



Erbismühle-Weilrod, Germany  
May 15, 2012

# Aqueous Chemistry - Results and Instrumentations -

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1. Introduction
2. Liquid-phase experiments with a partition method
3. Experimental achievement and problems
4. New experimental approach
  - Electrochemistry
  - Coupling with a recoil separator
5. Perspective - Complex-formation experiments
  - Redox experiments

## Liquid-phase chemistry

- ▶ Clarification of basic chemical properties of SHE ionic charge and radius, redox potential, complex formation, *etc.*
- ▶ Elucidation of the influence of relativistic effects on chemical properties of SHE

## Chemical characterization with single atoms

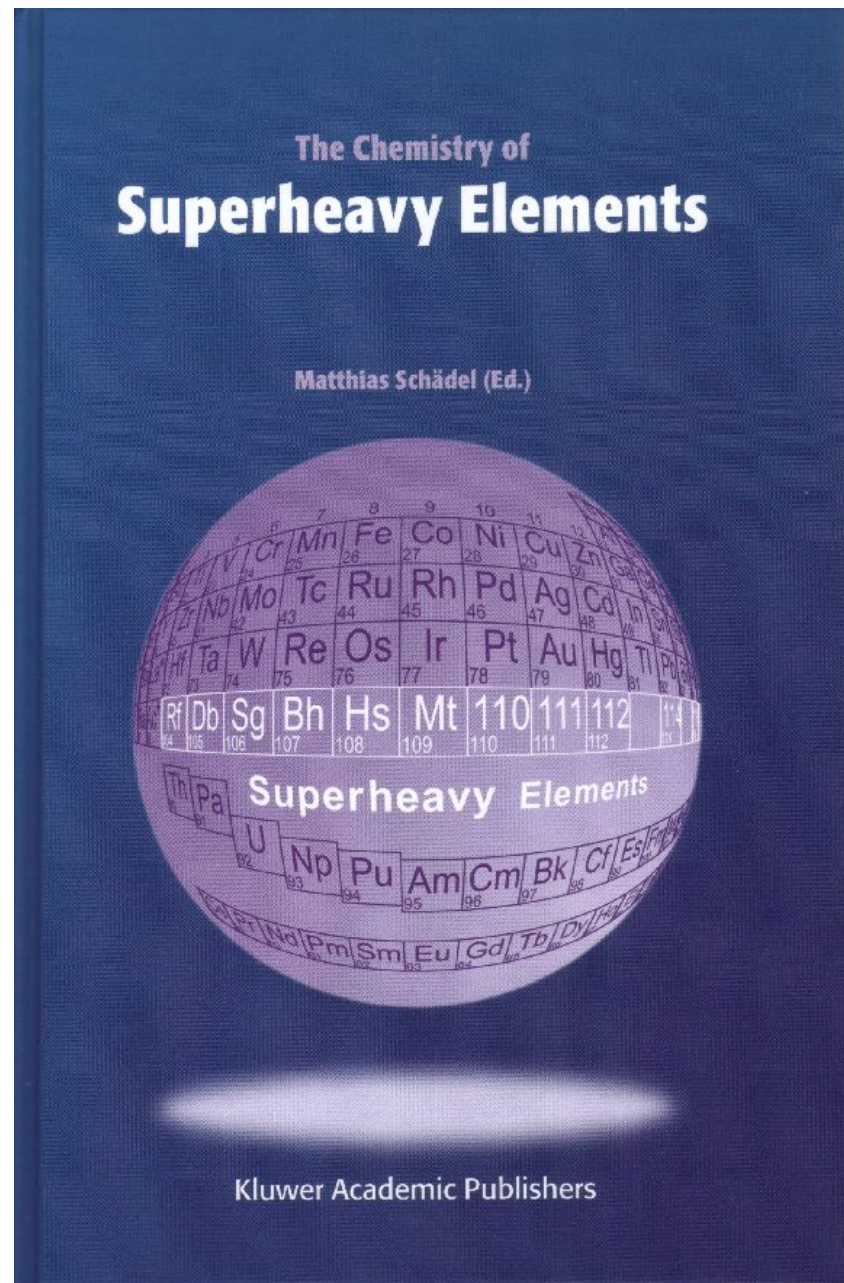
- ▶ Partition method  
Liquid-liquid extraction, Ion-exchange chromatography, Reversed-phase extraction chromatography
- ▶ Comparative study with lighter homologues

J. V. Kratz,  
In Chapter 5: Liquid-phase chemistry

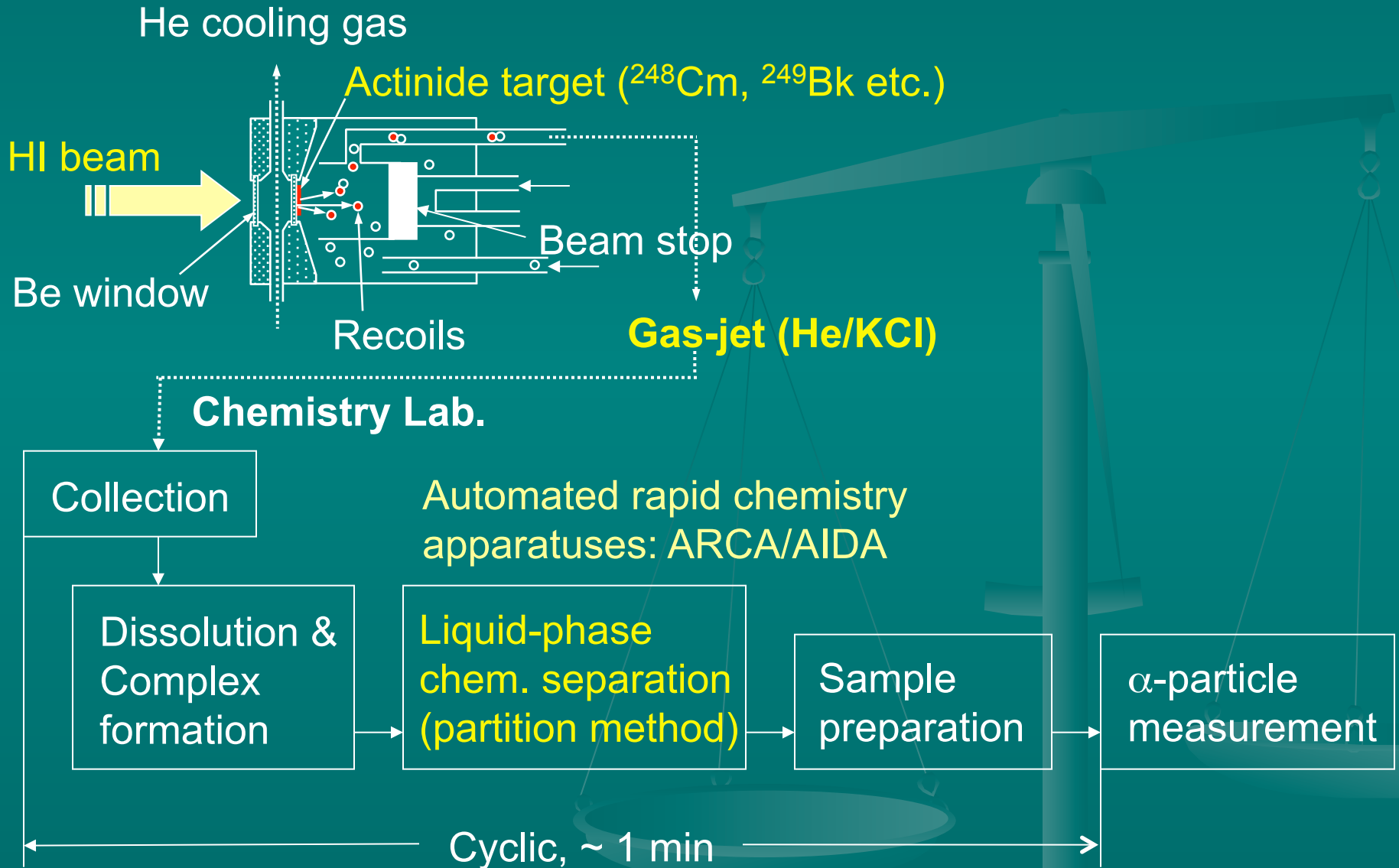
The ultimate goal of the partition experiments is to determine the so-called distribution coefficient ( $K_d$ ) as a function of ligand concentration.

