Studies on Separation of Actinides And Lanthanides by Extraction Chromatography Using 2,6-BisTriazinyl Pyridine

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GULMARG (Jammu & Kashmir)
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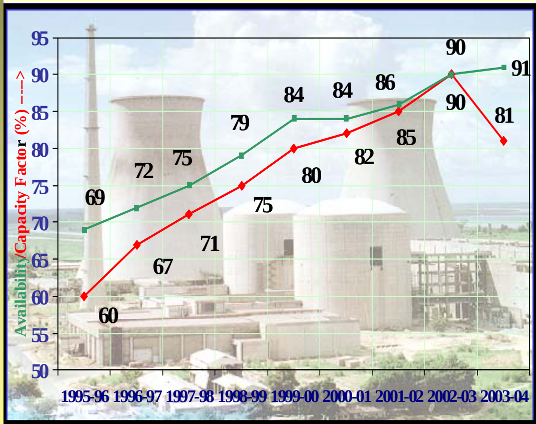
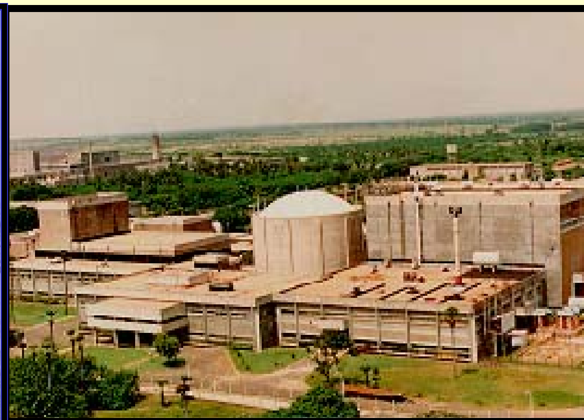
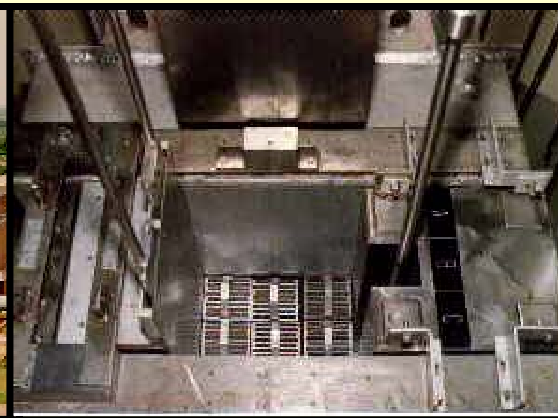
BRNS : Board of Research in Nuclear Sciences
HBNI : Homi Bhabha National Institute
NBHM : National Board for Higher Mathematics
SSSF : Solid Storage Surveillance Facility
WIP : Waste Immobilisation Plant
AEES : Atomic Energy Education Society
ACTREC : Advanced Centre for Treatment, Research & Education in Cancer
TIFR : Tata Institute of FundamentalResearch
TMC : Tata Memorial Centre
DCS&EM : Directorate of Construction, Services & Estate Management
DPS : Directorate of Purchase & Stores
Research & Development Organisations
Public Sector Undertakings
Industrial Facilities
Grant-in-aid Organisations
Service Organisations

THREE STAGE NUCLEAR POWER PROGRAM







Stage – I PHWRs

- 12- Operating
- 6 - Under construction
- Several others planned
- Scaling to 700 MWe
- Gestation period being reduced
- POWER POTENTIAL ≅ 10,000 MWe

LWRs

- 2 BWRs Operating
- 2 VVERs under construction

Stage - II
Fast Breeder Reactors

- 40 MWth FBTR - Operating since 1985 Technology Objectives realised
- 500 MWe PFBR- Under Construction
- POWER POTENTIAL ≅ 530,000 MWe

DAE Presentation on 24-06-04

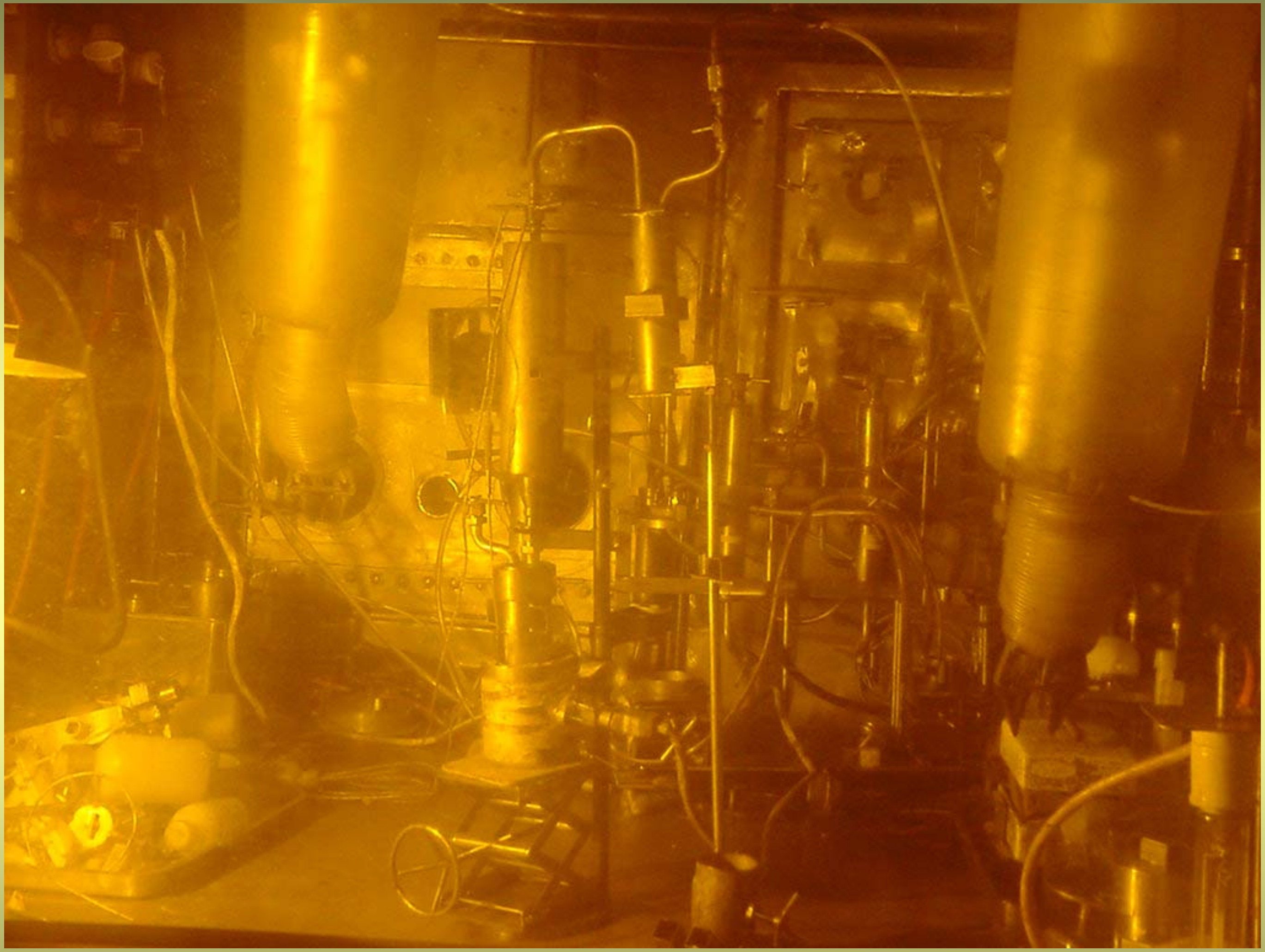
Stage - III
Thorium Based Reactors

- 30 kWth KAMINI- Operating
- 300 MWe AHWR- Under Development

POWER POTENTIAL IS VERY LARGE
Availability of ADS can enable early introduction of Thorium on a large scale

