
| Ragi | 3.00 ppm | 2.86 ppm | 95.33 |
| Green gram | 4.05 ppm | 3.98 ppm | 98.27 |
| Ferrous fumerate(300mg) | 114.10 | 113.54 | 99.51 |
| Ferrous dextrin(50mg) | 100.22 | 99.62 | 99.40 |

**REFERENCES**

[1] Lee, M.S Lee.K.J Sepn of Iron by extraction*, Hydrometallurgy*, **2005:** 80:163.

[2] B  Pospiech,W.Walkowiak, Michal J.Wozniak*. Physicochemical Problems of Mineral Processing,***2005**:39:89 .

[3] J.Saji,and  M.L.P.Reddy. *Hydrometallurgy* **2001**:61: 81.

[4] A Nasu, H Takagi, Y.Ohmiya And T Sekine. *Analytical Sciences* **1999**:15:177.

[5] DN Reddy. KV Reddy and KH Reddy *J Chem. Pharm. Res*., **2011**:3(3):205

[6]  RS Dave, GB Dave VP Mishra Mk Pandya  *J Chem. Pharm. Res.,***2011**:3(3):271

[7] JK.Tufun,J K Bentum D K Essuman and JE Koranaterg  *J Chem. Pharm. Res*., **2011:** 3(2): 397.

[8] ST Natarajan,R jayaraj, PTThanarajand PD Prasanth *J Chem. Pharm. Res*., **2011:** 3(2):595.

[9] AVLNSH Hariharan and DMuralikrishna *J. Chem. Pharm. Res*. **2011**:3(2): 576.

[10] B.Gupta,  A.Deep,V Singh and SN  Tandon,. *Hydrometallurgy* **2003**:70:121.

[11] J Saji, RT Prasad, C.S.P Iyer,and  M.L.PReddy, *Hydrometallurgy* **1998**: 49: 89.

[12] F.J Alguacil.,and S Martinez,  *Journal of Membrane Science* **2000** ;176: 249 .

[13] S K.atarzyna,.C Ryszard, P Krystyna, Polish. *J. Chem. Tech* **2011:** 13(1):1 .

[14] AIVogel, "A Text book of quantitative Inorganic Analysis" 3$^{rd}$ Edition, **1962**, P.311, Longman, London.

[15] E Hesford. and  H.A.C Mckay *Trans. Faraday Soc.,* **1958**: 54**:** 573,

[16] C.FColeman. KB Brown..,JGMoore. and KA Allen. Proc.2nd Intl. Conf., Peaceful uses of Atomic Energy, Geneva, **1958,** C.10, Paper 510.

[17] RW Cattrall and BO West, *J. Inorg. nucl. chem.,* **1966**: 28: 3035.

[18] WU Zhichun, YU Shuqin,  CHEN Jiayoung *Acta Mettallurgica Sinica* Series B, **1990**: 3(6): 391.