$K_d$  vs. [Ligand]  $\Rightarrow$  Chemical species

- Automated rapid chemical separation
- Data with good statistics



## 2. Liquid-phase experiments with a partition method



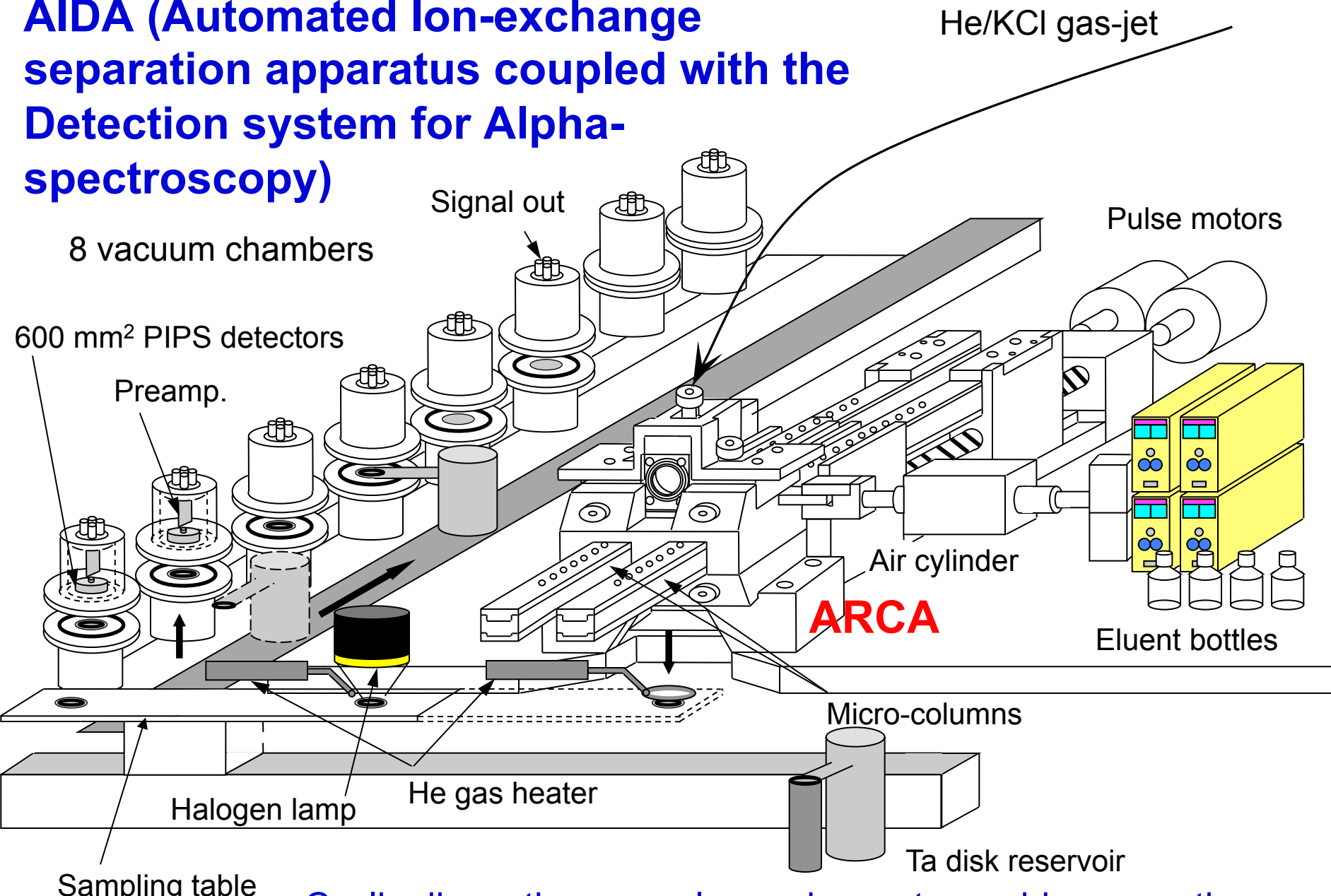
Element	Nuclide	$T_{1/2}$ (s)	Nuclear reaction	$\sigma$ (nb)	Chemical separation	Apparatus
$_{104}\text{Rf}$	$^{257}\text{Rf}$	4	$^{208}\text{Pb} (^{50}\text{Ti}, n)$	10	S.E.	SISAK
	$^{261}\text{Rf}$	68	$^{248}\text{Cm} (^{18}\text{O}, 5n)$	13	I.E., E.C.	ARCA, AIDA
$_{105}\text{Db}$	$^{262}\text{Db}$	34	$^{249}\text{Bk} (^{18}\text{O}, 5n)$	6	E.C. , I.E.	ARCA
			$^{248}\text{Cm} (^{19}\text{F}, 5n)$	1	I.E.	AIDA
$_{106}\text{Sg}$	$^{265}\text{Sg}$	10	$^{248}\text{Cm} (^{22}\text{Ne}, 5n)$	0.24	I.E.	ARCA
$_{108}\text{Hs}$	$^{269}\text{Hs}$	10	$^{248}\text{Cm} (^{26}\text{Mg}, 5n)$	0.007	Adsorption	CALLISTO

S.E. : Solvent Extraction

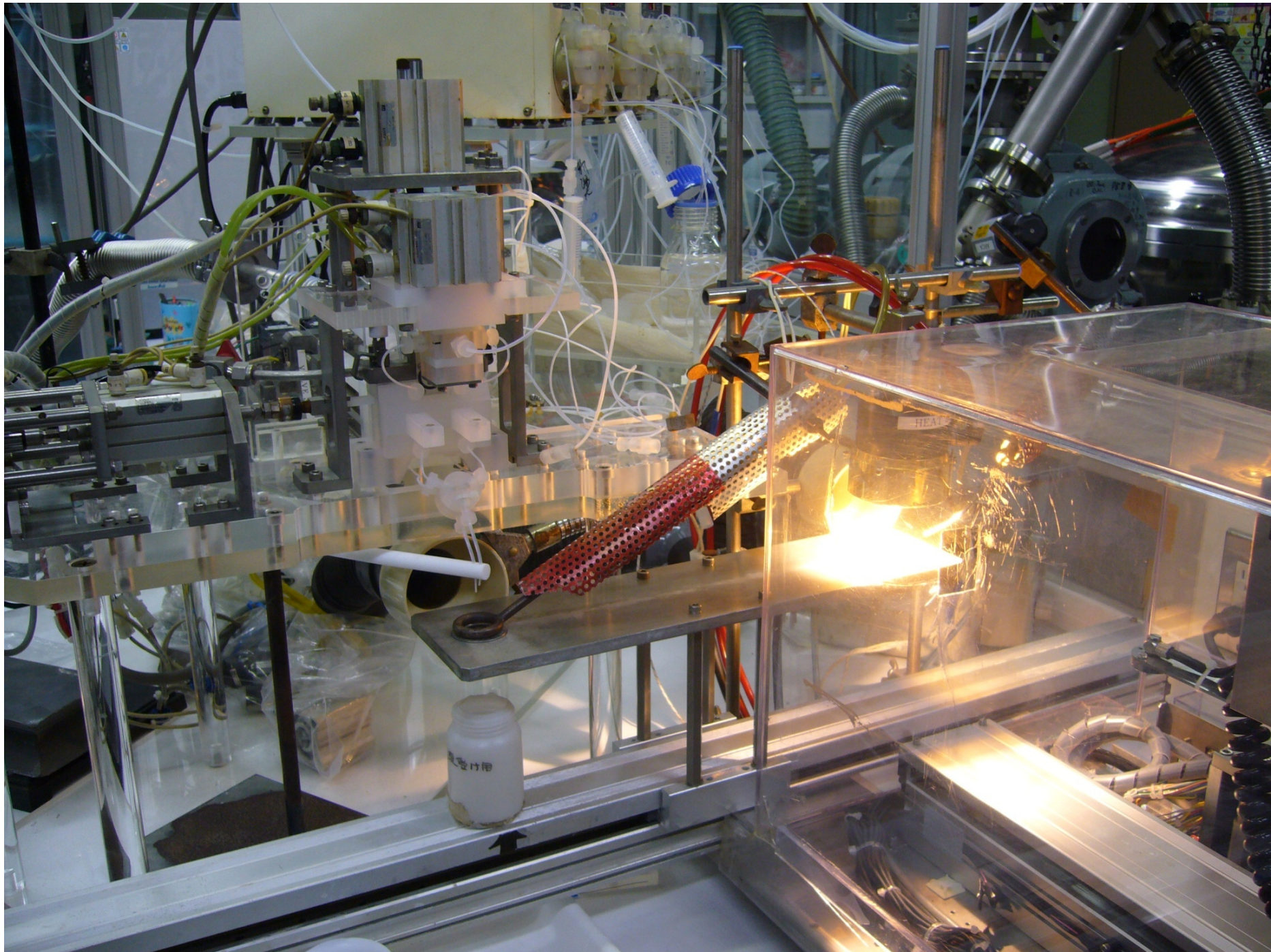
I.E. : Ion Exchange

E.C. : Extraction Chromatography

# AIDA (Automated Ion-exchange separation apparatus coupled with the Detection system for Alpha-spectroscopy)



Cyclic discontinuous column chromatographic separation of the short-lived heaviest nuclides





# Anion-exchange procedure in HF with AIDA

1. Collection of  $^{261}\text{Rf}$  and  $^{169}\text{Hf}$  for 125 s
2. Dissolution with 245(260)  $\mu\text{L}$  of HF and feed onto the column at 0.74(1.0) mL/min

3. 200  $\mu\text{L}$  of 4.0 M HCl at 1.0 mL/min

AIX column: MCI GEL CA08Y resin (25  $\mu\text{m}$ )  
1.6 mm i.d.  $\times$  7.0 mm (1.0 mm i.d.  $\times$  3.5 mm)

1st fraction ( $A_1$ )

2nd fraction ( $A_2$ )  $\Rightarrow$   $\alpha$ -spectrometry

Adsorption probability (%) =  $100 A_2 / (A_1 + A_2) \rightarrow K_d$

$^{169}\text{Hf}$  : elution behavior and chemical yields ( $\sim 60\%$ )

$^{85}\text{Zr}$  and  $^{169}\text{Hf}$  from Ge/Gd target: Ge/Gd( $^{18}\text{O}$ , xn)

Typical results on fluoro complex formation of Rf :

- ▶ Anion- and cation-exchange chromatography with ARCA/AIDA  
Fluoro complex formation and ionic radius