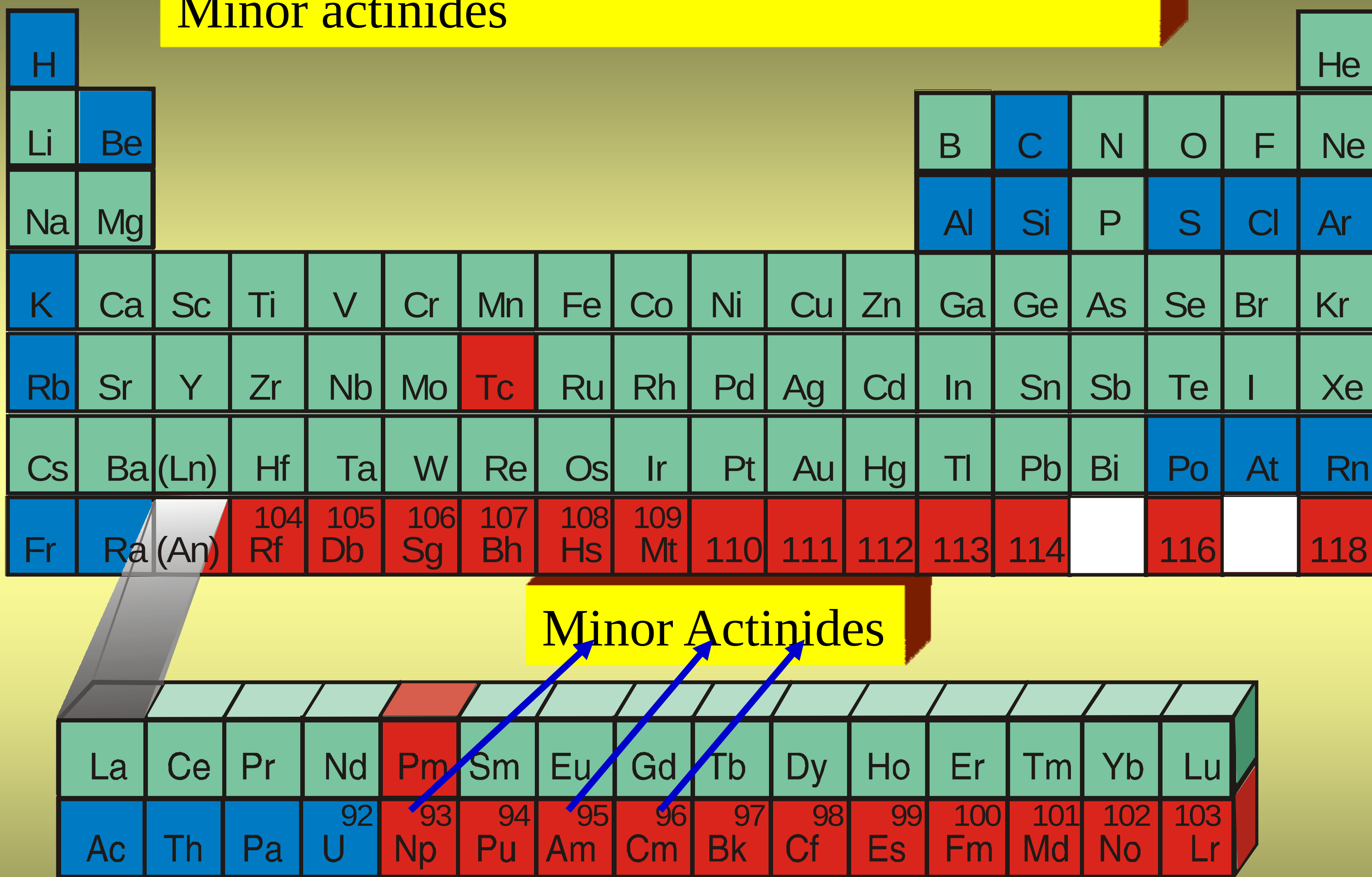
Fast Breeder Test Reactor
Kalpakkam

Radiochemistry Laboratory



Hot Cells

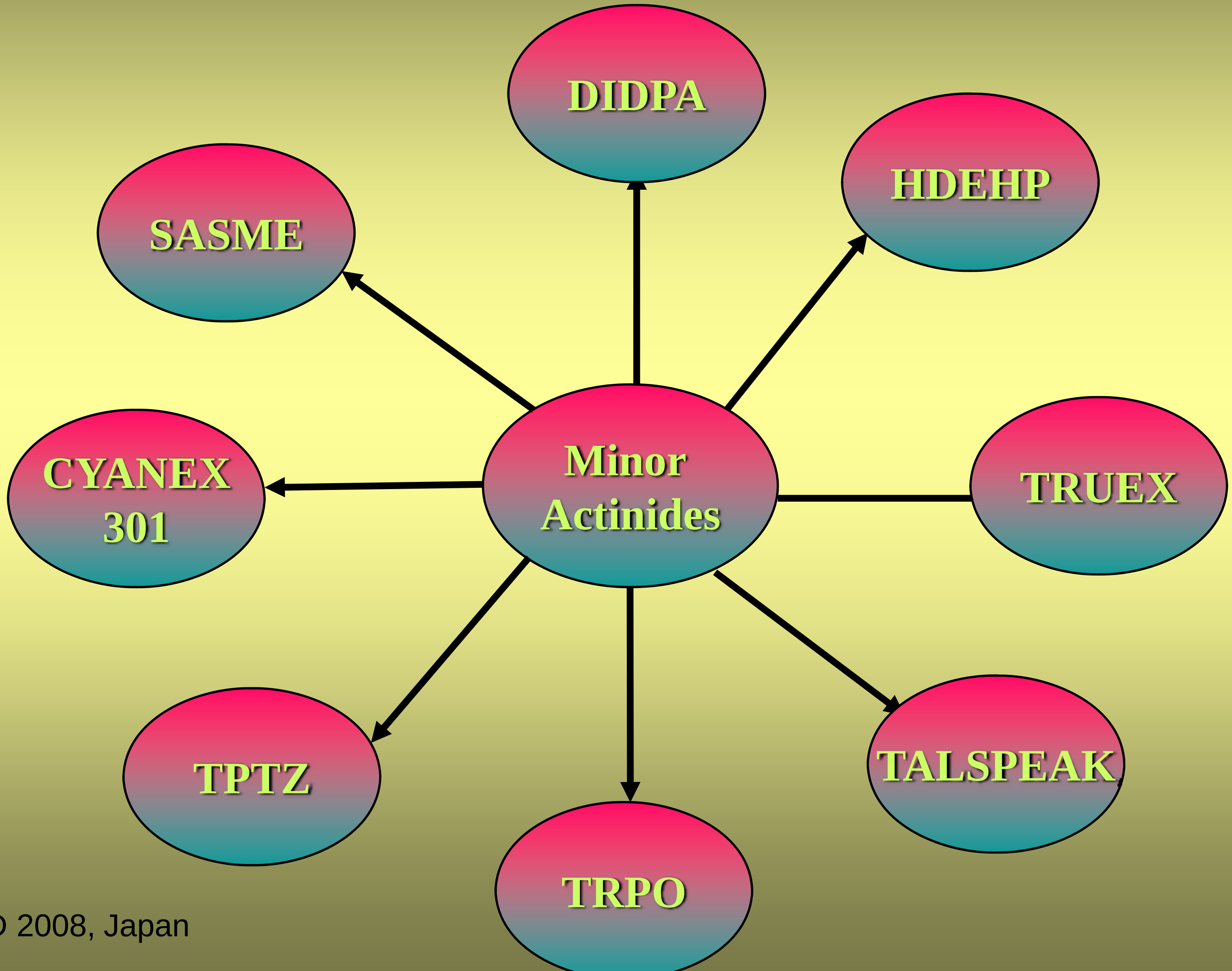
Minor actinides



Man-made Radioactive Elements

Naturally Radioactive Elements

*Separation of **MINOR** actinides by various techniques*



Extractants used in our Laboratory

for Co extraction of lanthanides and actinides

Truex process ---- CMPO ------ Solvent Extraction

Diamides ----- DMDBMA ------- Solvent Extraction
[Dimethyl Dibutyl Malonamide]

TEHDGA --- Tetraethyl Hexyl Diglycoamide -- Solvent Extraction

DMDOHEMA ---- Solvent Extraction
[DimethylDioctylHexylEthoxyMAlonamide]

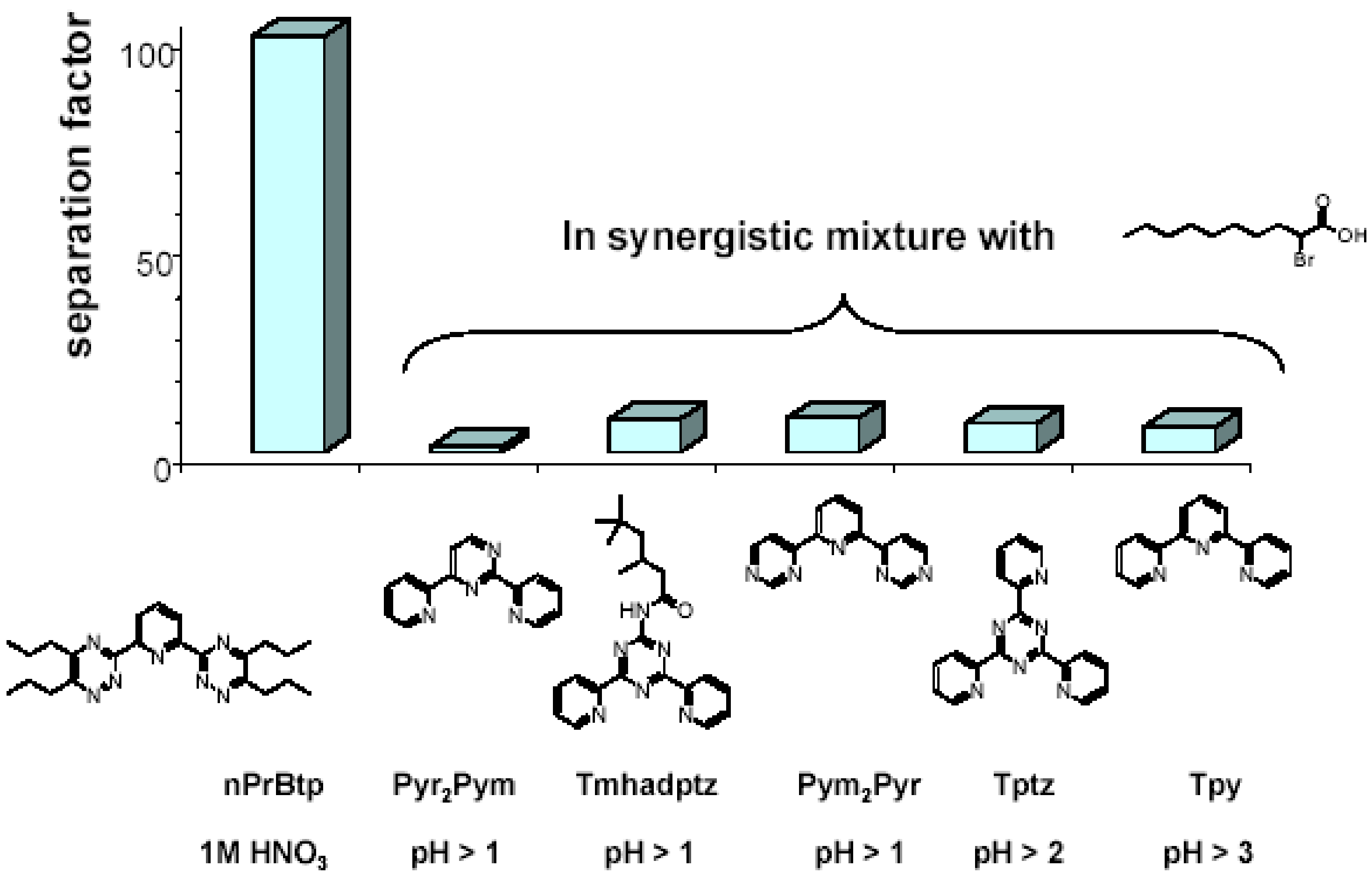
Other Techniques

- Extraction Chromatography
- Room Temperature Ionic Liquids
- Supercritical Fluid Extraction
- High Performance Liquid Chromatography

Actinide – Lanthanide Separation

- Bis Triazinyl Pyridine (BTP)

An(III) / Ln(III) SEPARATION BY POLYAZINES



Outline

- **Introduction**
  - Lanthanide-Actinide Separation.
  - Bis Triazinyl Pyridines (BTPs).
  - Advantages of Extraction Chromatography over Solvent Extraction.
- **Experimental Work**
  - Synthesis of 2,6-bis(5,6-dipropyl-1,2,4-triazin-3-yl)pyridine.
  - Preparation of the Extraction Resin.
  - Extraction Studies of Am (III) and trivalent lanthanides by XAD-7 impregnated with 2,6-bis(5,6-dipropyl-1,2,4-triazin-3-yl)pyridine.
- **Conclusions**

