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## Research Article

# SOLVENT EXTRACTION STUDY OF PRASEODYMIUM FROM SALICYLATE MEDIUM BY CYANEX 301

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### ABSTRACT

Solvent extraction of praseodymium (III) from sodium salicylate medium using organophosphorous extractant cyanex 301 in chloroform was studied. The effects of various parameters like sodium salicylate concentration, extractant concentration, shaking time, diluents and stripping agent on the extraction efficiency of Pr (III) were investigated. Diverse ion study was also performed in order to check the influence of other ions in the extraction. The extraction of Pr (III) was quantitative using 0.003 M Cyanex 301 and 0.01M sodium salicylate. The extracted Pr (III) was stripped out quantitatively from the organic phase with 1.0 M hydrochloric acid and determined spectrophotometrically with arsenazo (III) at 655 nm. Separation of Pr (III) from binary mixture other was achieved. The method was extended for the separation and determination of Pr(III) in magnet leach solution. The method is simple, rapid and selective with good reproducibility.

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### INTRODUCTION

Praseodymium is valued for its magnetic, electrical, chemical, and optical properties (Rare earth elements 101 2012). The Rare Earth Elements (REE) permanent magnets made using praseodymium are applied in hybrids, plug-in, electric vehicles, wind and hydro power generation, computer disc drives; cordless power tools and medical imaging-MRI (Xie, F. et al 2014). Other application of praseodymium is for improved magnet corrosion resistance; pigment; searchlights; airport signal lenses; photographic filters, control systems etc. Therefore, there is an analytical importance for the separation and determination of trace praseodymium in various types of samples ranging from geological to nuclear waste materials. Solvent extraction is the most widely used technique for the separation and recovery of praseodymium.

The extraction of praseodymium was investigated from chloride medium using different extractants such as D2EHPA, PC88A, Cyanex 272, Cyanex 921, Cyanex 923, Cyanex 301, Cyanex 302, LIX 841, LIX 622N, Alamine 336, Aliquat 336 and their mixtures. Among the extractants, the combination of cyanex 921 with cyanex 301 and combination of cyanex 923 with cyanex 301 showed best results (Padhan, E., et al., 2018). Extraction and separation of Ce(III) and Pr(III) was studied using two complexing agents with di-(2-ethylhexy) phosphoric

acid. (Shao H. et al., 2014). Hydrometallurgical route were implemented to separate Nd and Pr from permanent magnet scrap using NaD2EHPA (Parhi, P.K. et al., 2016). Studies for separation of lanthanum and cerium have been studied extensively using organophosphorous extractant (Basualto C. et al., 2013). Synergistic solvent extraction, the extraction of metal ions with two kinds of extractants, has attracted much attention in the last decades. It not only enhances the extraction efficiency but also improves the selectivity significantly (Batchu N.K. et al., 2015, Banda, R. et al., 2012, Padhan, E. et al., 2018). Cyanex 272, Alamine 336, TBP, LIX 63 etc. were used to study extraction in chloride medium (Liu, Y. et al., 2016, Liu, Y. et al., 2015, Liu, Y. et al., 2015a, Liu, Y. et al., 2014). Also, Cyanex 272 and its mixture with solvating, cationic and anionic extractants like TBP, TOPO, DOS, Cyanex 301, Versatic-10, Alamine 308, and Alamine 336 solvent have been studied for extraction of Pr and Nd from chloride solution containing La Saponified. Cyanex 272 showed better separation capabilities than unsaponified cyanex 272 (Banda, R. et al 2012). Extraction from chloride acetate media was studied using 8-Hydroxy quinoline (Wu, D. et al., 2007 and Wu, D. et al., 2007a). Pr (III) in nitrate media was studied using Cyanex 301 (Hefny, N.E, El. et al., 2004, Hsu, K.H. et al 1980). The stoichiometry of the metal species in the organic phase was reported as  $Pr(NO_3)_3 \cdot 2CYANEX\ 921$  and  $Pr(NO_3)_3 \cdot CYANEX\ 923$  by using cyanex 921 and cyanex 923 in

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kerosene (Panda, N. *et. al.*, 2014). Binary mixture of Cyanex 921 and Cyanex 923 as extractant for extraction study of Pr (III) and Nd (III) (Panda, N. *et. al.*, 2017). N,N-dihexyloxamic acid was found to serve as an effective extractant for La, Ce and Pr from hydrochloric acid. The extraction order was La < Ce < Pr (Guoa, C. *et. al.*, 2017)

The effect of various diluents on the extraction of Pr(III) and Sm(III) by cyanex 923 was studied by (Nadi, El.*et. al.*, 2010), who reported that the extraction increases with the decrease in the polarity of the investigated diluents. Hefny used cyanex 923 in various diluents for extraction.