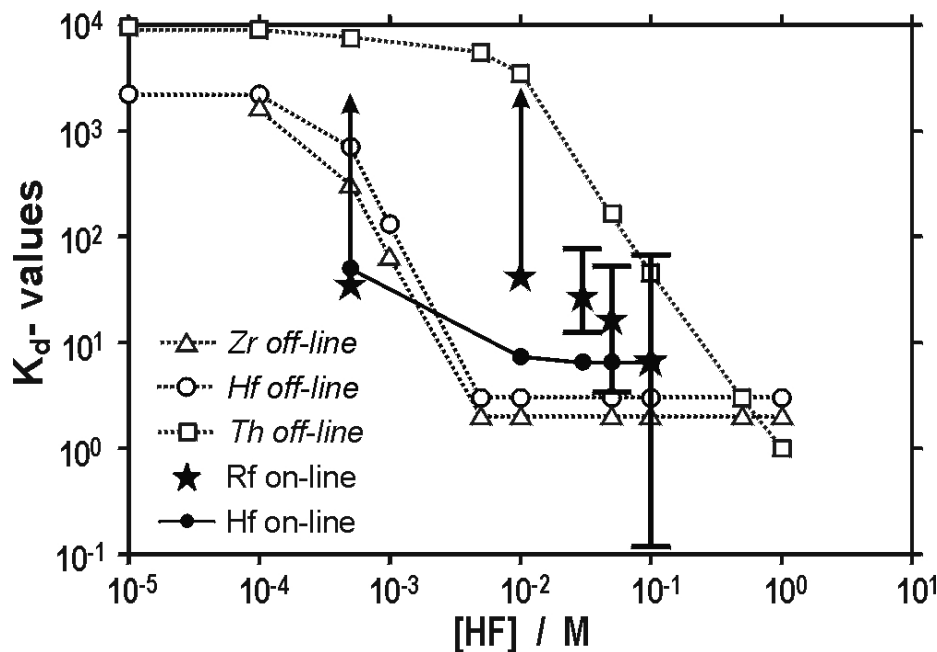
Problems :

- ▶ Reaction kinetics and chemical species
- ▶ Comparison with theoretical predictions

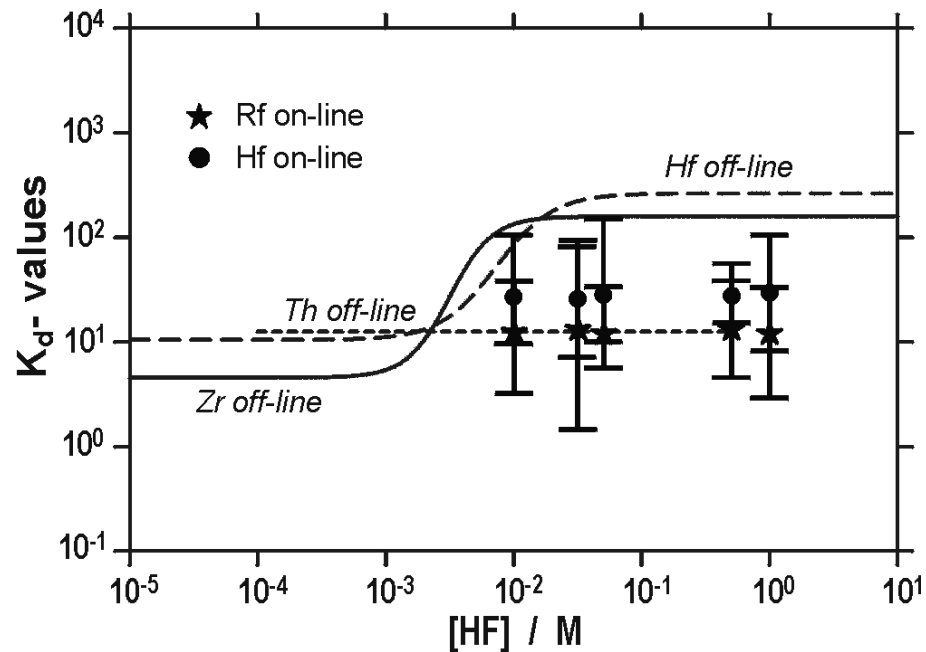
# Fluorido complex formation of Rf

Adsorption of Zr, Hf, Rf and Th on ion-exchange resin in 0.1 M HNO<sub>3</sub> at various HF concentrations.

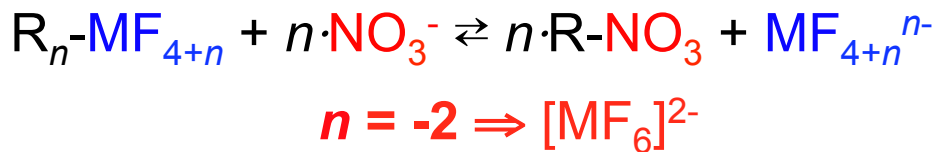
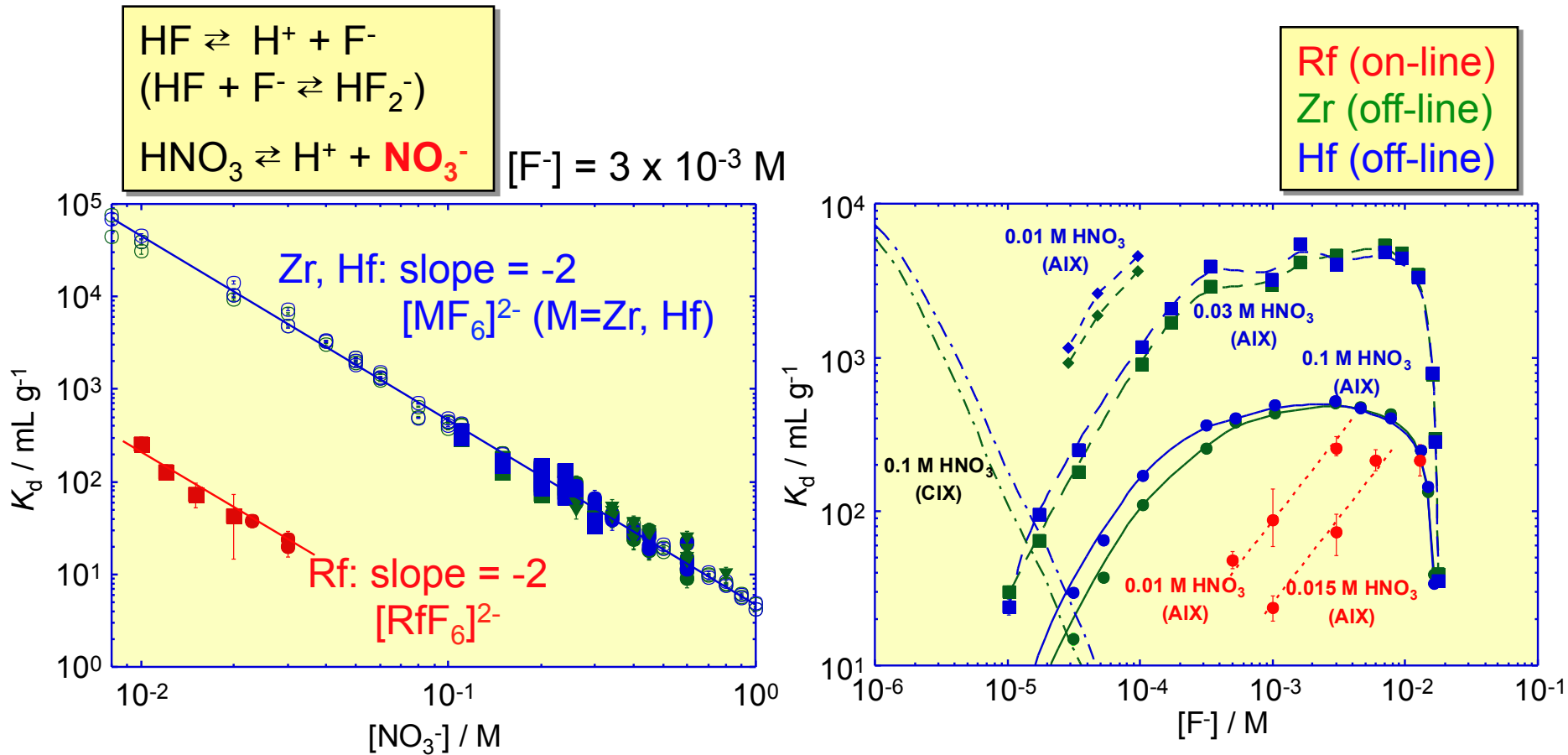
## Cation-exchange