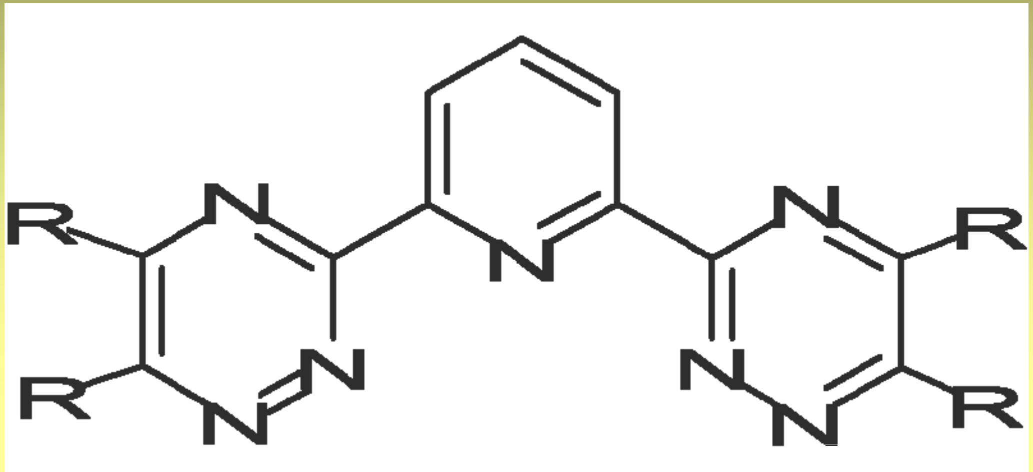
Introduction

Lanthanide – Actinide Separation

- *Need*
  - Partitioning and Transmutation (to reduce long-term radiological risks to the environment by transmutation of the minor actinides).

- *Difficulty*
  - Lanthanides and actinides have similar chemical properties due to similar ionic radii.

Bis Triazinyl Pyridines (BTPs)



First reported in 1999 by ***Kolarik, Mullich and Gassner*** that 2,6-di(5,6-dialkyl-1,2,4-triazin-3-yl)pyridines extract and separate Am(III) and Eu(III) very efficiently as nitrates.

(Solvent Extraction and Ion Exchange, 17(1), 23-22, 1999)

Limitations of solvent extraction –

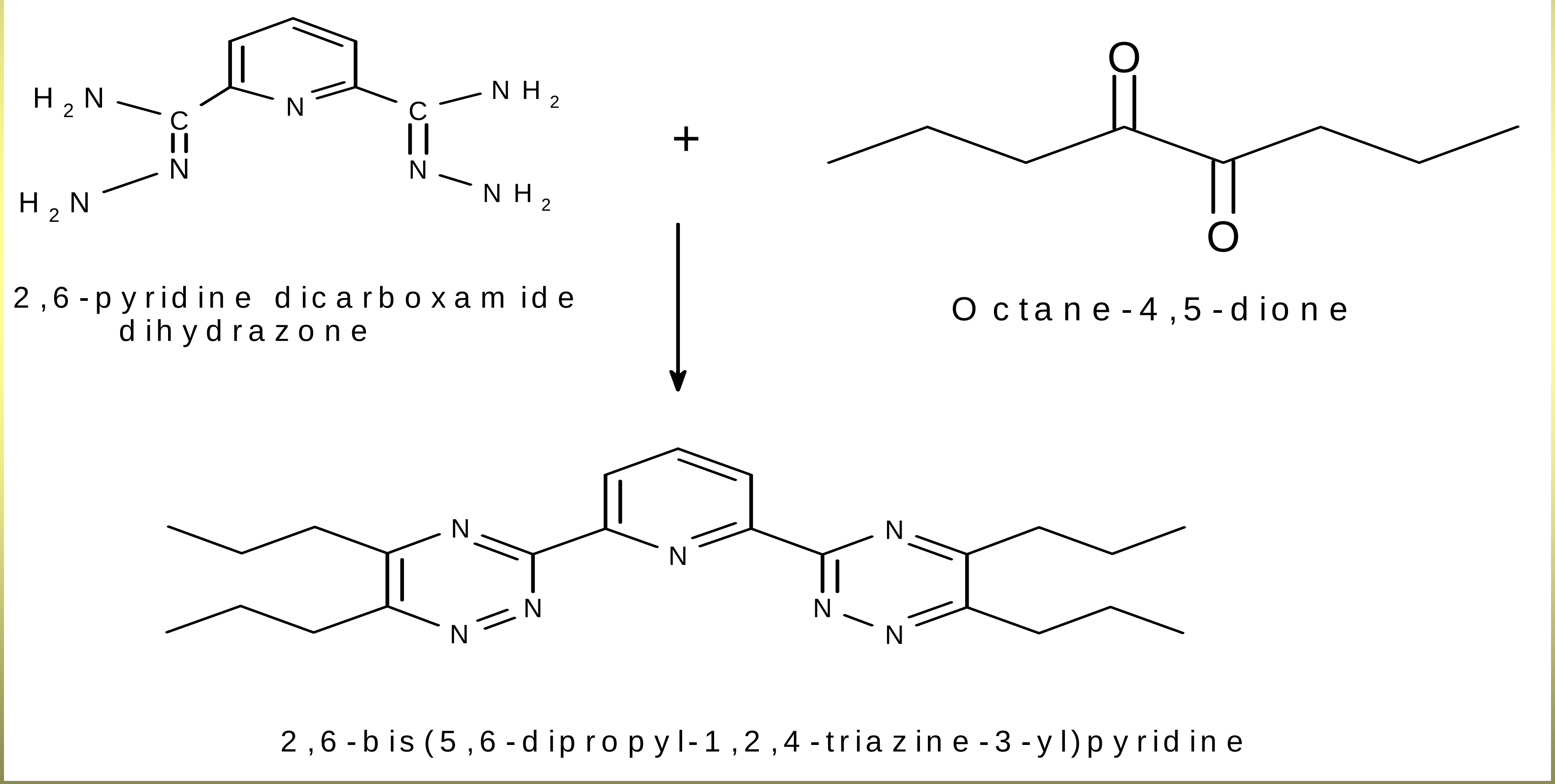
- Third Phase formation,
- Need for phase-modifiers,
- Disposal of large volumes of extractants and diluents,
- Tedious multi-stage extraction procedures.

Advantages of Extraction Chromatography

- No third phase formation,
- No need for a modifier,
- Reusability of the synthesized resin,
- Simple and compact equipment,
- Minimal loss of organic solvent.