In the present work, the solvent extraction of praseodymium (III) in sodium salicylate media using cyanex 301 in chloroform has been studied. The effects of several parameters, such as the sodium salicylate concentration, cyanex 301 concentration, shaking time, study of stripping agents, effect of diluents, influence of other REE and metal ion, binary separation and its application, are studied. The method is found to be selective and efficient.

## Experimental

### Materials

Cyanex 301 was procured from Cytec, Canada. sodium salicylate, nitric acid, hydrochloric acid, chloroform were of AR grade and arsenazo reagent was of LR grade.

A UV-visible spectrophotometer (1800 Shimadzu) was used to measure the absorbance of the metal-arsenazo complex and to establish its  $\lambda_{max}$  and its concentration. The absorbance was measured at 655 nm against reagent blank solution

Cyanex 301 was diluted in chloroform. Praseodymium solution, sodium salicylate solutions were prepared in milli Q water. Hydrochloric acid was used as a stripping agent.

### Procedure

#### Extraction method

The aqueous phase containing 50  $\mu$ g Praseodymium (III) was maintained at 0.01 M sodium salicylate solution in a total volume of 10 mL and then transferred to 125 mL separatory funnel. 10 mL of 0.003 M cyanex 301 in chloroform was added into separating funnel and shaken for 5 minutes. The two phases were allowed to separate. Praseodymium (III) was then stripped from the organic phase.

#### Back Stripping Method

The back stripping of praseodymium (III) was carried out by shaking 10 mL of 1.0 M hydrochloric acid (stripping agent) and the loaded organic phase containing Pr (III) in a separating funnel. Stripped praseodymium (III) was determined spectrophotometrically with arsenazo (III) at 655 nm. The concentration of praseodymium (III) was calculated from calibration graph

The metal concentration in the organic phase was calculated from the difference between its concentrations in the aqueous phase before and after extraction. The distribution ratio (D) was calculated from the equation:

$$D = \frac{(C_o - C) \times V}{(C \times V')}$$

Where  $C_o$  is the original metal concentration before extraction, C is the final metal concentration in solution after extraction, while V and V' are the volumes of the aqueous and organic phases, respectively.

The percentage of extraction (E/%) was determined from (D) values as:

$$\% E = \frac{100 D}{D + 1}$$

The percentage of stripping has been calculated using the formula:

$$\% \text{ Stripping} = \frac{[M]_s}{[M]_o - [M]} \times 100$$

Where

$[M]_o$  is the original concentration in the aqueous phase before extraction

$[M]$  is the concentration of metal in the aqueous phase after extraction

$[M]_s$  is the concentration of metal in the aqueous phase after stripping.

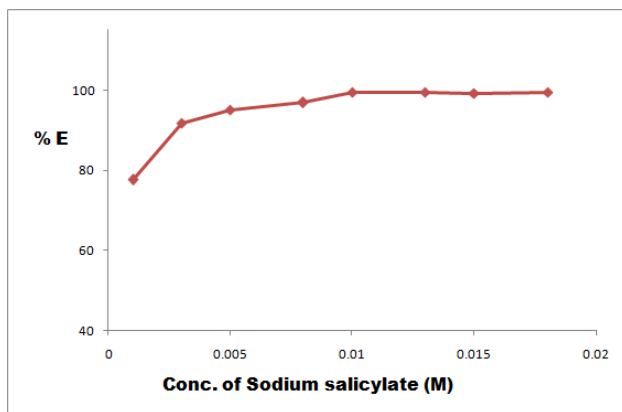
## RESULTS AND DISCUSSION

### Effect of sodium salicylate concentration

The extraction efficiency of praseodymium (III) with cyanex 301 in chloroform as a function of sodium salicylate concentration is tabulated in table 1 and plot is shown in fig. 1. The concentration of cyanex 301 in the organic phase was fixed at 0.003 M. On further decrease in concentration of sodium salicylate there was decrease in extraction of praseodymium (III) and with increased concentration there was not much change. Thus, confirming direct proportionality between sodium salicylate concentration and extraction of praseodymium (III). The subsequent extraction studies of praseodymium (III) were carried out with 0.01 M sodium salicylate.