## Anion-exchange

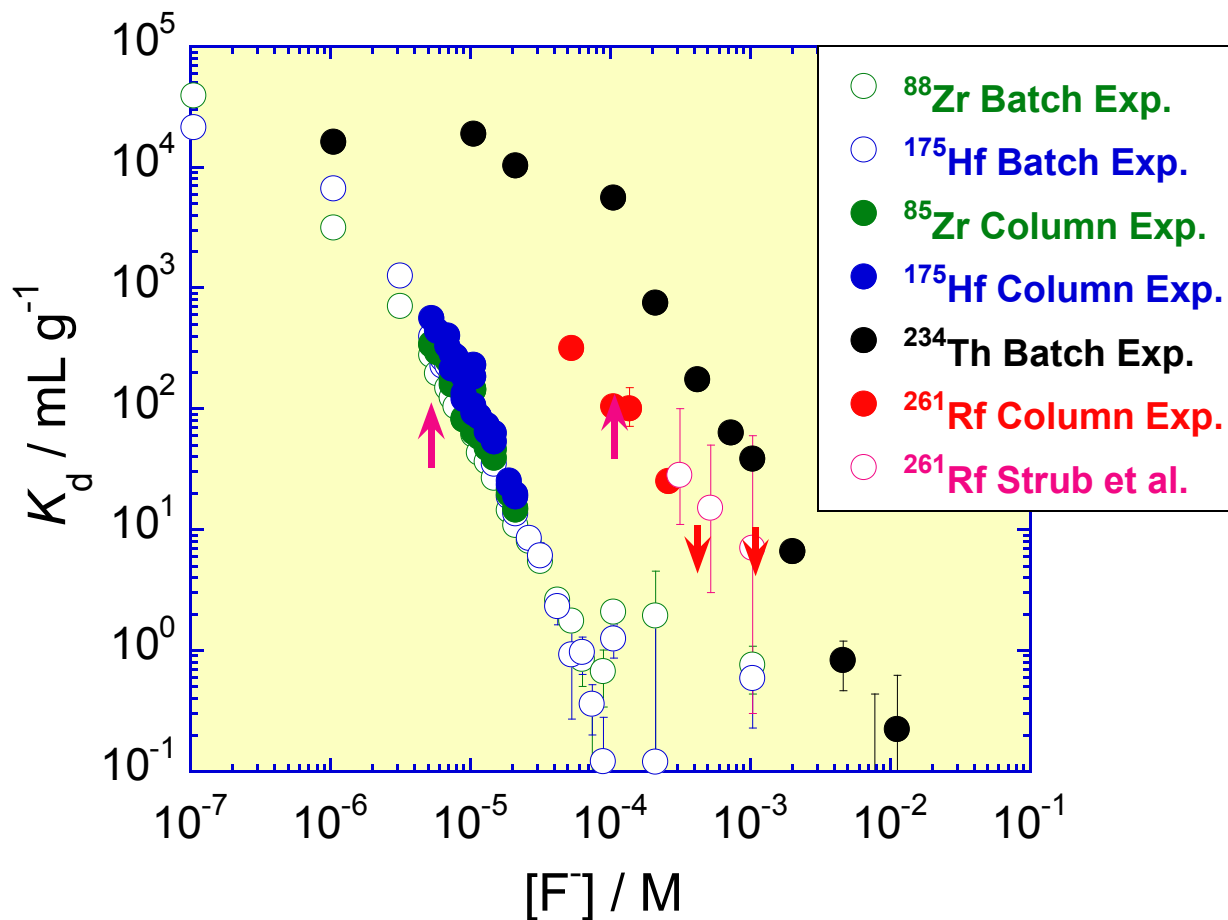


# Anion-exchange behavior of Rf in HF/HNO<sub>3</sub>



Formation of  $[\text{MF}_6]^{2-}$  : Zr  $\approx$  Hf > Rf

# Cation-exchange behavior of Rf in HF/0.1 M HNO<sub>3</sub>



The fluoro complex formation of Rf successively proceeds as those with the homologues.

The strength of the coordination of the fluoride ions to Rf is significantly weaker than that to Zr and Hf.

# Fluorido complex formation of Rf

1. We clarified that Rf is present as the hexafluorido complex,  $[\text{RfF}_6]^{2-}$  in  $[\text{F}^-] = 3 \times 10^{-3} \text{ M}$ .
2. The strength of the fluorido complex formation was clearly demonstrated:  $\text{Zr} \approx \text{Hf} > \text{Rf} > \text{Th}$ .
3. Theoretical predictions by V. Pershina:  
Predominant electrostatic interaction  
→ Correlation between ionic radii and strength of complex formation  
 $\text{Zr} (72 \text{ pm}) \approx \text{Hf} (71 \text{ pm}) < \text{Rf} (76 \text{ pm: cal.}) \ll \text{Th} (94 \text{ pm})$   
→ The ionic radius of  $\text{Rf}^{4+}$  is in between  $\text{Zr}^{4+}/\text{Hf}^{4+}$  and  $\text{Th}^{4+}$ .

## Chemical behavior of lighter homologues

- Batch experiment with relatively long-lived nuclides

→  $K_d^{\text{Batch}}$



- On-line column experiment with short-lived nuclides

→  $K_d^{\text{Column}}$



$$K_d^{\text{Batch}} = K_d^{\text{Column}}$$

Reaction with column exp. reaches equilibrium.

## Superheavy elements

- On-line column experiment

↓ good statistics ↓  
 $K_d$                       %ads.



- Chemical species
- Complex formation



Theoretical prediction

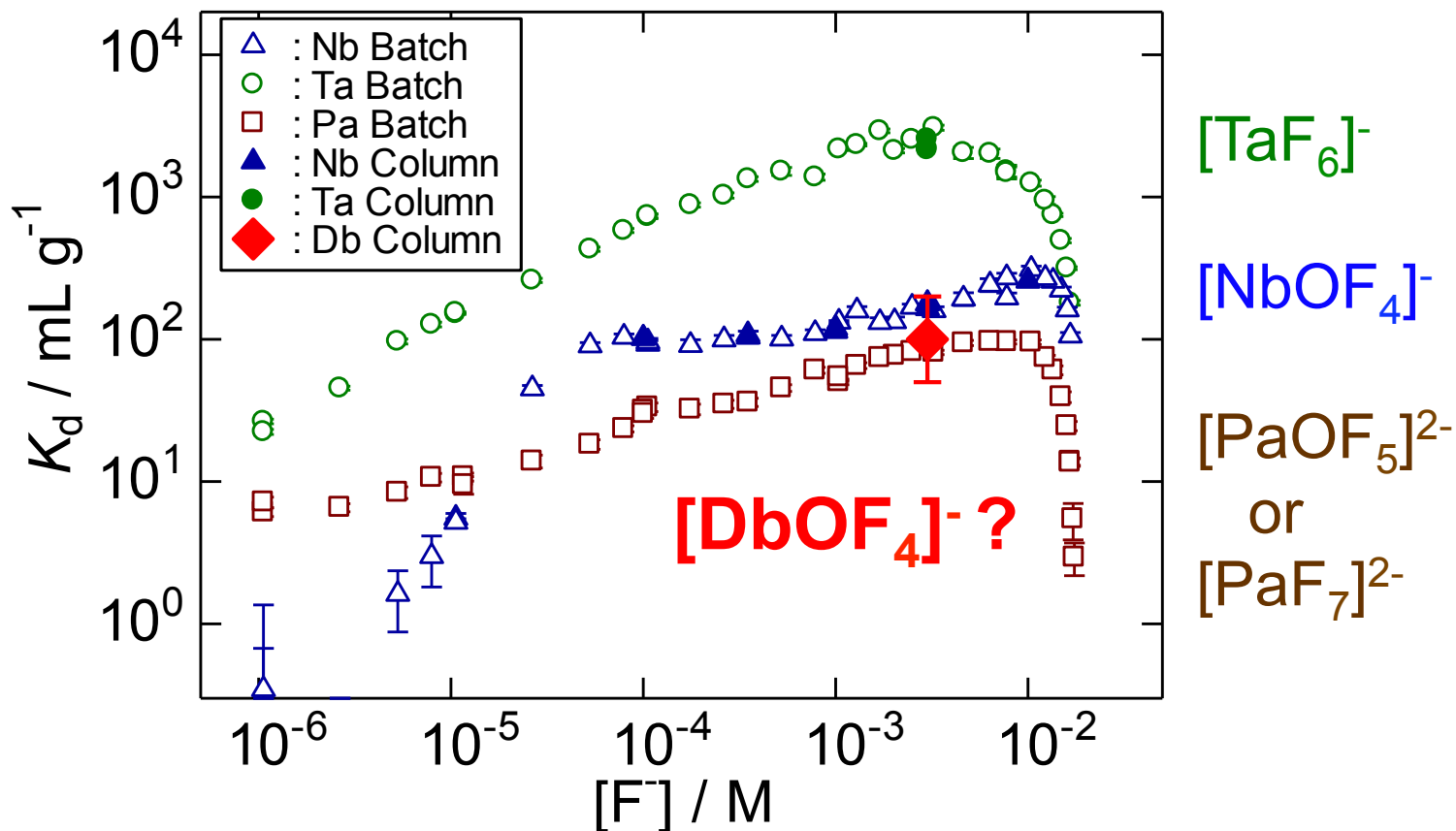
Yes

No

Complex formation	Chromatography	Chemical quantity	Chemical species	Formation strength
Chlorido	AIX	%ads	$[\text{RfCl}_6]^{2-}$ ?	$\text{Rf} \geq \text{Zr} > \text{Hf}$
TBP	Reversed-phase	%ads	$\text{RfCl}_4(\text{TBP})_2$ ?	$\text{Rf} < \text{Zr} \approx \text{Hf}$
TOTO	Reversed-phase	%ads	$\text{RfCl}_4(\text{TOPO})_2$ ?	$\text{Rf} < \text{Zr} \approx \text{Hf}$
Nitrate	AIX	%ads	$\text{Rf}(\text{NO}_3)_4$ ?	$\text{Rf} \approx \text{Zr} \approx \text{Hf}$
Fluorido	AIX & CIX	$K_d$	$[\text{RfF}_6]^{2-}$ $[\text{RfF}_2]^{2+}/[\text{RfF}]^{3+}$	$\text{Rf} < \text{Zr} \approx \text{Hf}$
Sulfate	CIX	%ads ( $K_d$ )	$[\text{Rf}(\text{SO}_4)]^{2+}$ ?	$\text{Rf} < \text{Zr} < \text{Hf}$



# Anion-exchange behavior of Db and its lighter homologues



# Comparative study with the homologues

## 1. Reaction kinetics:

Ion-exchange reaction processes of SHE taking place in the column experiments have to reach equilibrium.

