A Novel Chromatographic Separation Technique using Tertiary Pyridine Resin for the Partitioning of Trivalent Actinides and Lanthanides

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<Background>

Partitioning of An(III) and Ln(III)

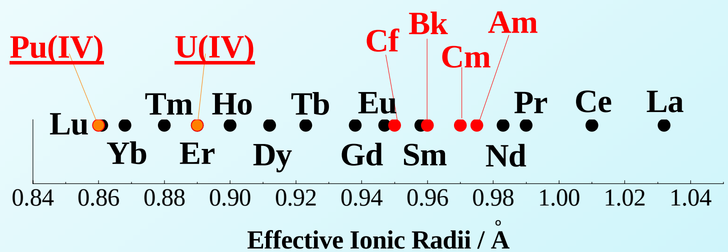
(* An(III): trivalent actinides, Ln(III): lanthanides)

~ What is the An and the Ln?? Where are they in the periodic table??~

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H																	He
2	Li	Be											B	C	N	O	F	Ne
3	Na	Mg											Al	Si	P	S	Cl	Ar
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba	Ln	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra	An	Rf	Db	Sg	Bh	Hs	Mt	Unn	Uuu	Unb	(Riken)	Uuq				

* Red symbols: Trivalent cations (M^{3+}) in solution

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr



R. D. Shannon, *Acta Cryst.*, A32, 751 (1976)

Same oxidation states, similar ionic radii.

They are not separated in reprocessing process.

<Background>

~ *Why is the partitioning of An(III) and Ln(III) required??*~

Transmutation strategy for reducing high-level wastes (HLW)
(Targets: ^{99}Tc, ^{129}I, ^{135}Cs, ^{241}Am, ^{244}Cm……)

➡ **The transmutation of Am & Cm requires;**

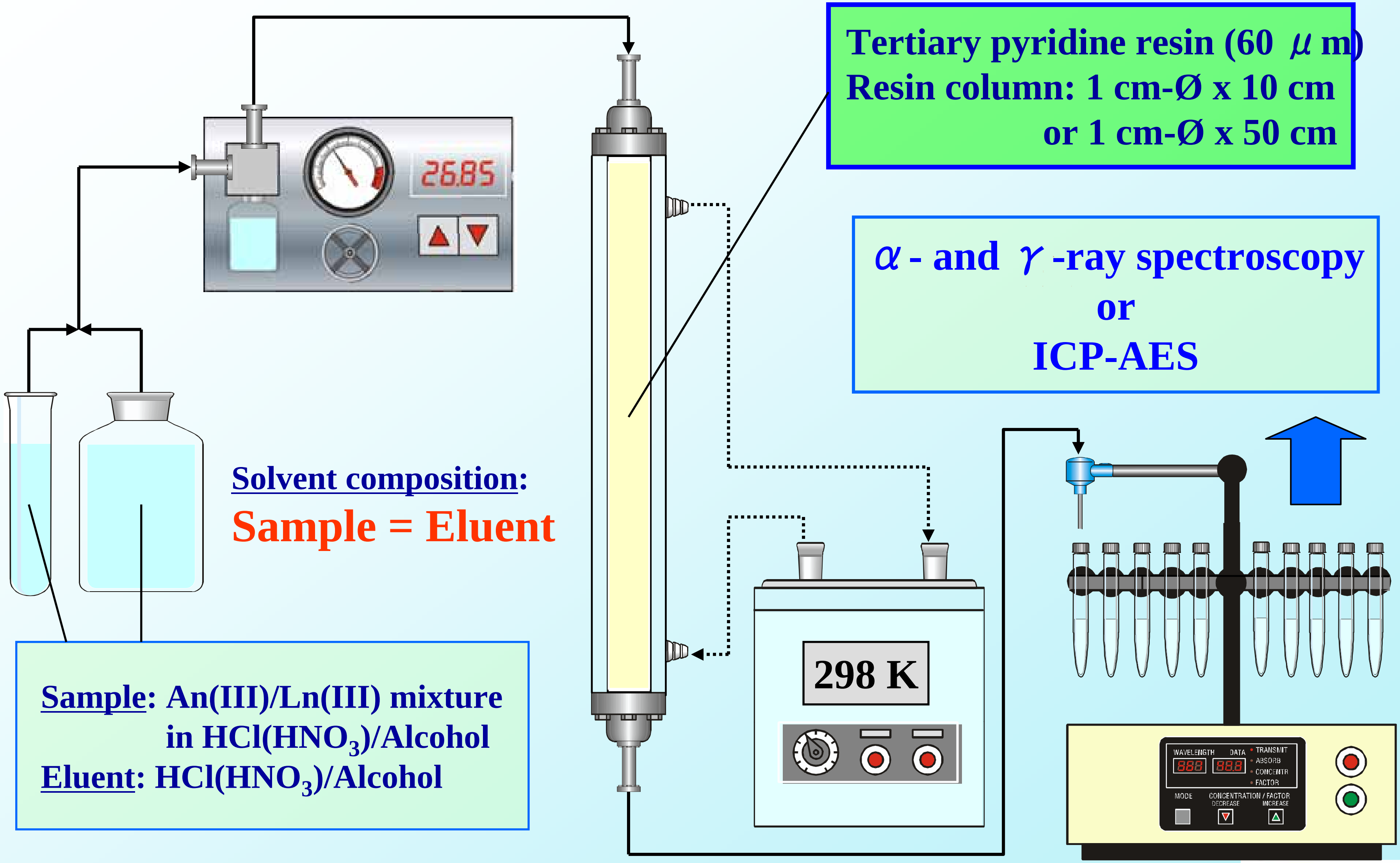
Separation of An(III) from Ln(III) (Intergroup separation)
&
Individual separation of An(III) (Intragroup separation).

⬆

Chromatographic separation technique using a tertiary pyridine resin
(Liquid-Solid extraction chromatography)

<Experimental>

~Apparatus~



Tertiary pyridine resin (60 μm)
Resin column: 1 cm-Ø x 10 cm
or 1 cm-Ø x 50 cm

α - and γ -ray spectroscopy
or
ICP-AES

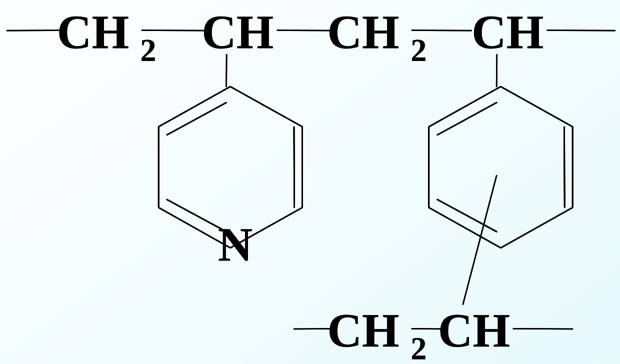
Solvent composition:
Sample = Eluent

Sample: An(III)/Ln(III) mixture in $HCl(HNO_3)$/Alcohol
Eluent: $HCl(HNO_3)$/Alcohol