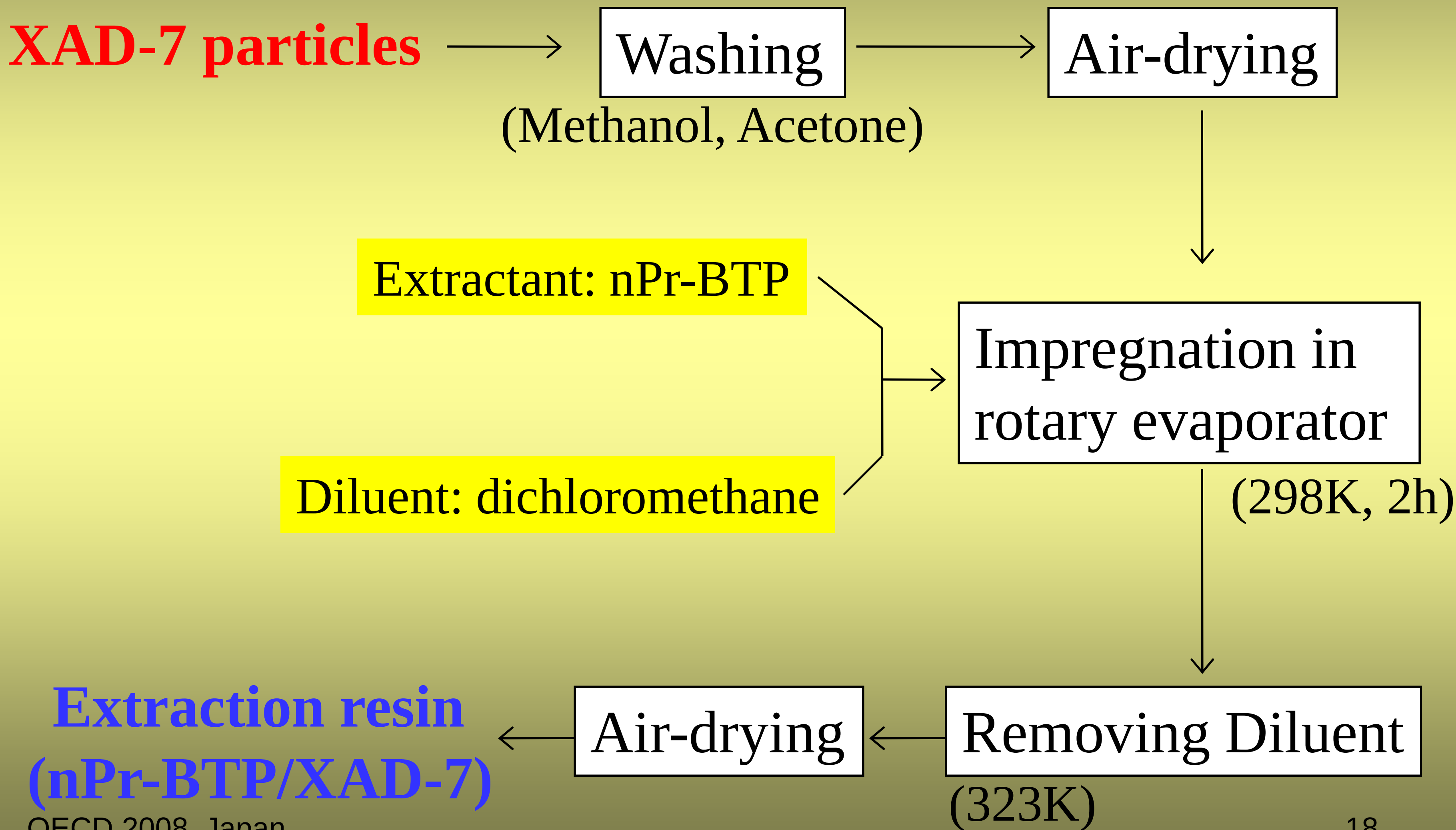
Experimental Work

Synthesis of 2,6-bis(5,6-dipropyl-1,2,4-triazine-3-yl)-pyridine



Preparation of the Extraction Resin

Resin Impregnation



"Extraction Studies of Am (III) and trivalent lanthanides by XAD-7 impregnated with 2,6-bis(5,6-dipropyl-1,2,4-triazin-3-yl)pyridine"

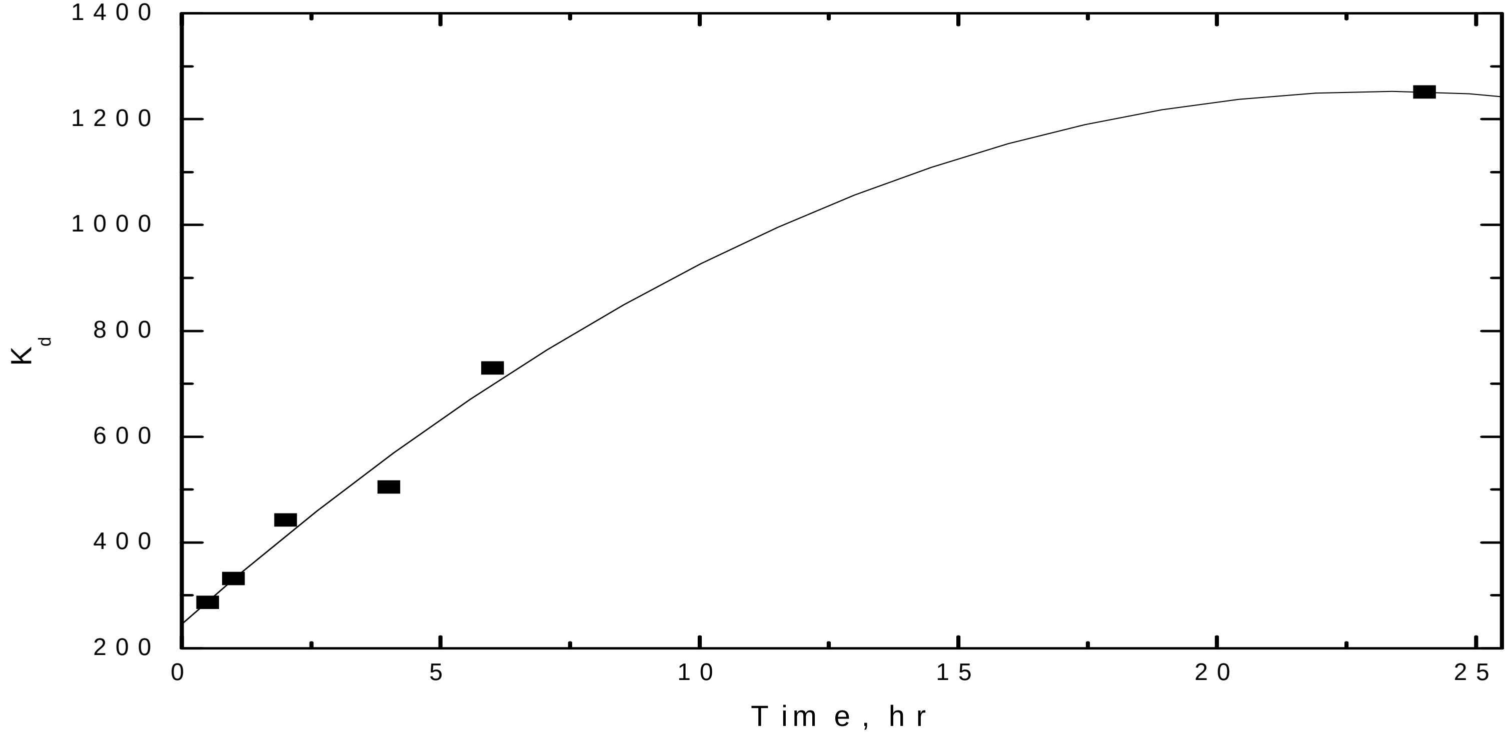


Figure : Kinetics of the uptake of Am (III) by nPr-BTP/XAD-7 resin (0.25g nPr-BTP/XAD-7, 0.1M HNO_3, 2M NH_4NO_3, 303K)