$$\Rightarrow K_d$$

## 2. Chemical forms of SHE in solution should be clarified.

different species  $\rightarrow$  different adsorption

**$\Rightarrow$  Fluorido complex formation**

## 4. Development of a new apparatus - Electrochemical approach

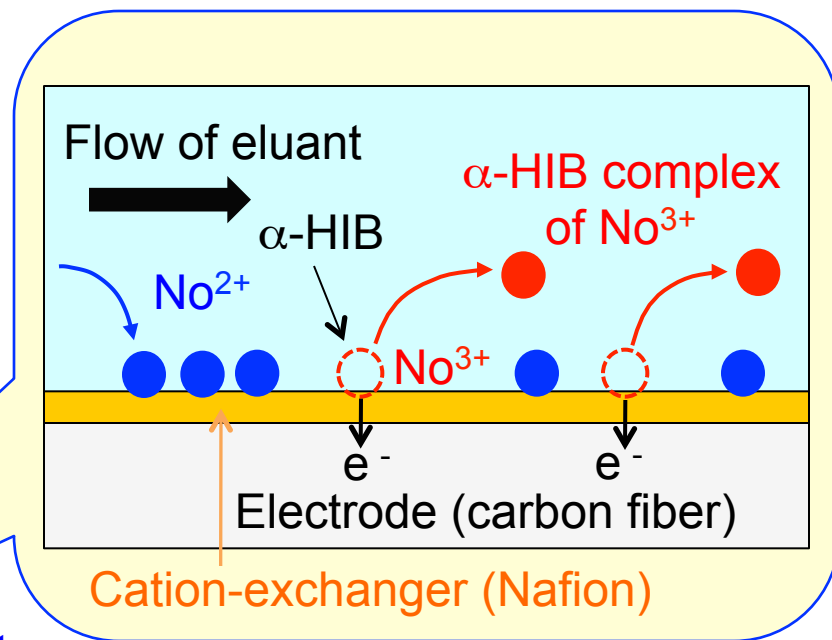
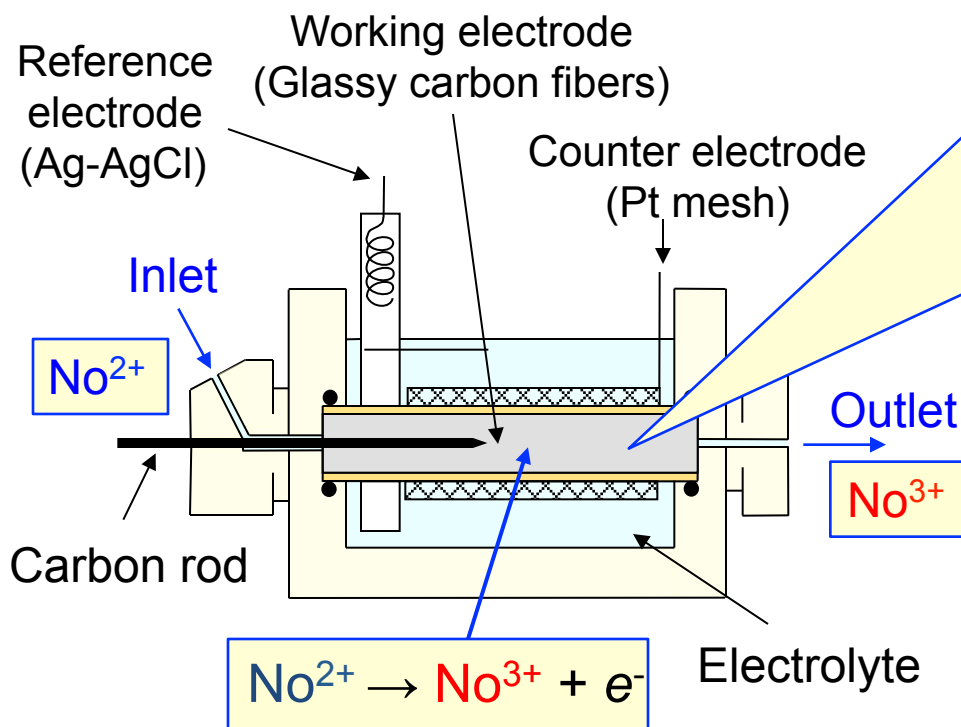
- Development of a rapid electrochemical apparatus
- Oxidation of No & reduction of Md

$^{248}\text{Cm}(^{12}\text{C}, 5n)^{255}\text{No}$  (3.1 min)

$^{248}\text{Cm}(^{11}\text{B}, 4n)^{255}\text{Md}$  (27 min)



## Flow electrolytic column with cation-exchanger



### Oxidation of $\text{No}^{2+}$

Complex formation of  $\text{No}^{3+}$  with  $\alpha\text{-HIB}$

# Experimental procedure: Oxidation of No

JAEA tandem accelerator

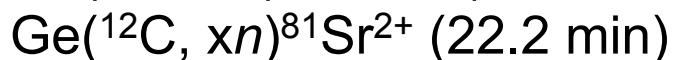


gas-jet transport

2) 0.1 M  $\alpha$ -HIB (pH3.9)

1) Collection for 10 min

collection and dissolution

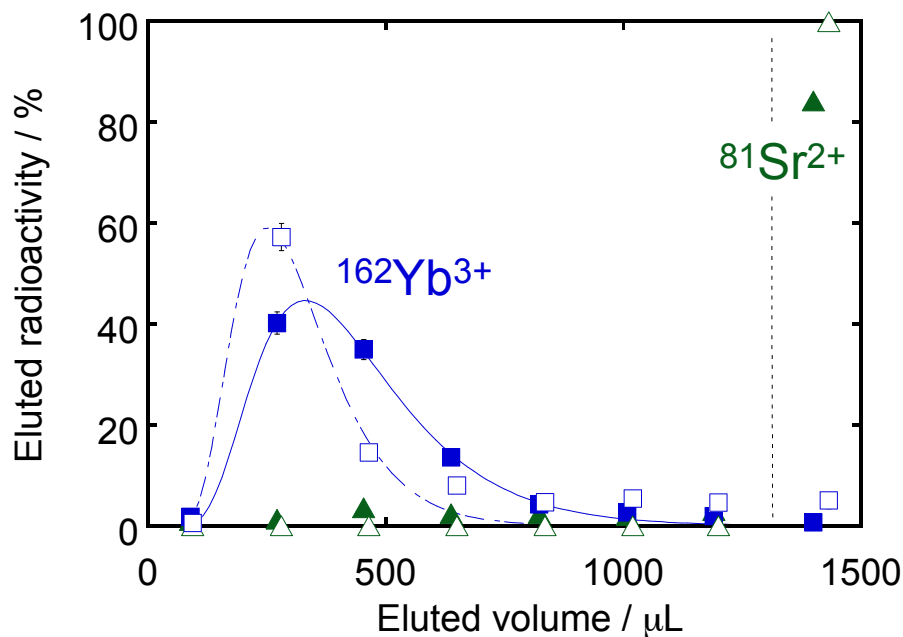


3) 3.0 M HCl

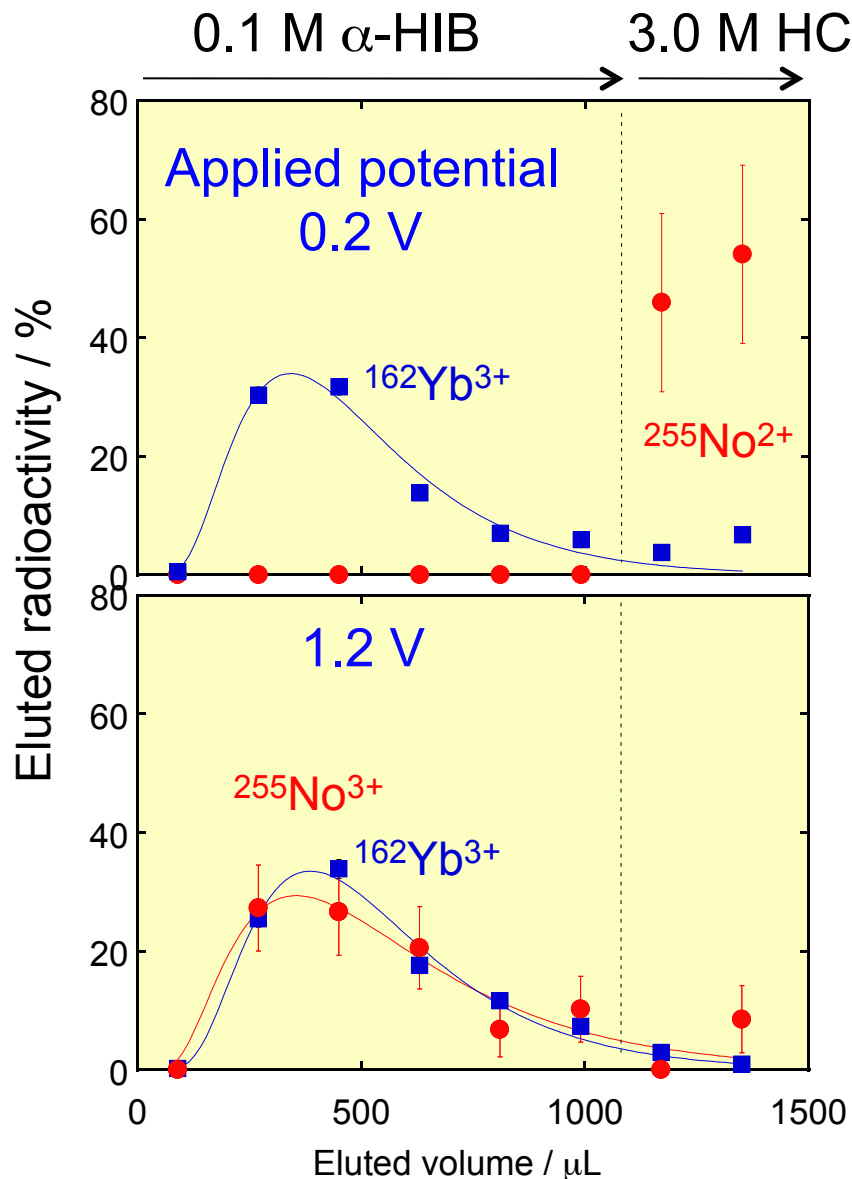
Flow electrolytic-column (500  $\mu\text{L}$ )  
(chemically modified electrode)  
Applied potentials: 0.2 - 1.2 V