<Experimental>

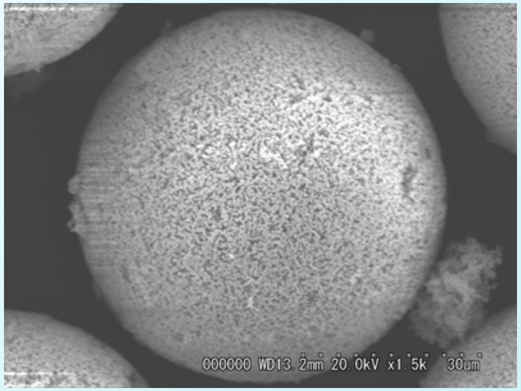
~Materials~

Tertiary pyridine resin impregnated in silica beads



<Tertiary pyridine resin>

impregnated



<Silica beads (60 μm)>

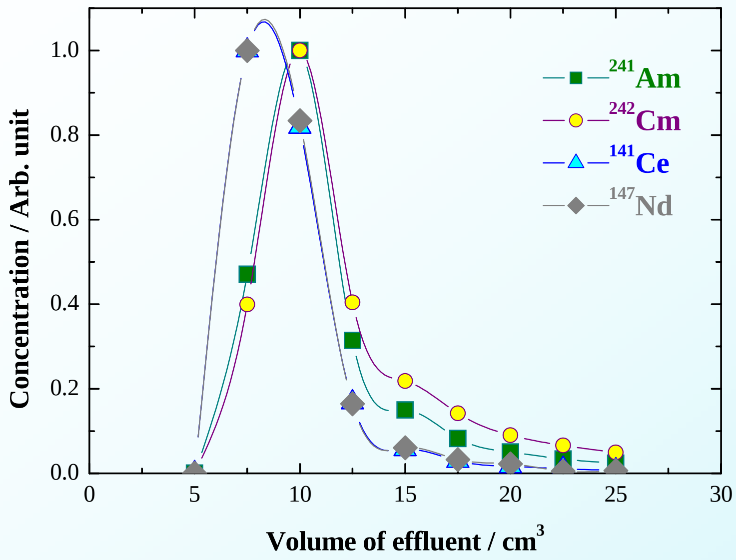
- **Soft-donor type extractant**
  (Effective for An/Ln separation)
- **High acid-resistance**
- **High radiation-resistance**

- **Structurally strong**
  (No swelling and shrinking)
- **High acid-resistance**
- **High radiation-resistance**

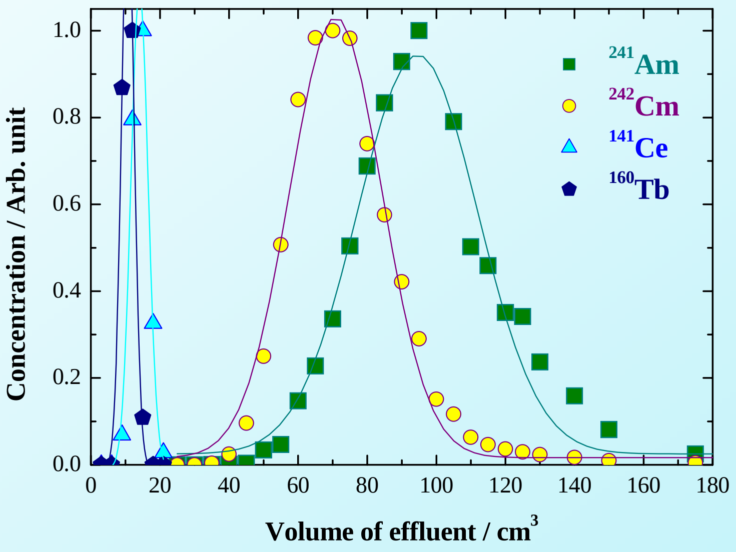
Favorable for practical uses!!

<Results (Chloride system)>

~*Intergroup separation of An(III) and Ln(III)*~



Typical chromatogram of An(III) and Ln(III)
by using anion exchange resin (Dowex 1X8)
(Solvent: conc.HCl : MeOH = 7 : 3
Size of resin column: 1 cmØ × 10 cm)



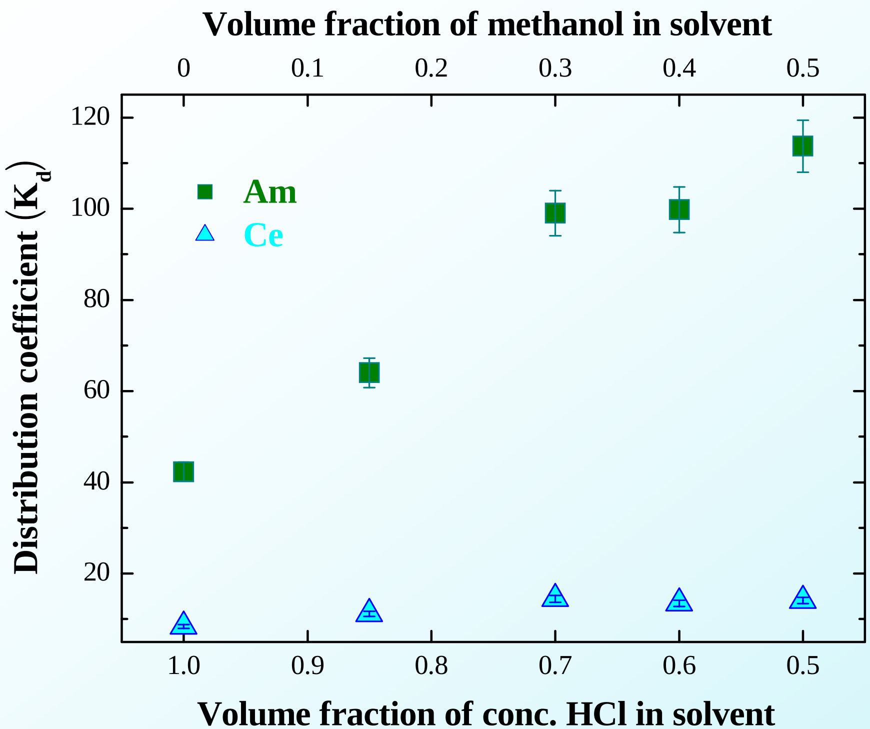
Typical chromatogram of An(III) and Ln(III)
by using tertiary pyridine resin
(Solvent: conc.HCl : MeOH = 7 : 3
Size of resin column: 1 cmØ × 10 cm)