**Table 1** Effect of sodium salicylate concentration

Concentration of Sodium salicylate (M)	%E
0.001	77.6
0.003	91.7
0.005	95.1
0.008	96.9
0.010	99.4
0.013	99.4
0.015	99.3
0.018	99.4



**Fig 1** Effect of concentration sodium salicylate

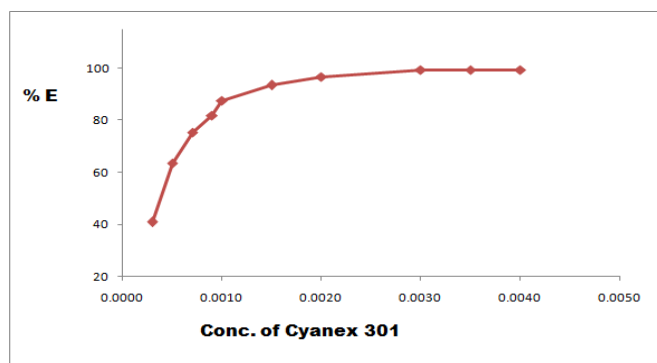
Pr(III) - 50  $\mu$ g/mL, Cyanex 301 – 0.003M, Stripping agent- 1.0 M HCl

**Effect of concentration of Cyanex 301**

In order to ascertain the optimum concentration of cyanex 301 required for the quantitative extraction of praseodymium (III), studies were conducted by varying the concentration of cyanex 301 in the range of 0.0003 to 0.004M by fixing concentration of sodium salicylate at 0.01M. The results are tabulated in table 2 and plot shown fig. 2. It was found that the extraction of praseodymium (III) was quantitative from 0.003 M to 0.004 M. With the decrease in concentration of cyanex 301, extraction of praseodymium (III) decreases. Hence, for further extraction studies of praseodymium (III) concentration of cyanex 301 selected was 0.003M.

**Table 2** Study of effect of concentration of cyanex 301

Concentration of Cyanex 301 (M)	%E
0.0003	40.83
0.0005	63.66
0.0007	75.5
0.0009	81.9
0.0010	87.7
0.0015	93.5
0.0020	96.7
0.0030	99.4
0.0035	99.4
0.0040	99.4



**Fig 2** Study of effect of concentration of cyanex 301

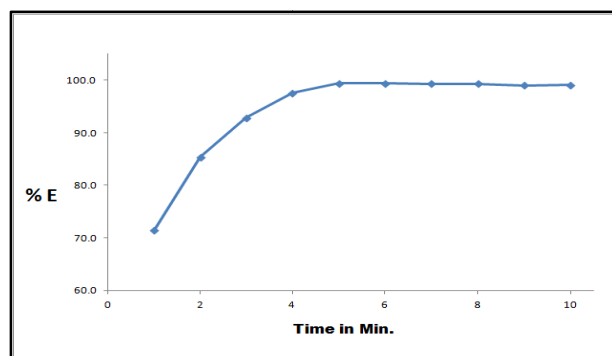
Pr(III) - 50  $\mu$ g/mL, sodium salicylate – 0.01M, Stripping agent- 1.0 M HCl.

**Effect of shaking time**

The shaking time was optimized by performing extraction for various periods of time (1-15 min.). The results showed that with 5 minutes of shaking there was quantitative extraction of praseodymium (III) (Table 3 & Fig. 3). However, with prolonged shaking there were no adverse effect on the extraction of praseodymium (III) in the presence of sodium salicylate. Hence, for practical purpose 5 minutes equilibration time was selected.

**Table 3** Effect of shaking time

Time in min.	% E
1	71.5
2	85.3
3	92.8
4	97.6
5	99.4
6	99.4
7	99.3
8	99.3
9	99.0
10	99.1



**Fig 3** Effect of shaking time

Pr(III) - 50  $\mu$ g/mL, sodium salicylate – 0.01M, Cyanex 301 – 0.003M  
Stripping agent- 1.0 M HCl

**Effect of diluents**

In order to study the effect of diluents on the extraction behavior, various diluents as shown in Table 4 were investigated. Chloroform was found to be best diluent amongst all as it gave quantitative extraction. Hence for all further studies, chloroform was selected as diluent.