$\text{No}^{3+}$  ( $\text{Yb}^{3+}$ )  $\text{No}^{2+}$  ( $\text{Sr}^{2+}$ )  
(6 fractions) (2 fractions)

$\alpha$ -source preparation and  
 $\alpha$ -particle measurements

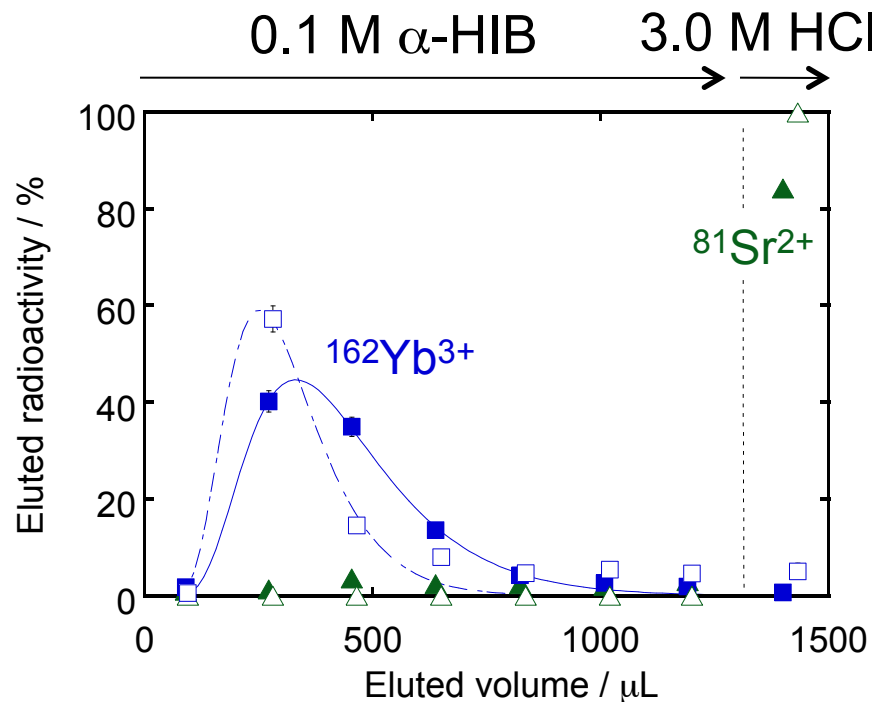


# Oxidation of $\text{No}^{2+}$



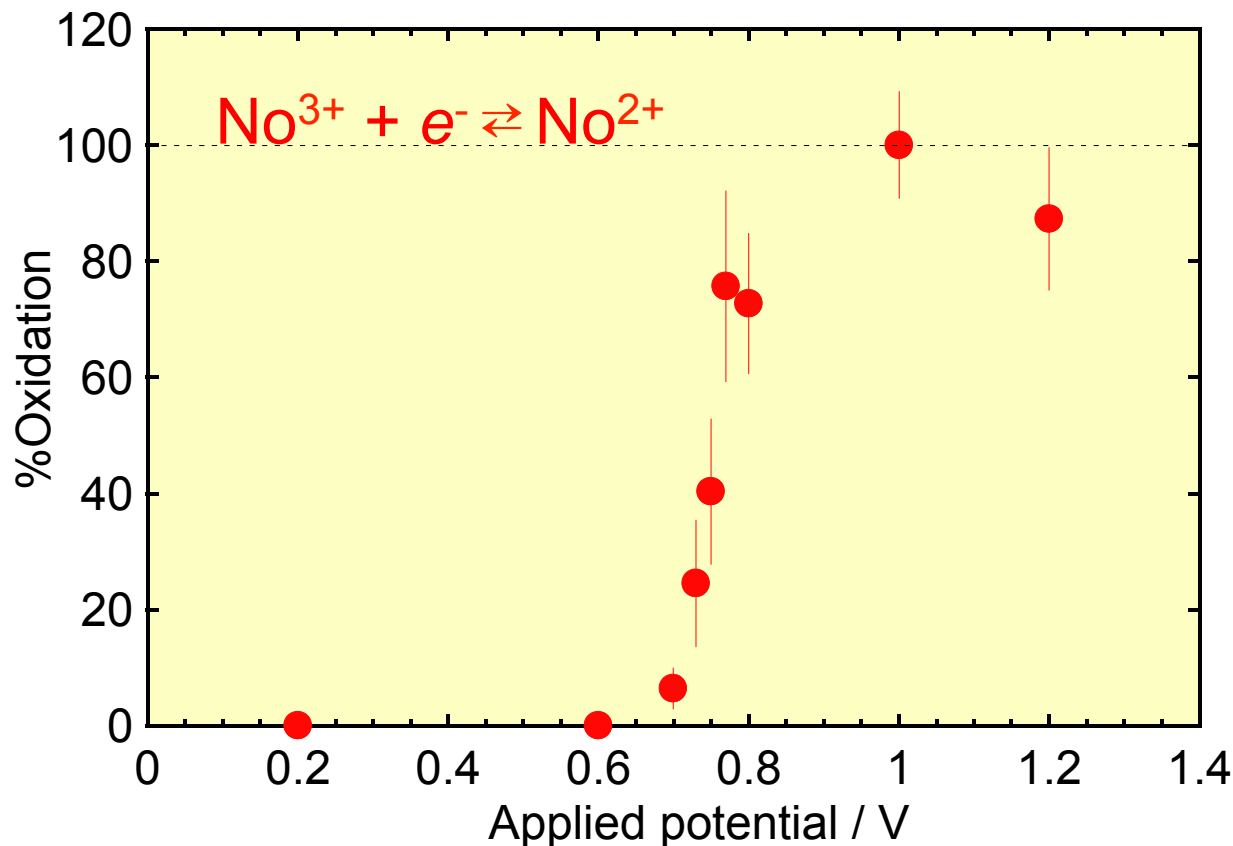
the number of  $^{255}\text{No}$  atoms  
 $\approx 100$  atoms ( $10^{-21}$  M)

Elution behavior of  $^{81}\text{Sr}^{2+}$  and  $^{162}\text{Yb}^{3+}$



# Variation of oxidation rates

$$\%Oxidation = \frac{[No^{3+}]}{[No^{2+}] + [No^{3+}]}$$



$$E = E_0 + \frac{RT}{nF} \ln \frac{[No^{3+}]}{[No^{2+}]}$$

$$E = E_0$$

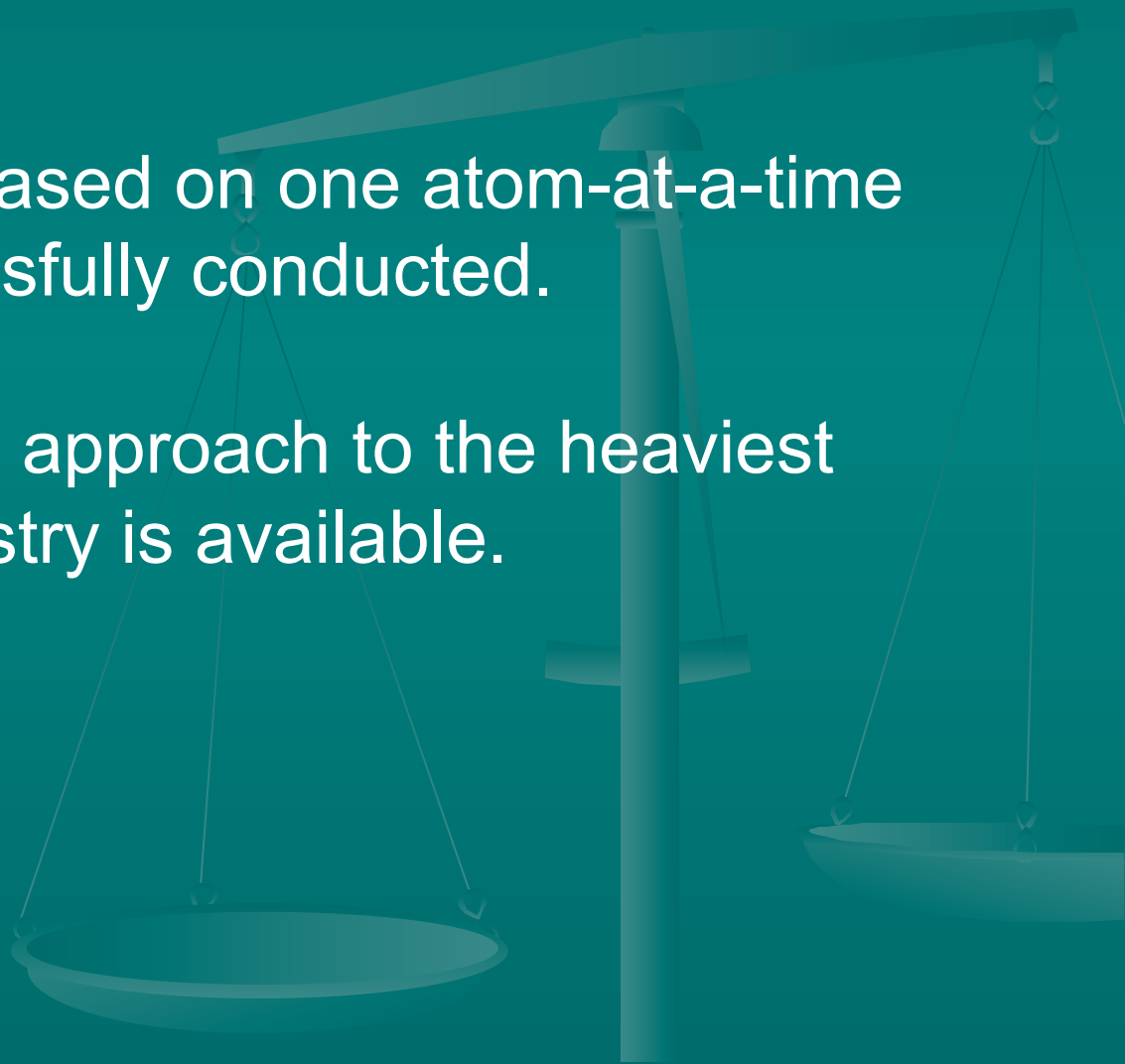
at  $[No^{3+}] = [No^{2+}]$

$$E_0 \approx 0.75 \text{ V}$$

# Electrochemistry of the heaviest elements

Redox reactions based on one atom-at-a-time scale were successfully conducted.