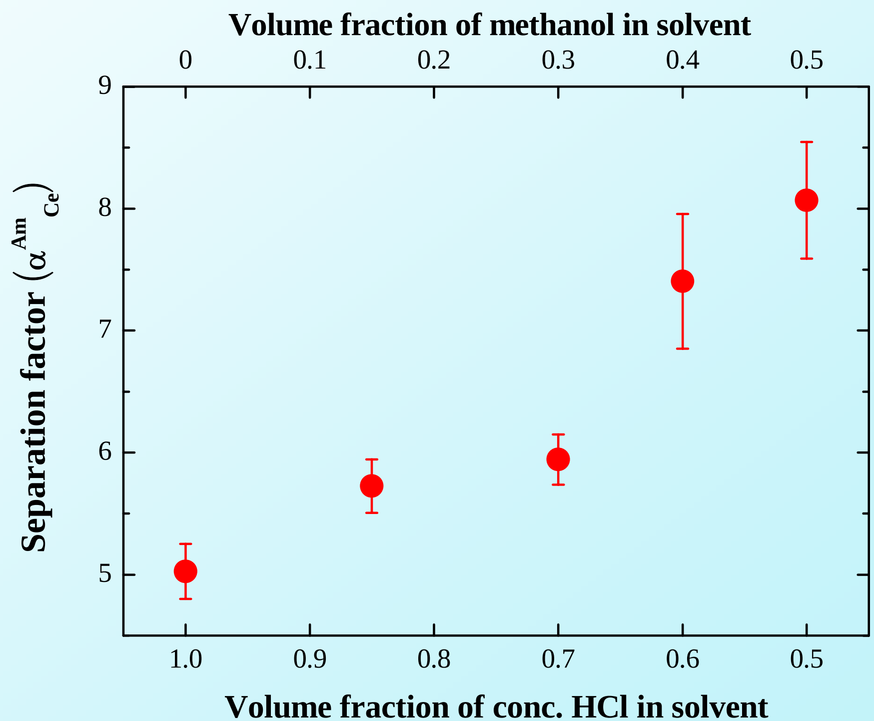
The pyridine resin adsorbs An(III) far more strongly than Ln(III) in HCl/MeOH system.

→ An(III) are separated from Ln(III)!!

<Results (Chloride system)>

~Effect of alcohol content in solvent~



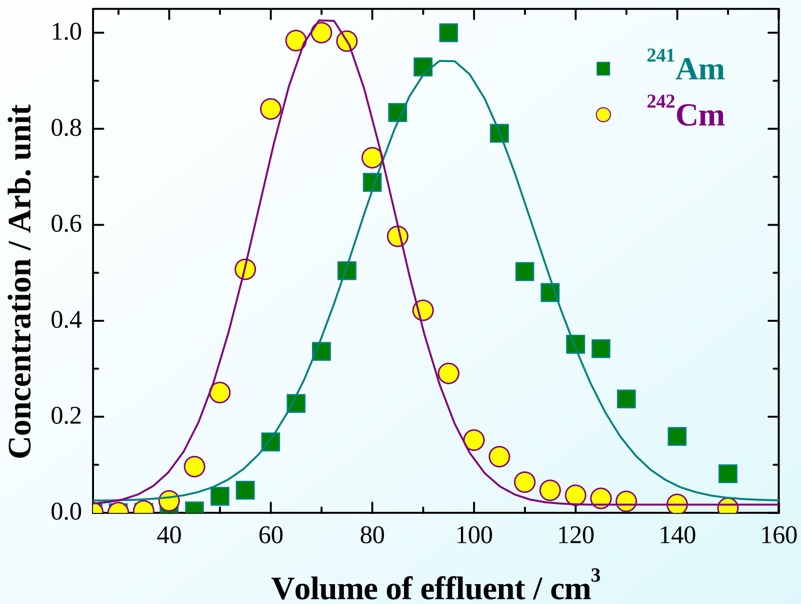


Adding alcohols in solvent promotes;

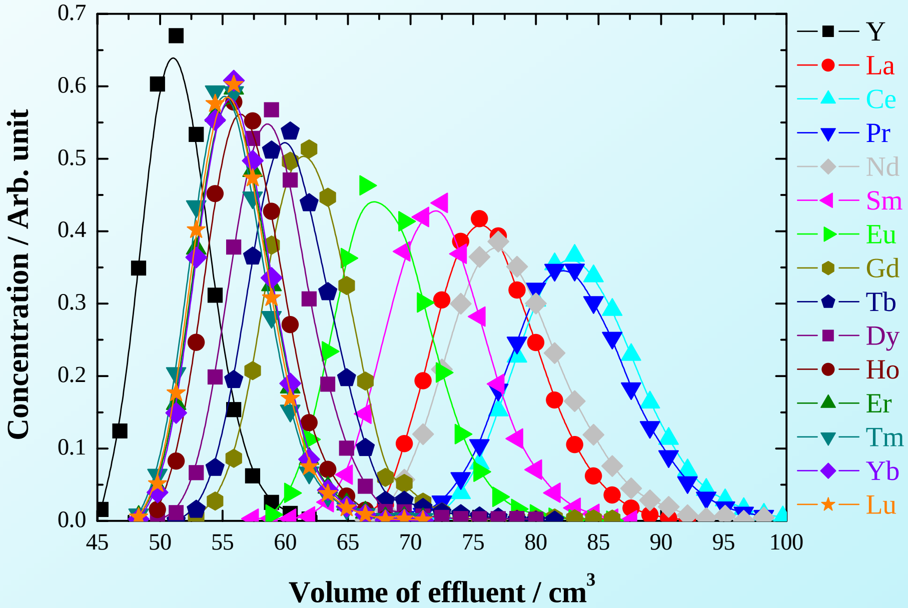
1. **<u>adsorption</u> of An(III) and Ln(III) in pyridine resin,**
2. **<u>separation</u> between An(III) and Ln(III).**

<Results (Chloride system)>

~*Intragroup separation of An(III) and Ln(III)*~



Typical chromatogram of An(III)
by using tertiary pyridine resin
Solvent: conc.HCl : MeOH = 7 : 3
Size of resin column: 1 cmØ × 10 cm

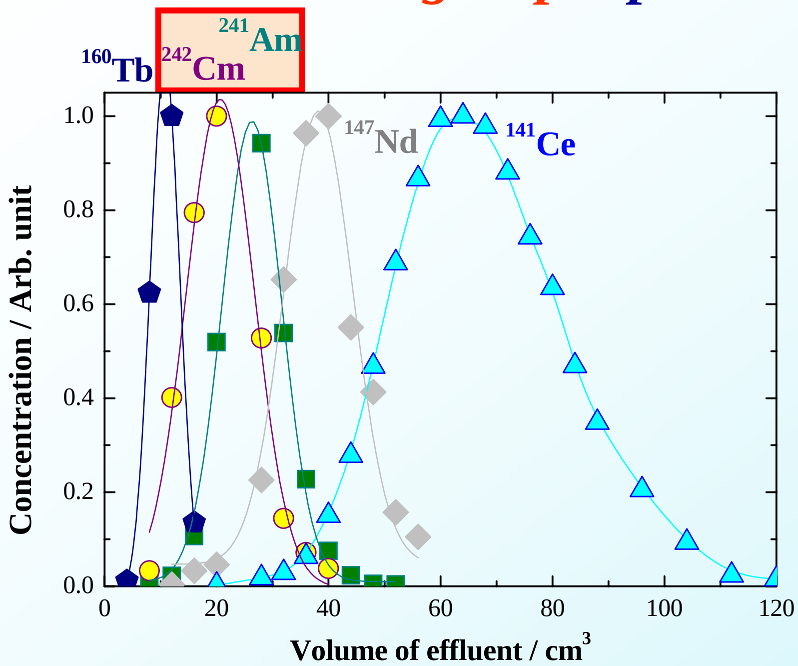


Typical chromatogram of Ln(III)
by using tertiary pyridine resin
Solvent: conc.HCl : MeOH = 5 : 5
Size of resin column: 1 cmØ × 100 cm

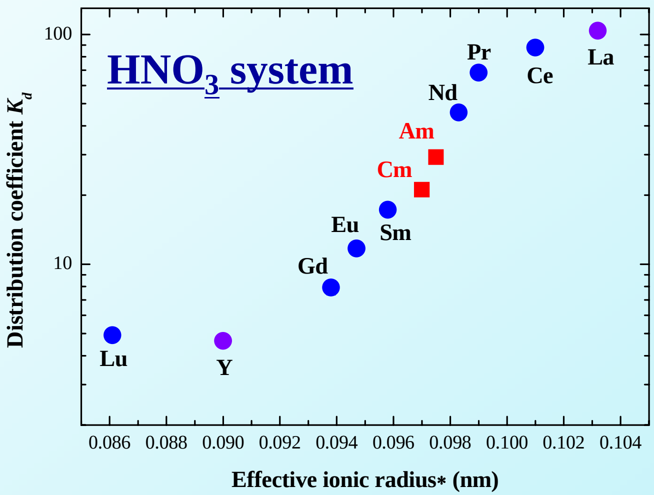
Although each elution peak is separated individually,
it appears that individual separation is difficult in the chloride system.