- **Distribution coefficient (K_d) values increased with increasing time of equilibration and equilibrium is reached in 24 hours.**
- **For K_d measurements, we have equilibrated for 3 hours.**

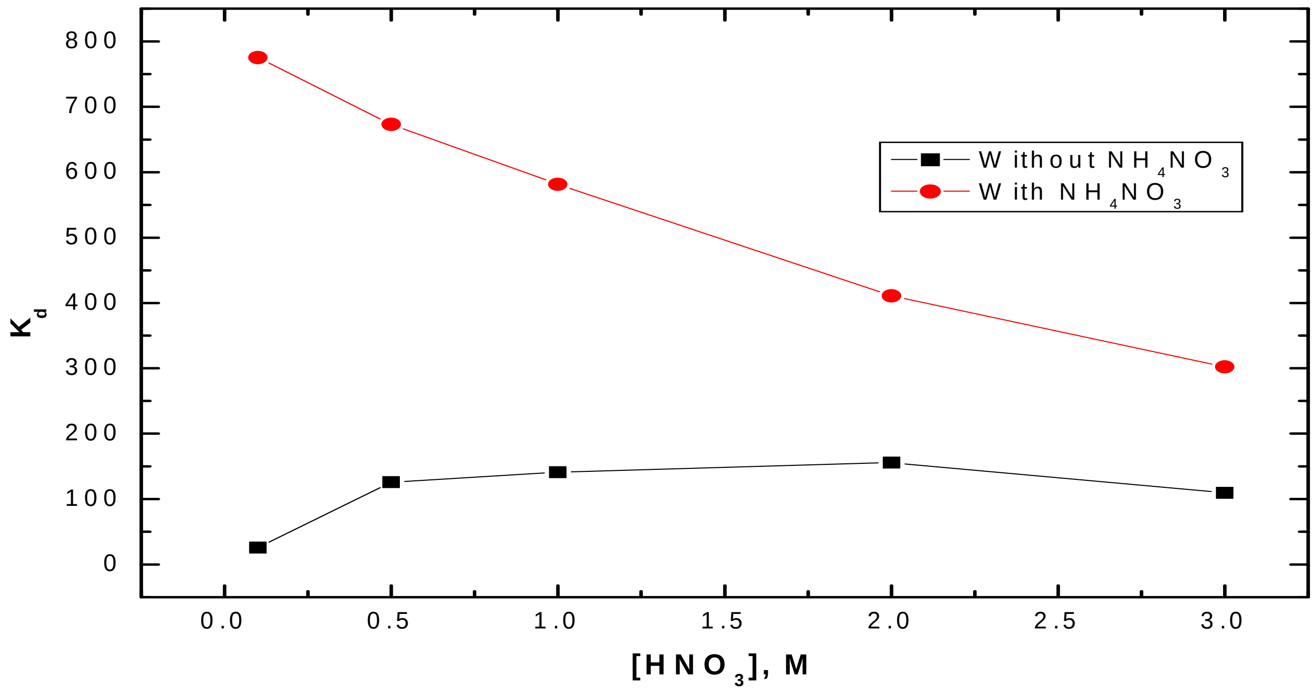


Figure: Effect of nitric acid concentration on the uptake of Am(III) by nPr-BTP/XAD-7 resin with and without 2M NH4NO3 (0.25g nPr-BTP/XAD-7, 303K, 3h).

- **K_d values for the extraction of Am(III) from nitric acid with ammonium nitrate are significantly higher.**

- **The increase of Am(III) adsorption with increasing nitrate concentration can be explained by the following adsorption equilibrium represented by Equation (1),**

$$M^{3+} + 3NO_3^- + n(\text{nPr-BTP}) = M(NO_3)_3(\text{nPr-BTP})_n \qquad (1)$$

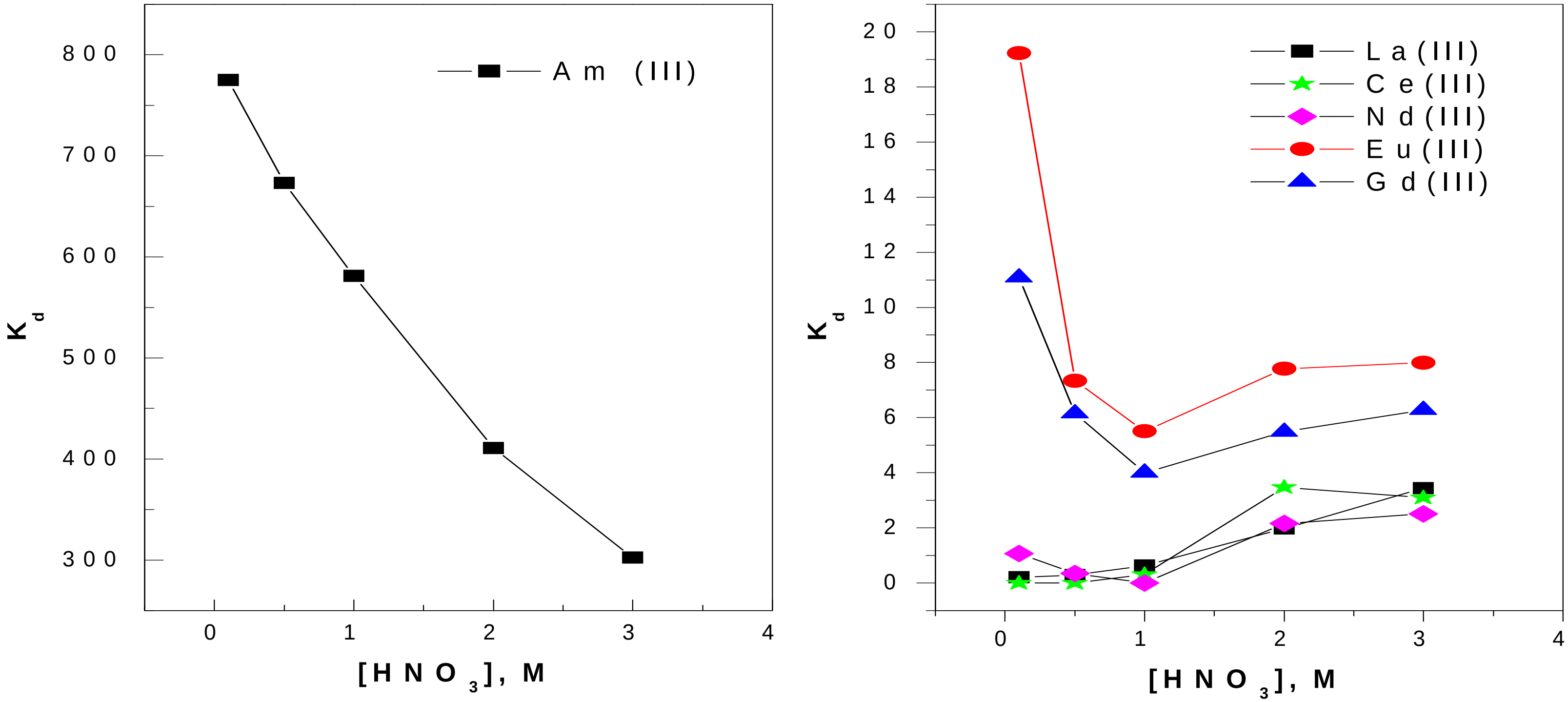


Figure : Effect of nitric acid concentration on the uptake of Am(III) and lanthanides by nPr-BTP/XAD-7 resin (0.25g nPr-BTP/XAD-7, 2 M NH_4NO_3, 303K, 3h)