⇒ A new technical approach to the heaviest element chemistry is available.





# - Coupling with a recoil separator

## Continuous liquid-liquid extraction with SISAK

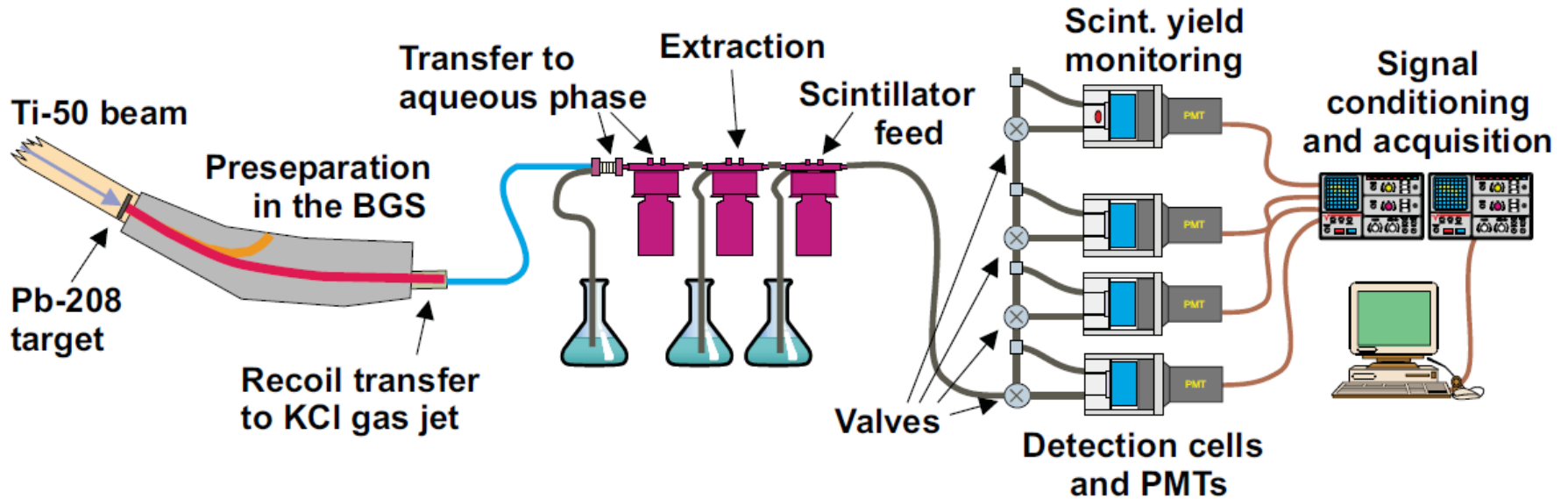
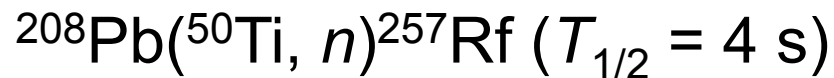
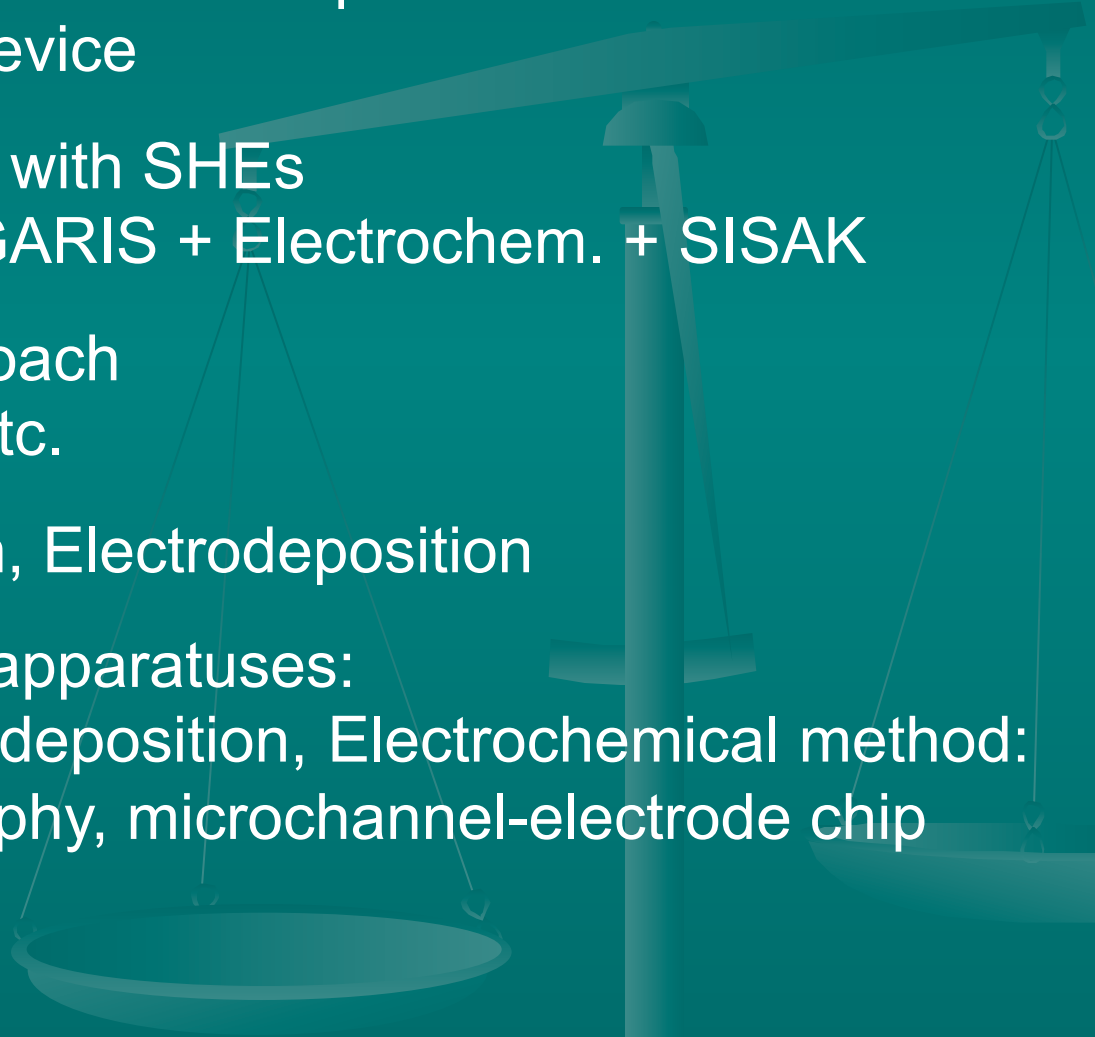


Figure 1. Overview of the SISAK-BGS setup.

BGS + SISAK + Scintillation counting

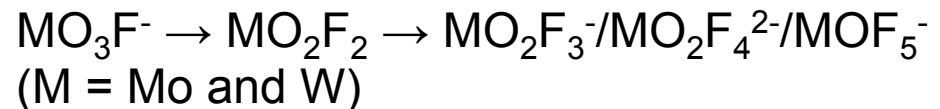
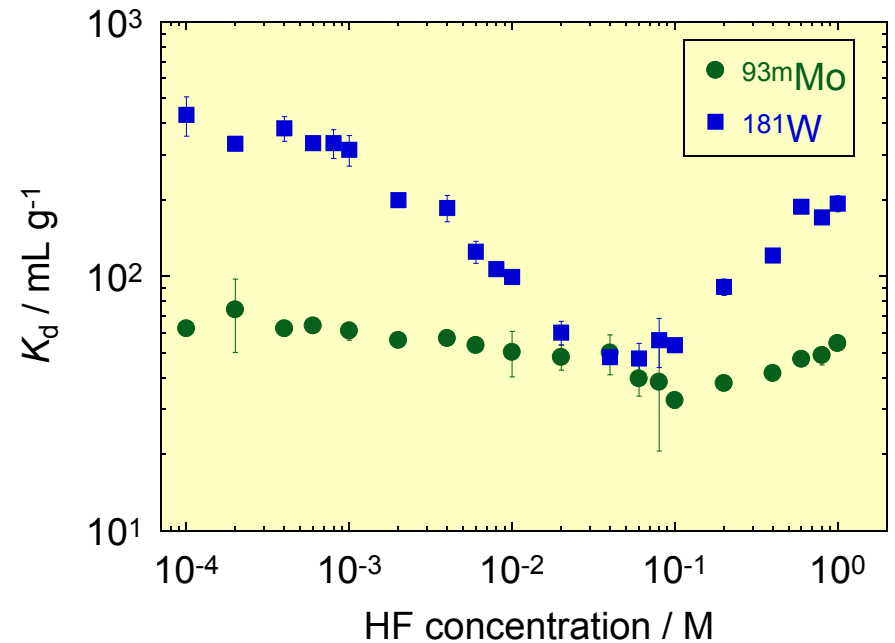
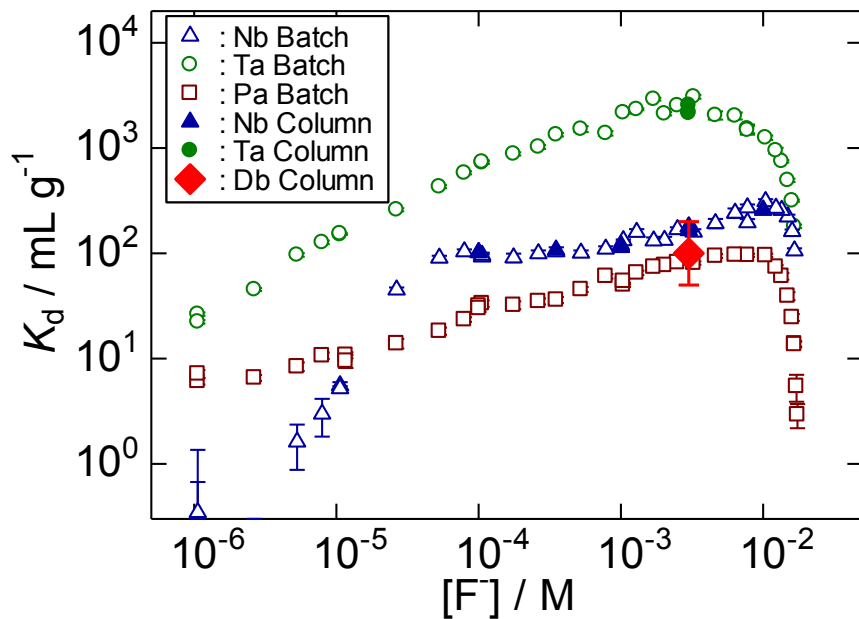