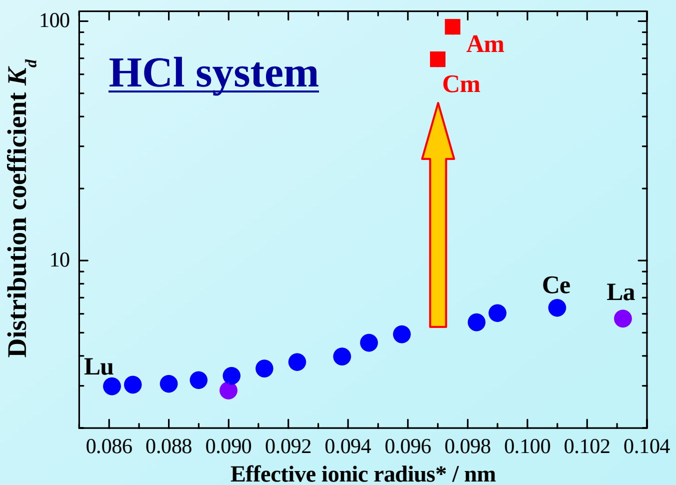
<Results (Nitrate system)>

~*Intergroup separation of An(III) and Ln(III)*~



Typical chromatogram of An(III) and Ln(III)
by using tertiary pyridine resin
(Solvent: conc.HNO_3 : MeOH = 7 : 3
Size of resin column: 1 cmØ × 10 cm)



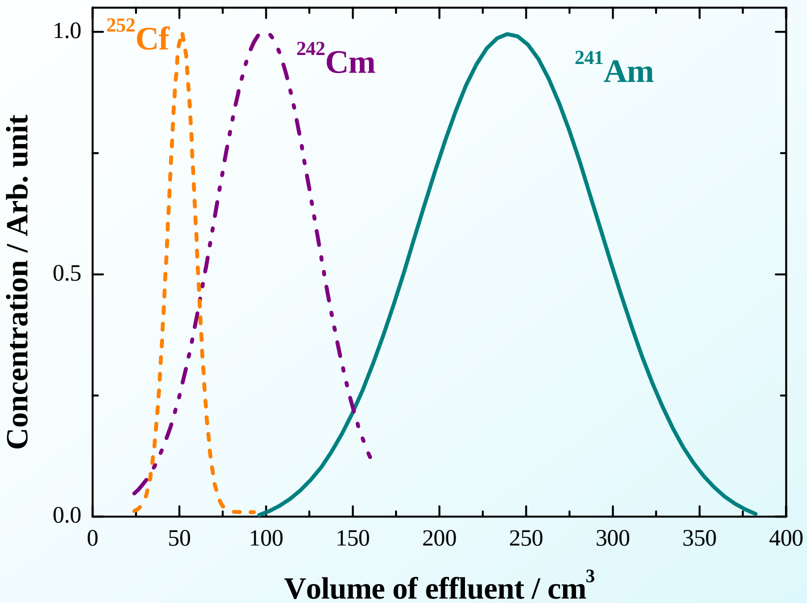


(* R. D. Shannon, *Acta Cryst.*, A32, 751 (1976))

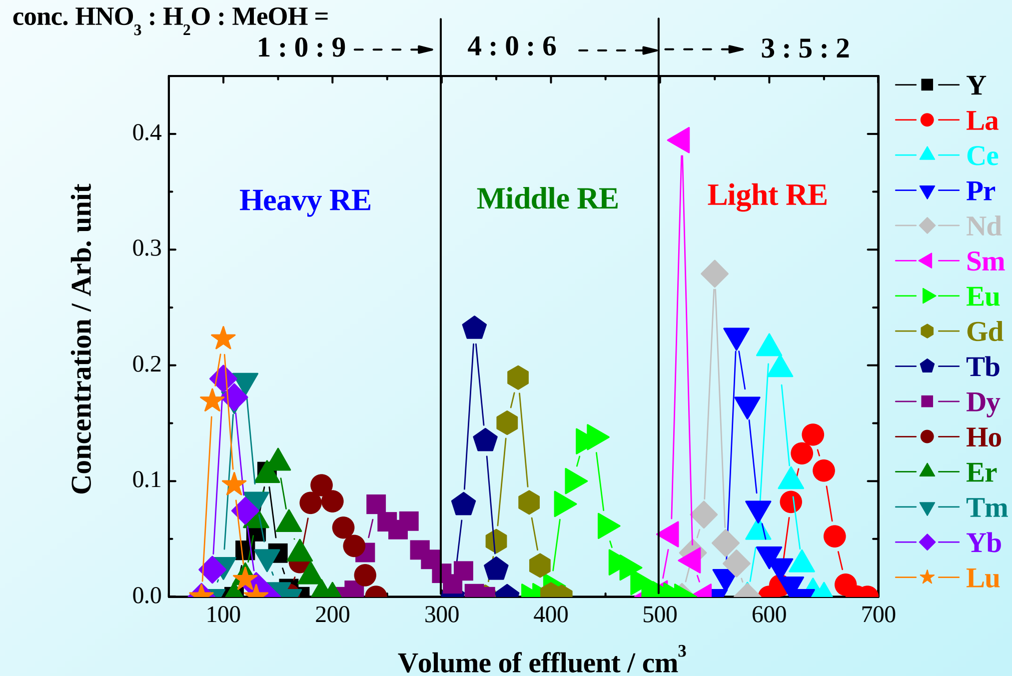
The nitric acid system is not applicable to An(III)/Ln(III) separation.

<Results (Nitrate system)>

~Intragroup separation of An(III) and Ln(III)~



Typical chromatogram of An(III)
by using tertiary pyridine resin
(Solvent: conc.HNO_3 : MeOH = 4 : 6
Size of resin column: 1 cmØ × 10 cm)

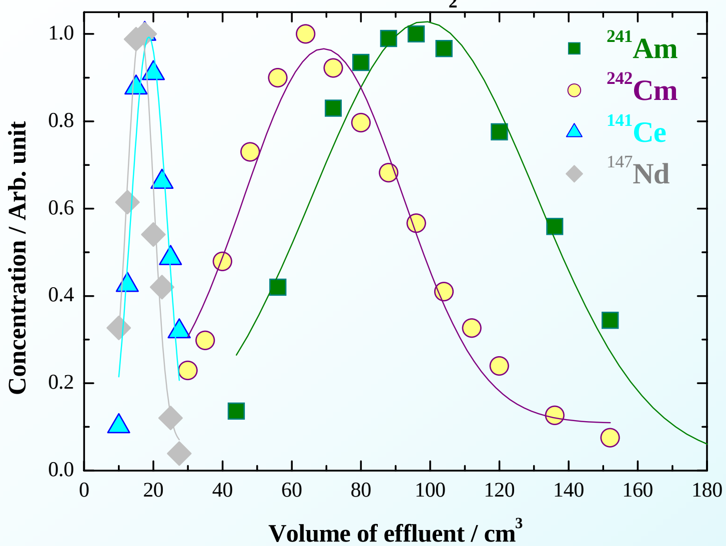


Typical chromatogram of Ln(III)
by using tertiary pyridine resin
(Size of resin column: 1 cmØ × 50 cm)

The nitric acid system is useful for
the individual separation of An(III) and Ln(III)!!