**Table 4** Effect of diluents

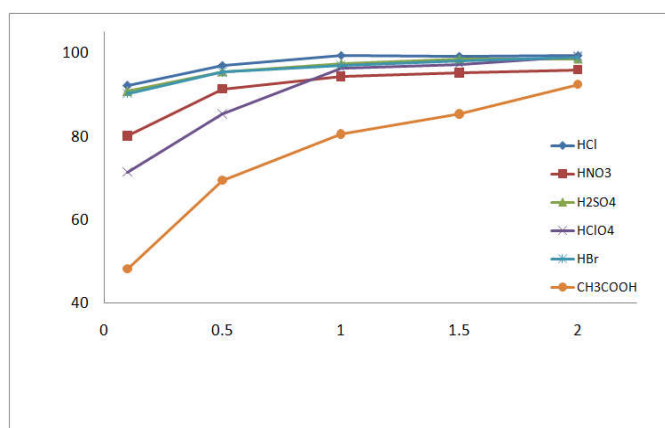
Diluents	Dielectric constant	Percentage Extraction
Carbontetrachloride	2.24	73.1
Chloroform	4.80	99.4
Dichloroethane	10.50	64.3
n-Dodecane	2.00	80.7
Nitrobenzene	34.80	41.2
Tetrachloroethane	8.20	42.0
Toluene	2.38	94.5
Xylene	2.30	85.4
Kerosene	2.02	86.0

**Study of stripping agents**

After extraction, back extraction was carried out to remove praseodymium (III) from the organic phase, for which various stripping agents were tried. The concentration of strip pants was varied from 0.1-2.0 M. Back extraction of praseodymium (III) was quantitative with 0.5-2.0 M hydrochloric acid. In further studies 1.0 M hydrochloric acid was used as stripping agent. The results are tabulated in table 5 and plot in shown fig. 4.

**Table 5** Study of stripping agents

Conc. (M)	Percentage Stripping of praseodymium (III)					
	HCl	HNO <sub>3</sub>	H <sub>2</sub> SO <sub>4</sub>	HClO <sub>4</sub>	HBr	CH <sub>3</sub> COOH
0.1	92.1	80.1	90.8	71.4	90.2	48.2
0.5	97.0	91.3	95.5	85.3	95.4	69.4
1.0	99.4	94.3	97.4	96.4	97.0	80.5
1.5	99.3	95.2	98.5	97.3	98.2	85.3
2.0	99.4	96.0	98.6	99.2	98.9	92.4

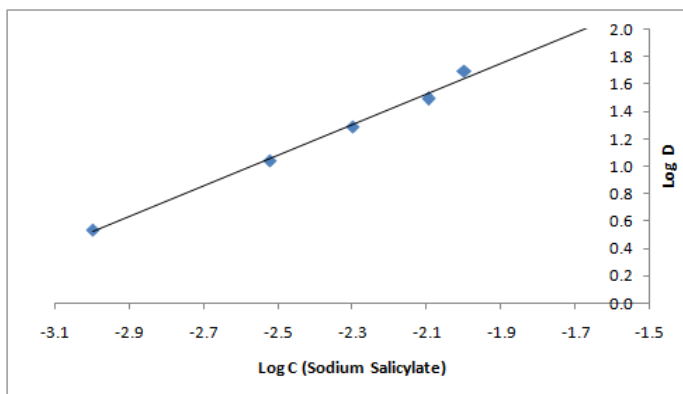


**Fig 4** Study of stripping agents

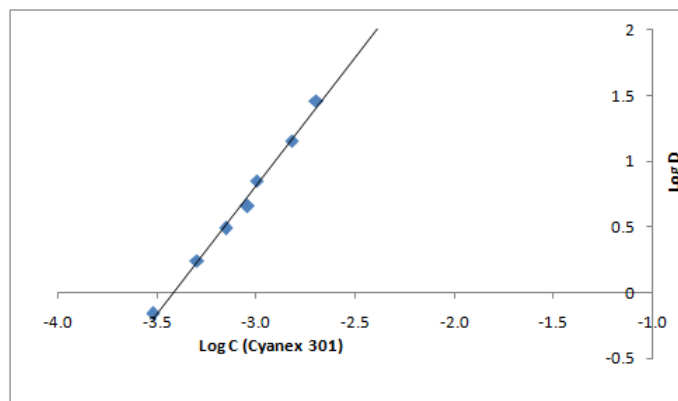
Pr(III) - 50 μg/mL, Cyanex 301- 0.003M, Sodium salicylate- 0.01M

**Nature of extracted species**

An attempt was made to find out the probable composition of the extracted species, from a plot of log D vs log C (sodium salicylate) at fixed cyanex concentration (0.003 M) shown in fig. 5 and log D vs log C (Cyanex 301) at fixed sodium salicylate concentration (0.01 M), shown in fig. 6. The slope of this plot was found to be 1.1 and 1.95 respectively indicating the one salicylate ion react with one mole of praseodymium and two cyanex molecules are used in extraction process.