# 5. Perspective on liquid-phase chemistry

1. Successive study on fluoro complex formation:  
Db and Sg → new device
  2. First electrochemistry with SHEs  
Reduction of  $\text{Sg}^{6+}$  : GARIS + Electrochem. + SISAK
  3. Electrochemical approach  
Ionic radius of  $\text{No}^{3+}$  etc.
  4. Hs: Solvent extraction, Electrodeposition
  5. Development of new apparatuses:  
MicroSISAK, Electrodeposition, Electrochemical method:  
electro-chromatography, microchannel-electrode chip
- 

# Successive fluoro complex formation: $^{262}\text{Db}$ ( $T_{1/2} = 34$ s) and $^{265}\text{Sg}$ (10 s)

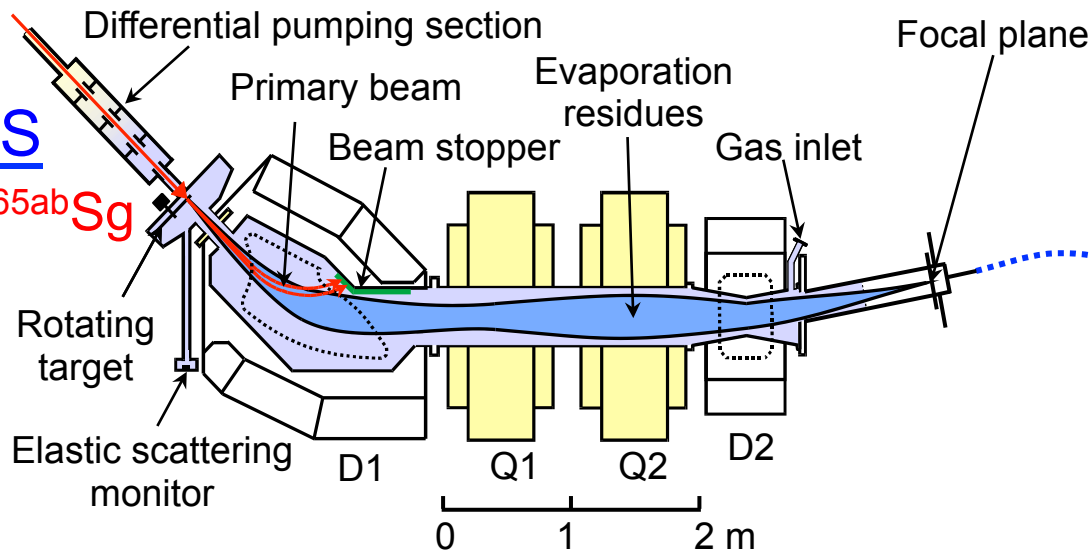
Anion-exchange behavior of Db and Sg ?



X.H. Liang *et al.*, J. Radioanal. Nucl. Chem. **292**, 917  
 (2012).

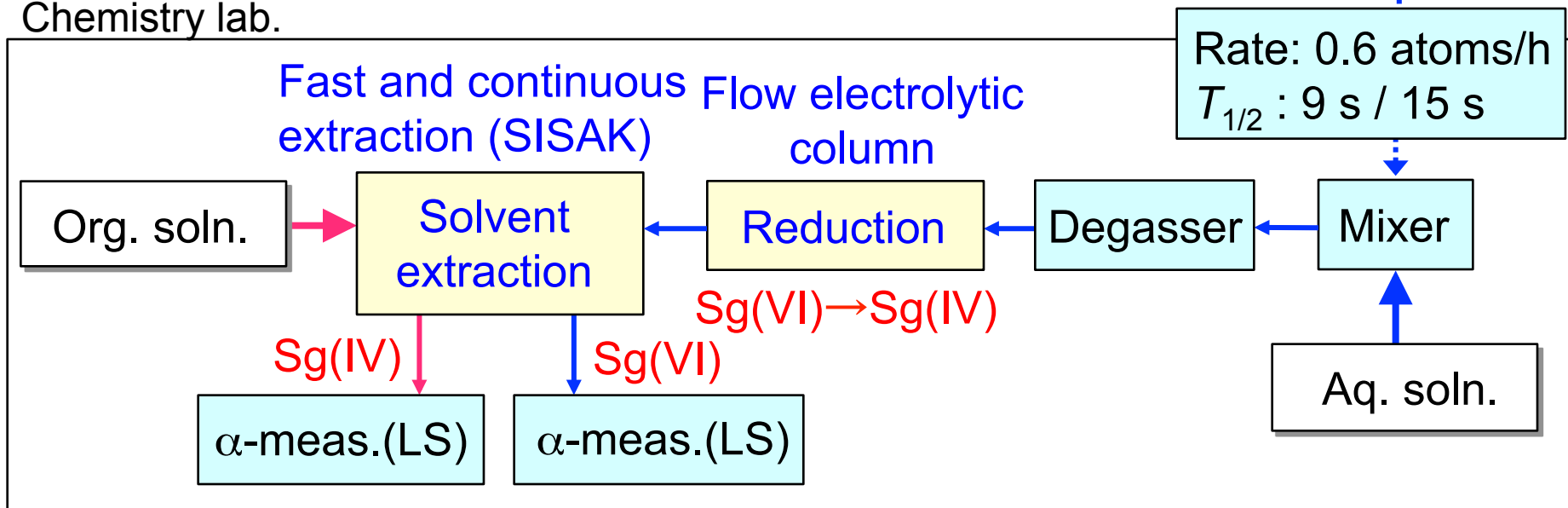
Further improvement of the apparatus is required.

## RIKEN GARIS



Irradiation cave

Chemistry lab.



P. Pyykkö  
PCCP 13, 161 (2011)

1	1 H	2											13	14	15	16	17	2 He	1s	
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne	2s2p	
3	11 Na	12 Mg	3	4	5	6	7	8	9	10	11	12	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar	3s3p	
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr	4s3d4p	
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe	5s4d5p	
6	55 Cs	56 Ba	57-71	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn	6s5d6p	
7	87 Fr	88 Ra	89-103	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113	114	115	116	117	118	7s6d7p	
8	119	120	121-	156	157	158	159	160	161	162	163	164	139	140	169	170	171	172	8s7d8p	
9	165	166												167	168					9s9p

6	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	4f
7	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	5f
8	141	142	143	144	145	146	147	148	149	150	151	152	153	154	155	6f

8	121	122	123	124	125	126	127	128	129	130	131	132	133	134	135	136	137	138	5g
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Fig. 3 The new, compact Periodic Table for elements 1–172. The numbers 1–18 are the Groups. For Periods 8 and 9, the Groups 13–14 are interpreted as  $p^*$  ( $p_{1/2}$ ) states and the Groups 15–18 as  $p$  ( $p_{3/2}$ ) states. Please note that, in this most compact version and respecting the ‘Orbitals’ assignment in the right-hand marginal, the Z values do not increase systematically. An alternative were to break present Period 8 into the pieces 8a (119–120), 8b (139–140) and 8c (156–164, 169–172).

8th Workshop on Chemistry of Superheavy Elements  
September 19-21, 2013, Takayama, Japan  
M. Schädel (chair)  
A. Toyoshima (secretary)

5th Asian-Pacific Symposium on Radiochemistry  
(APSORC 13)  
September 22-27, 2013, Kanazawa, Japan  
Y. Nagame (chair)  
M. Yamamoto (co-chair)

# Acknowledgements

JAEA - M. Asai, Z. J. Li, K. Ohe, N. Sato, T. K. Sato,  
A. Toyoshima, K. Tsukada and M. Schädel

RIKEN - H. Haba and H. Kikunaga

Osaka Univ. - Y. Kasamatsu and A. Shinohara

Niigata Univ. - S. Goto and H. Kudo

Tokyo Metropolitan Univ. – K. Akiyama and Y. Oura  
Univ. Tsukuba – K. Sueki

Kanazawa Univ. – W. Sato and A. Yokoyama

GSI - Ch. E. Düllmann, V. Pershina and A. Yakushev  
Univ. Mainz - J. V. Kratz

IMP, China - F. L. Fan and Z. Qin

Oslo Univ. - J. P. Omtvedt