<Results (Effect of acid concentration)>

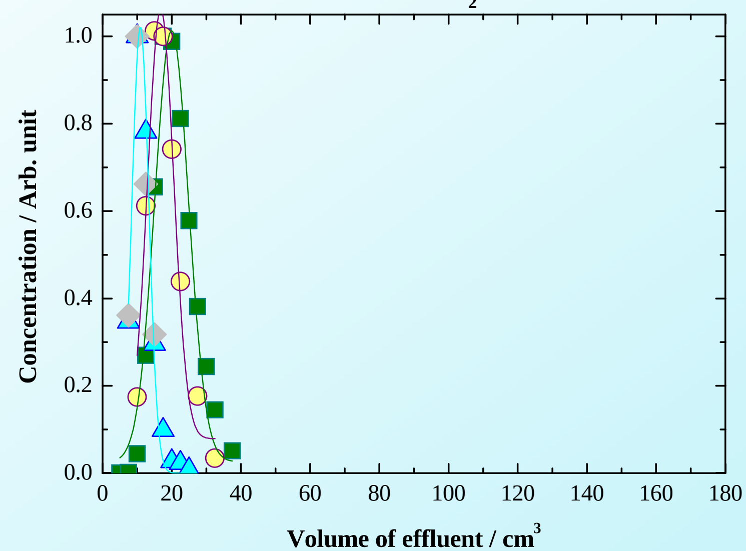
Solvent: conc. HCl : H_2O : MeOH = 6 : 0 :4

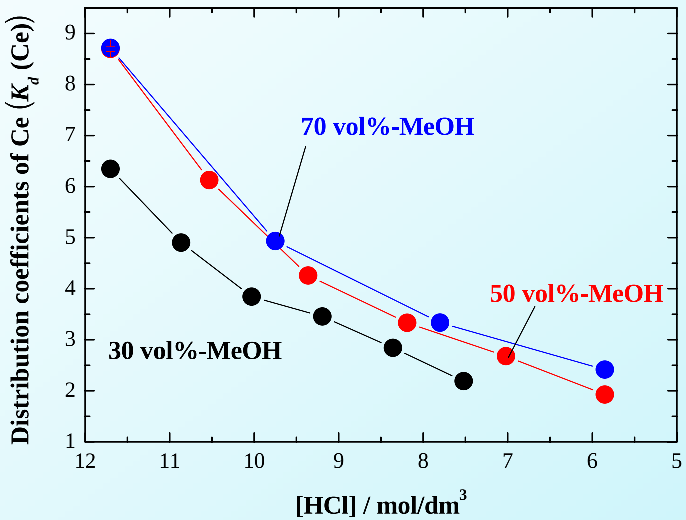


+10 vol%

water

Solvent: conc. HCl : H_2O : MeOH = 5 : 1 :4



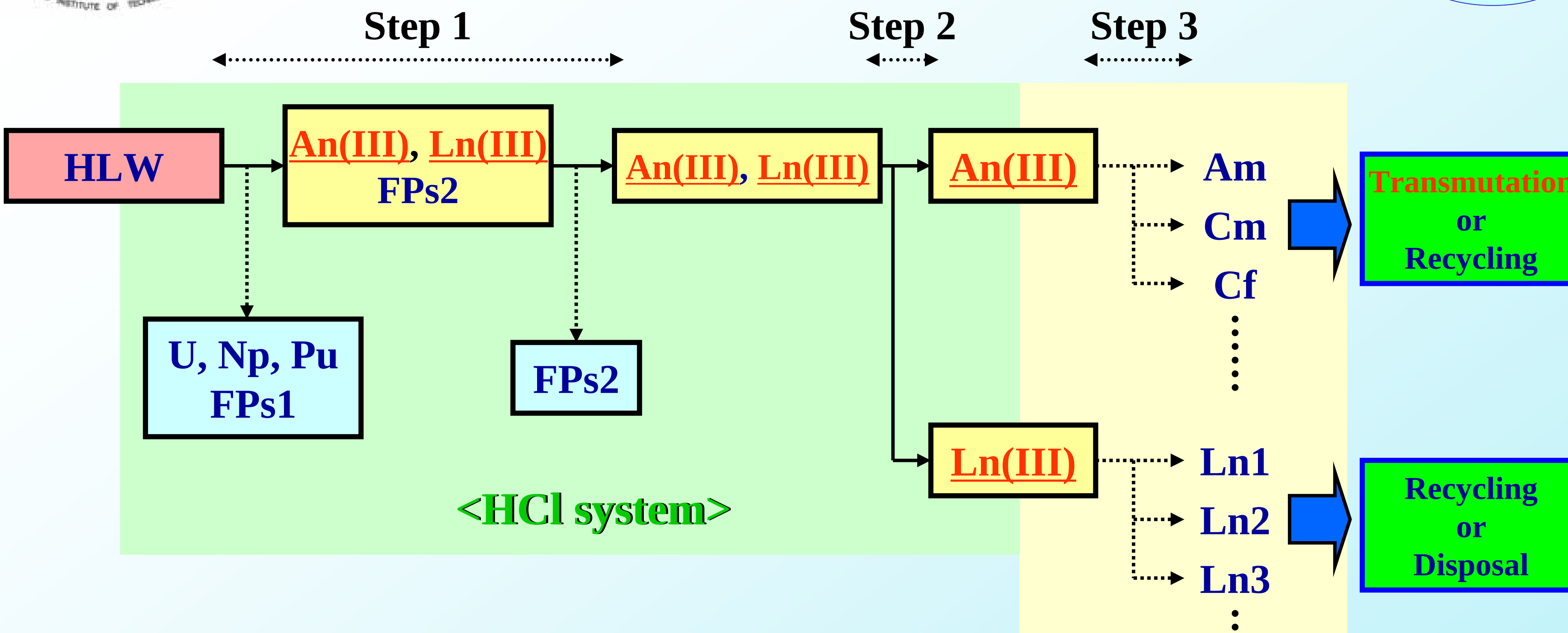


Decreasing tendencies of K_d & α :

HCl system >> HNO_3 system

Efficient separation requires higher concentration of HCl (HNO_3). (lower water activity)

<Partitioning process using tertiary pyridine resin>



<u>Step 1</u>: Separation of An(III) & Ln(III)
from other An and FPs
(U~Pu can be separated from An(III) & Ln(III).)

<u>Step 2 & 3</u>: Inter- and Intragroup separation of An(III) and Ln(III) (This work)

<u>Problems to be solved</u>: Separation of FPs from An and Ln(III)!!