- **The lanthanides are not extracted by the resin at any acidity.**
- **K_d value for the extraction of Am(III) is maximum at 0.1M nitric acid in the presence of ammonium nitrate.**

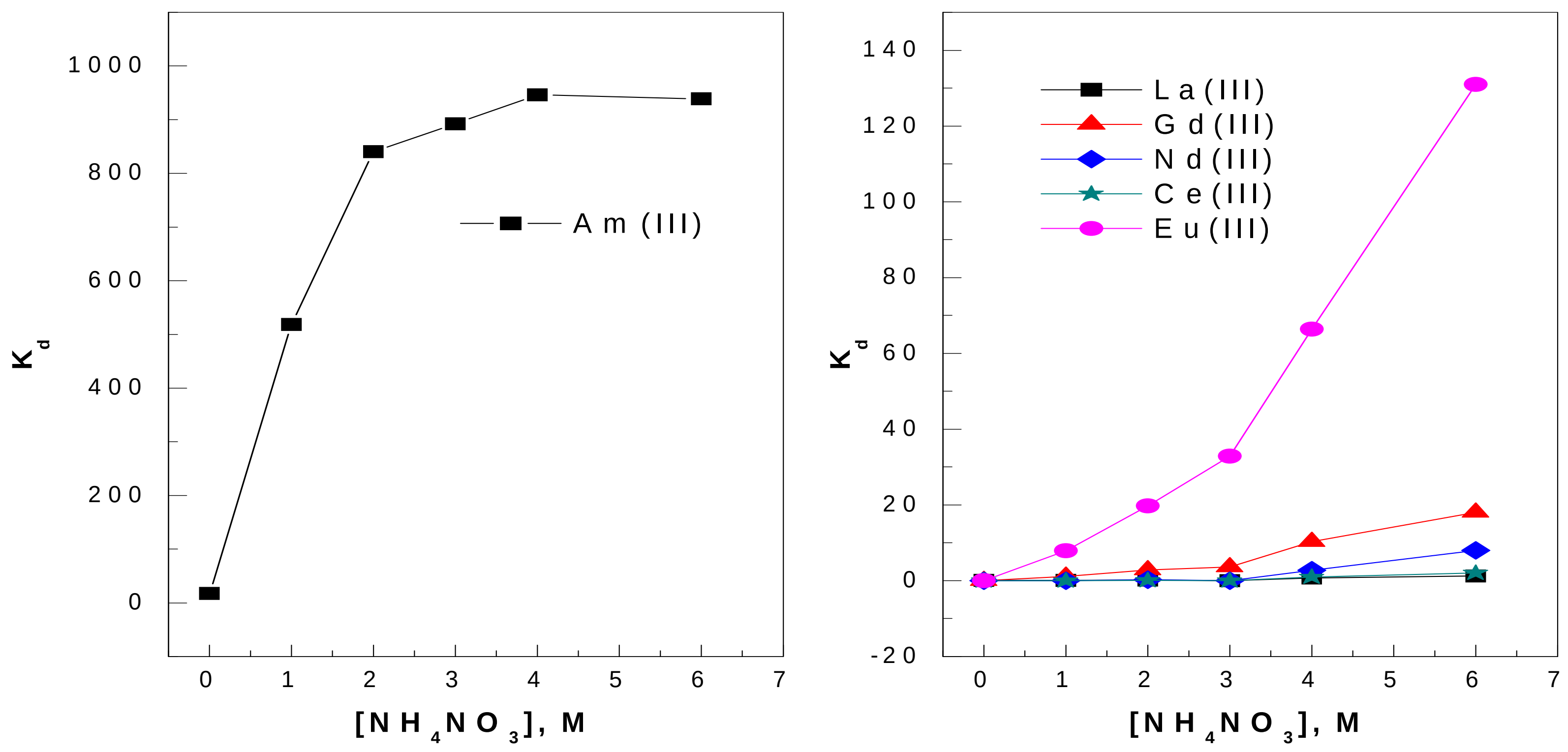


Figure : Effect of nitrate concentration on the uptake of Am(III) and Lanthanides by nPr-BTP/XAD-7 resin (0.25g nPr-BTP/XAD-7, 0.1M HNO_3, 303K, 3h)

The distribution coefficient (K_d) value of Am (III) increases with increase in NH_4NO_3 concentration, which can be explained by equation (1),

$$M^{3+} + 3NO_3^- + n(\text{nPr-BTP}) = M(NO_3)_3(\text{nPr-BTP})_n \qquad (1)$$

$[NH_4NO_3]$ M	Separation Factor (K_d Am / K_d Ln)				
	La	Ce	Nd	Eu	Gd
0	192	173	173	173	173
1	2730	5187	5187	66	451
2	2471	7638	1400	43	296
3	8925	8926	8926	27	246
4	1412	937	347	14	92
6	770	465	117	7	52

Table: Separation Factors for Americium-Lanthanide Separations (0.25g nPr-BTP/XAD-7, 0.1M HNO3, 303K, 3h)