**Fig 5** log D vs log C (sodium salicylate) at fixed cyanex concentration (0.003 M)



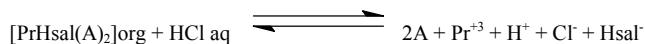
**Fig 6** log D vs log C (Cyanex 301) at fixed sodium salicylate concentration (0.01 M)

Therefore, on the basis of the above studies, the probable mechanism for the complex formation can be proposed as follows;



Where Hsal stands for the salicylate ion  
 H<sub>2</sub>sal stands for salicylic acid  
 HA stands for the active component of Cyanex 301

The probable extracted species PrHsal(A)<sub>2</sub> formed in organic phase was stripped out using 1M hydrochloric acid. Reaction occurring in stripping mechanism could be given as, Stripping mechanism:



In conclusion, we can say that, there is formation of a mixed complex, of the type PrHsal(A)<sub>2</sub>. Praseodymium was stripped from the organic phase and detected using Arsenazo.

**Effect of diverse ions**

Praseodymium (III) was extracted with 0.003M cyanex 301 in chloroform from 0.01M sodium salicylate in the presence of wide range of diverse ions (Table 6). The tolerance limit was set such that the amount of diverse ions required causing ±2% error in the recovery of Praseodymium (III). It was observed that, a large number of cations and anions were tolerated.

**Table 6** Praseodymium (III) extracted with 0.003M cyanex 301 in chloroform from 0.01M sodium salicylate in the presence of diverse ions

Tolerance Ratio	Diverse Ions		
	Cations	Anions	REE
Pr(III) : Diverse ions			
1:10	Cd <sup>2+</sup> , Mn <sup>2+</sup>	Thiourea, Urea, F <sup>-</sup>	- - - -
1:15	K <sup>+</sup> , Pb <sup>4+</sup> , Ca <sup>2+</sup>	Oxalate, NO <sub>3</sub> <sup>-</sup> , NO <sub>2</sub> <sup>-</sup>	Sm <sup>3+</sup>
1:20	Mg <sup>2+</sup> , Na <sup>+</sup>	PO <sub>4</sub> <sup>3-</sup> , I <sup>-</sup> , Tartarate	Nd <sup>3+</sup>
1:25	Pt <sup>4+</sup> , Ba <sup>2+</sup> , Cu <sup>2+</sup> , Cr <sup>3+</sup>	Cl <sup>-</sup> , Br <sup>-</sup>	Eu <sup>3+</sup>
1:30	Ni <sup>2+</sup> , Be <sup>2+</sup> , Zn <sup>2+</sup> , Mo <sup>6+</sup> , V <sup>5+</sup>	EDTA, SO <sub>4</sub> <sup>2-</sup> , SO <sub>3</sub> <sup>2-</sup>	Gd <sup>3+</sup> , Dy <sup>3+</sup> , Y <sup>3+</sup>

**Separation of praseodymium (III) from binary mixtures**

Based on the partition data, the separation of Praseodymium (III) from some commonly associated metal ions obtained in the leach solution obtained from permanent magnet of rare

earth like Nd (III), Sm (III), Co (II), Mn (III) and Th(IV) using Cyanex 301 in chloroform can be achieved by taking advantage of difference in extraction conditions. Praseodymium (III) extracted in organic phase was stripped out using 1M HCl and determined spectrophotometrically. The recoveries of Pr (III) and that of the added ions were obtained about 99.4% as shown in Table 7.

**Table 7** Separation of praseodymium (III) from binary mixture

Sr. No.	Composition µg/mL	Recovery of Pr(III) %	Recovery of added ion*
1	Pr(III) : Nd (III) (50 : 400)	99.4	99.9
2	Pr(III) : Sm (III) (50 : 30)	99.3	99.5
3	Pr(III) : Co (III) (50 : 500)	99.3	99.5
4	Pr(III) : Mn (III) (50 : 200)	99.4	99.4
5	Pr(III) : Th (IV) (50 : 30)	99.4	99.4

\*Estimated procedure for added ion by ICP

### Analysis of praseodymium (III) in leach solution of magnet scrap

An aliquot of sample solution was analyzed as per the proposed method and known method. Praseodymium (III) content was determined and the % recovery of praseodymium (III) was found to be 99.4%.

### CONCLUSION

- A simple method has been developed for the extraction, separation and determination of praseodymium (III) using cyanex 301 in chloroform from sodium salicylate medium.
- The important feature of this method is that it permits the separation of praseodymium (III) from other rare earth elements such as Nd (III) and Sm (III). Also Co (II), Mn(II) and Th (IV) which are usually associated with rare earth in the leach solution of magnet scrap
- The method was extended for the analysis of praseodymium in leach solution.
- The method is simple, rapid and selective with good reproducibility (approximately  $\pm 2\%$ ).

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