<Summary>

- A novel chromatographic separation technique using a tertiary pyridine resin is effective for the partitioning of An(III) and Ln(III).

- The separation technique is applicable both to the intergroup separation of An(III) and Ln(III) and to the intragroup separation of these elements by using several solvent systems.

- The intergroup separation of An(III) and Ln(III) can be achieved in HCl/alcohol system and their intragroup separation can be roughly achieved in HNO_3/alcohol system.

- Adding alcohols in solvent improves the efficiency of separation.

- Effective separation requires high acid concentration.

<Acknowledgements>

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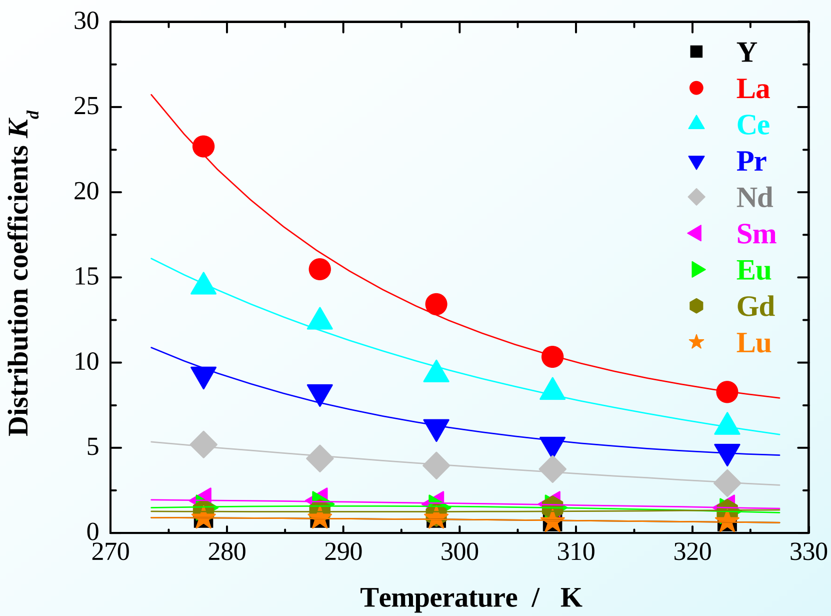
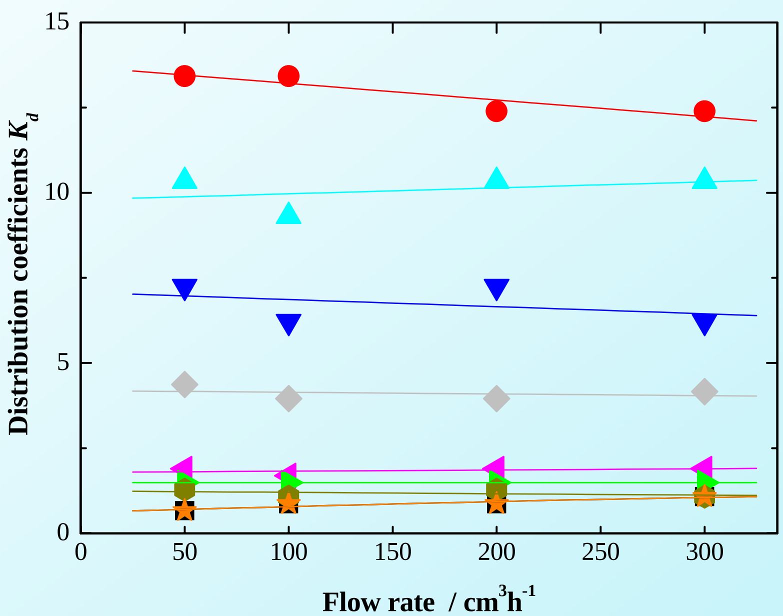
Mr. Kouhei Otake
(***Tokyo Institute of Technology***)

And thank you for all of your attention!!

<Results (Effect of temperature & flow rate)>



Variation in distribution coefficients of Ln(III) against temperature
(Solvent: conc.HNO_3 : H_2O : MeOH = 3 : 5 : 2)



Variation in distribution coefficients of Ln(III) against flow rate
(Solvent: conc.HNO_3 : H_2O : MeOH = 3 : 5 : 2)

For efficient separation;
Lower temperature is required.

Flow rates have almost no effect.
➡ Rapid operation is possible.

<Advantages & disadvantages>

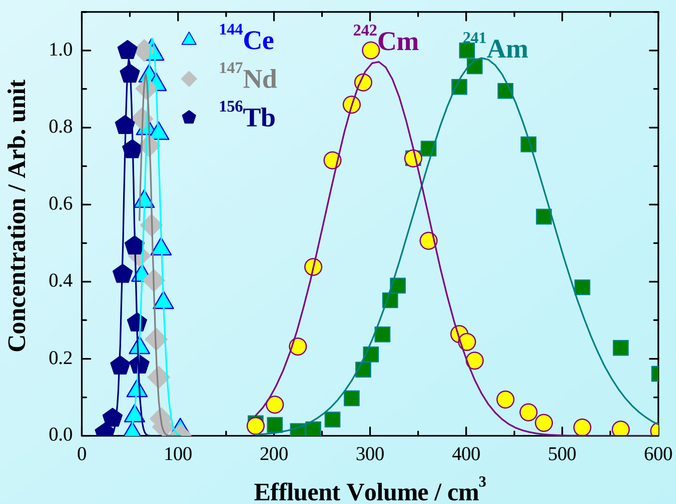
Advantages

- Simple apparatus
- Simple separation procedure
- Simple solvents
  (HCl, HNO_3, Alcohols)
- Simple extractant
  (Pyridine resin: **C, H, N, SiO_2**)
- **Recyclable** extractant
- Effective for An(III)/Ln(III) separation