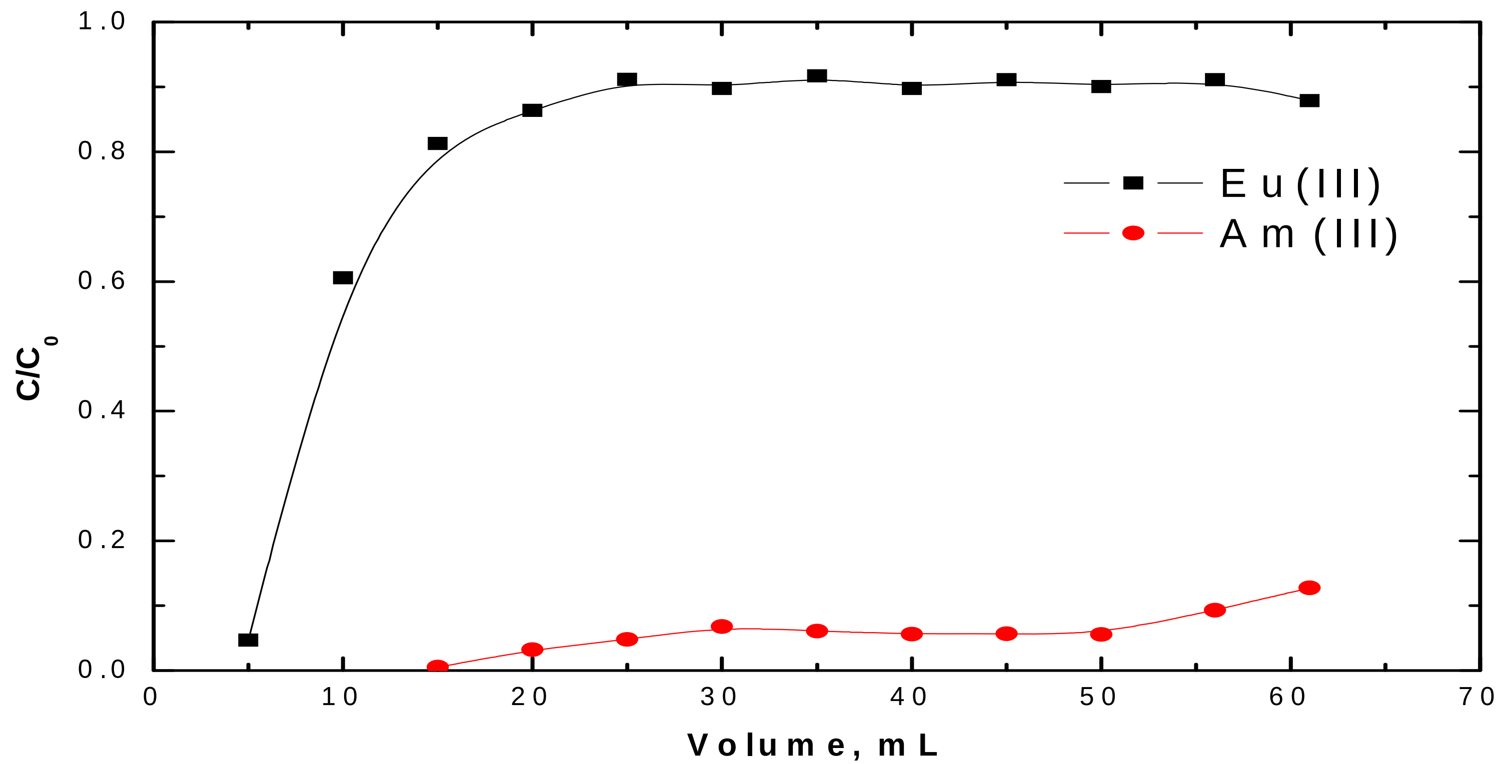


Figure : Loading of Am (III) and Eu (III) on to a column of nPr-BTP/XAD-7 resin.

Europium was not retained in the column and up to 99.4% of it was recovered at the loading stage itself. Up to 90% of the Am was retained in the column.

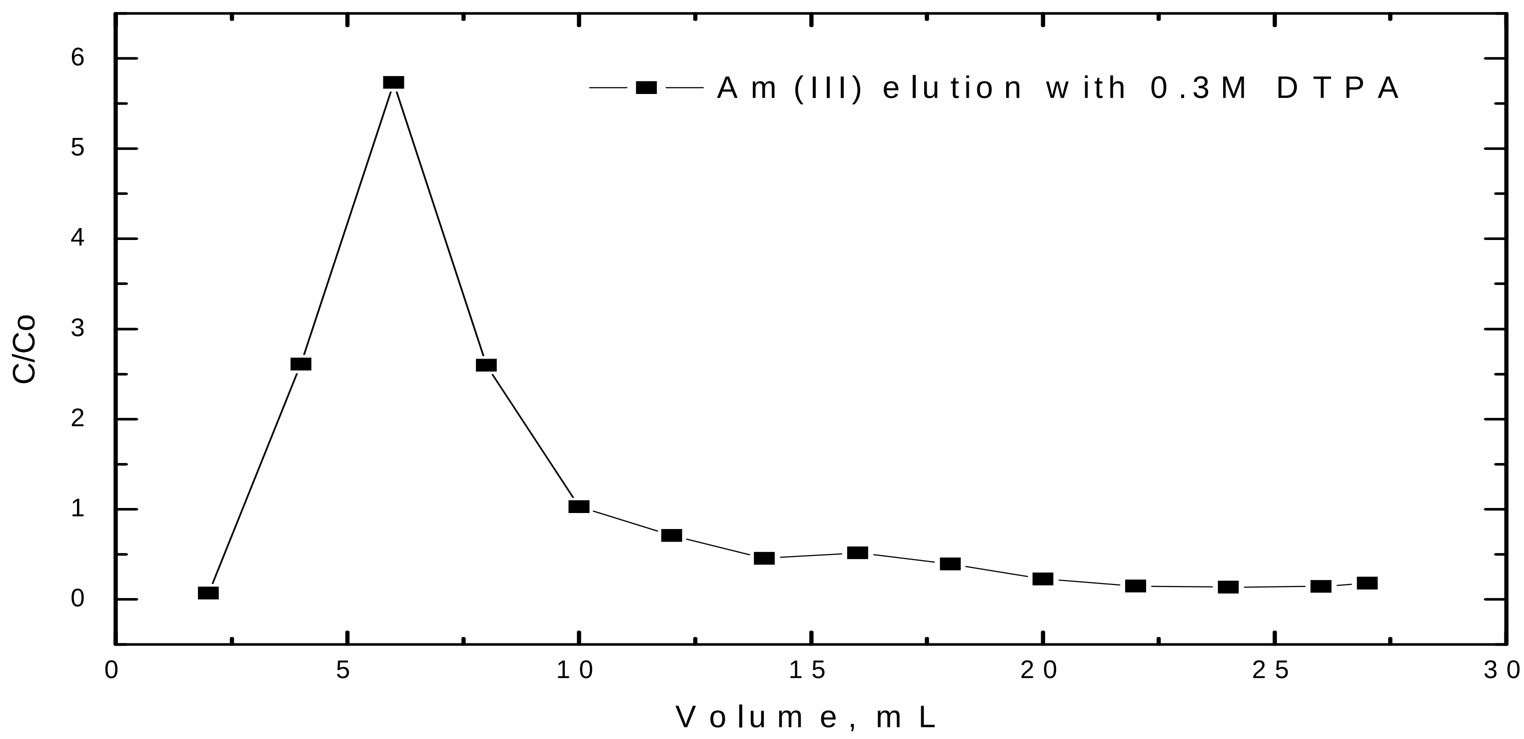


Figure : Elution of Am (III) from nPr-BTP/XAD-7 column with 0.3M DTPA.

- **Loaded Am(III) was recovered by passing 0.3 M DTPA solution (pH=4.0).**
- **60% of Am was recovered within the first three column volumes.**
- **Further tailing was observed.**

Conclusions -

- nPr-BTP impregnated XAD-7 resin displayed high selectivity for americium and good separation-factors for the separation of other lanthanides from the same.

- Column runs for the separation of americium from europium gave good results with 99.4% Europium being removed in the loading stage itself.

- The elution of Am from the column using DTPA was found to be 60% and efforts are on to improve the same.

Thank You……