Disadvantages

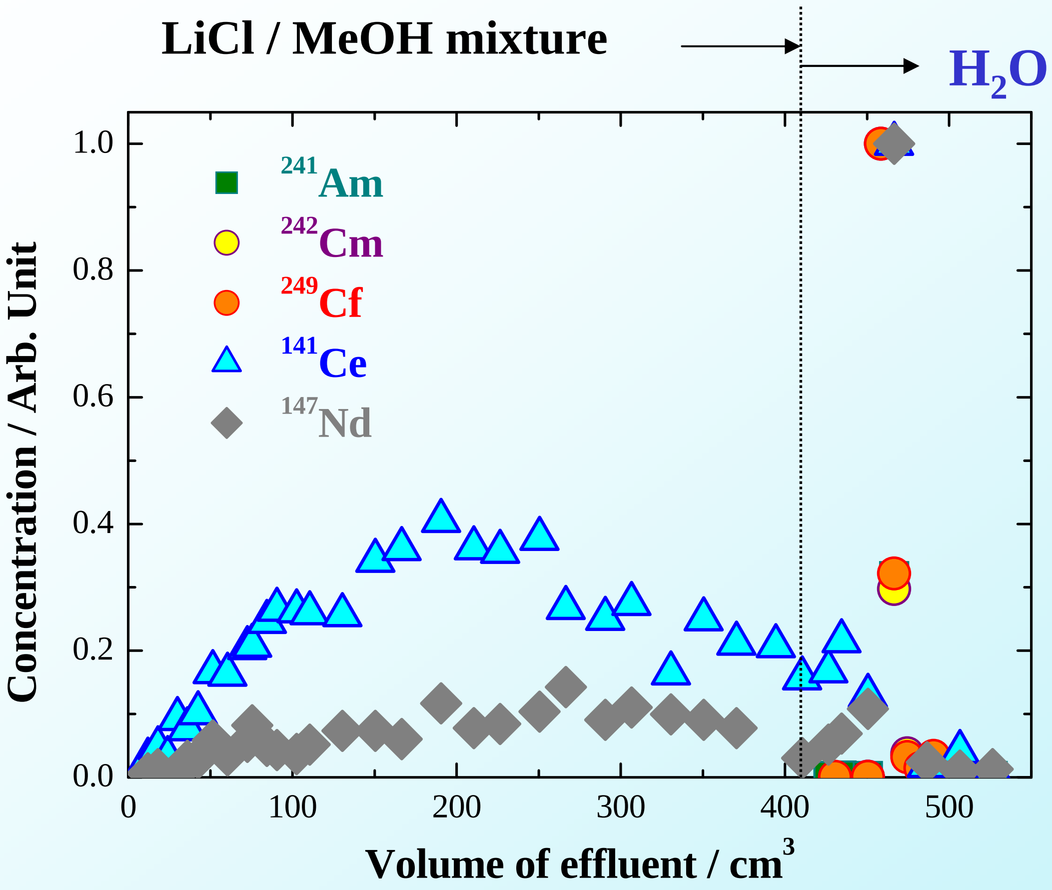
- **High acid concentration**
- Mixture of acidic solutions and alcohols
- Combination with PUREX

Solvent: conc. HCl : MeOH = 7 : 3



(Size of resin column: 1 cm-Ø × 50 cm)

<Lithium Chloride System>



Solvent:

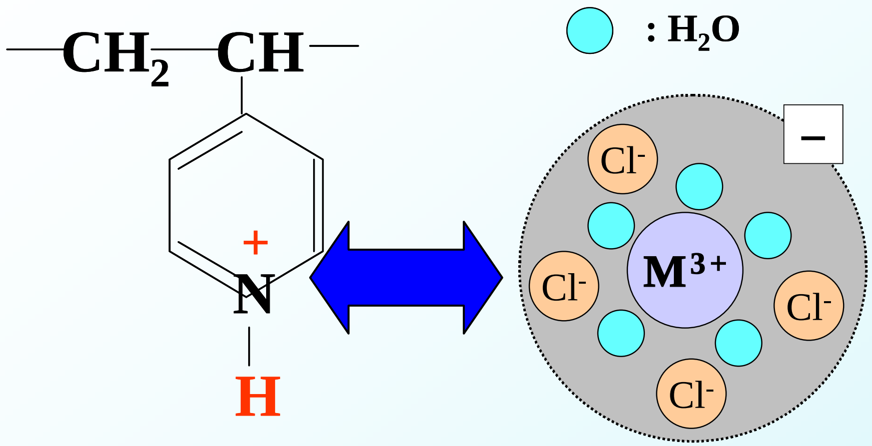
70 vol%-11.7 mol/dm^3-LiCl / 30 vol%-MeOH

Resin column : 1 cmØ × 10 cm

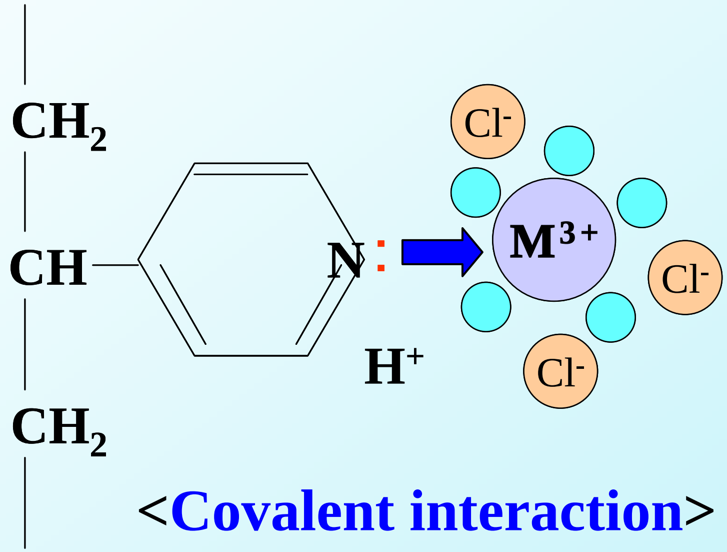
Distribution coefficient:

LiCl solvent >> HCl solvent

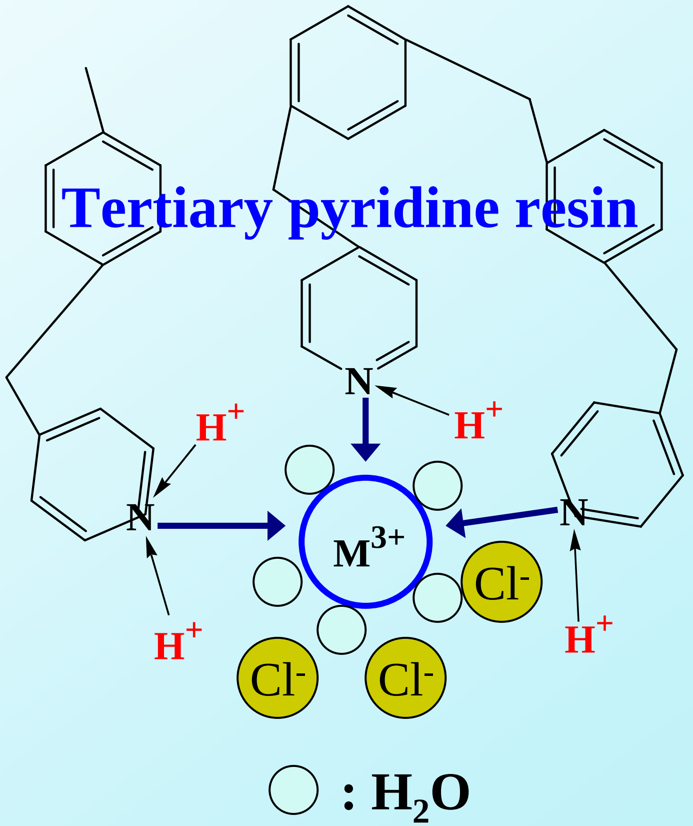
<Adsorption Mechanism>



<Ionic interaction>

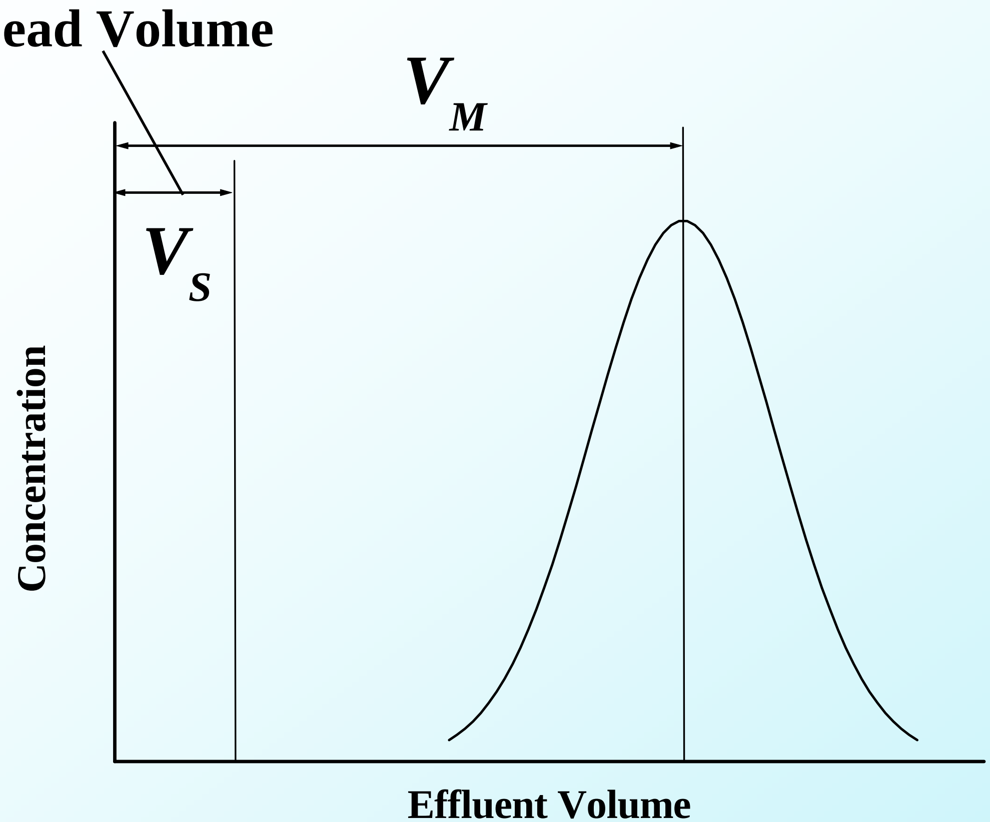


<Covalent interaction>



<Possible mechanism??>

<Calculation>

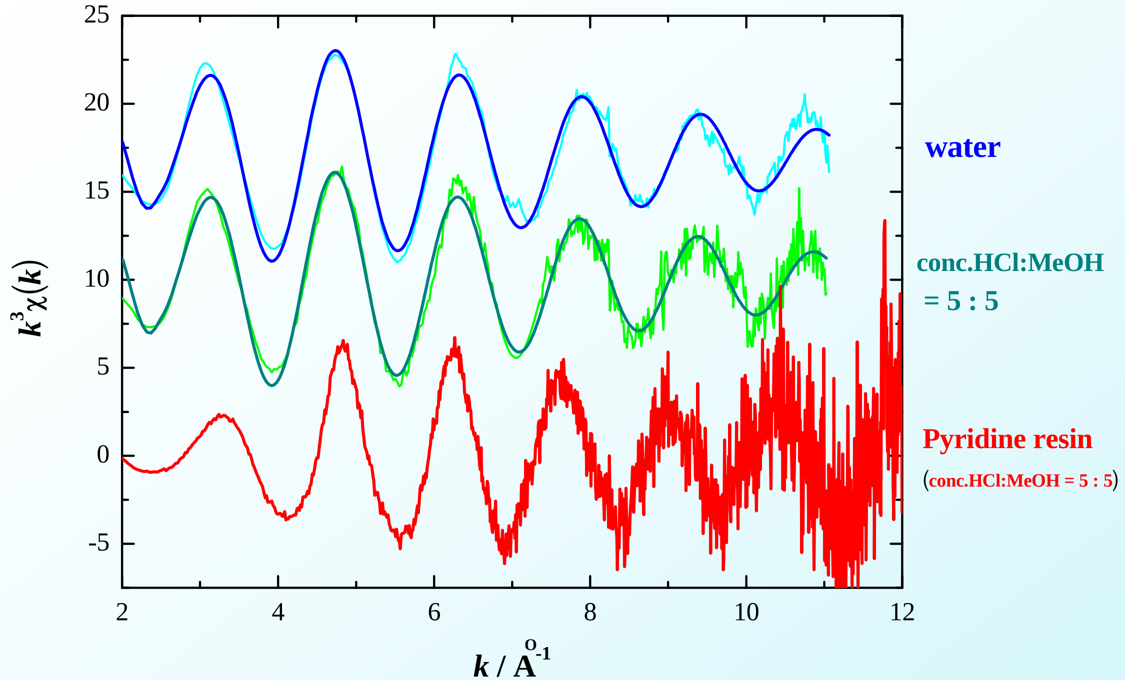


(V_R : Volume of Resin in Column)

$$K_d = (V_M - V_S) / V_R$$

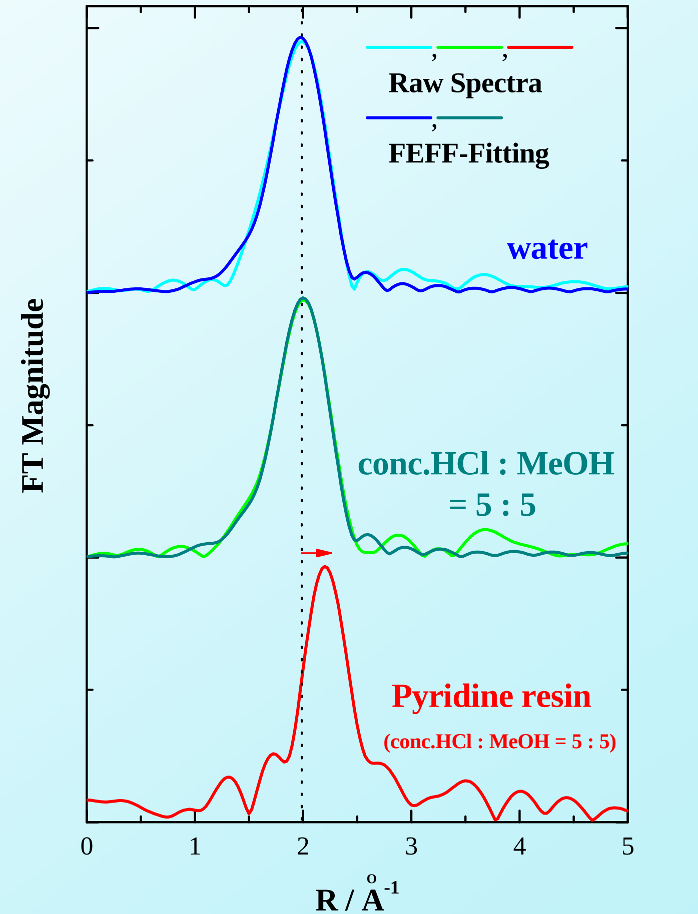
$$\alpha^{A}{}_{B} = K_d(\mathrm{A}) / K_d(\mathrm{B})$$

<Gadolinium-L_{III} EXAFS>



<k^3-weighted EXAFS spectra>

<Structural parameters>
N_{water}: 8.5~9.2 @ 2.42 Å
(in water & HCl/MeOH)



(* Phase shifts are not corrected.)

<Corresponding fourier transforms>

(All spectra were collected at BL-27B@PF-KEK.)

<Adsorption Mechanism>

Bulk (Solution phase)　　　　Resin phase