Liquid Phase Experiments with the Heaviest Elements

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Contents

Recent progress in aqueous chemistry of
the heaviest elements

1. Introduction
   Nuclides, Experimental apparatuses & procedures

2. Fluorido complex formation of $_{104}Rf$ and $_{105}Db$

3. Electrochemistry of the heaviest elements based on an atom-at-a-time scale
   Oxidation of $_{102}No$ and Reduction of $_{101}Md$
   ⇒Poster presentation by Atsushi Toyoshima

4. Perspective

1. Introduction

Transactinide nuclides used for aqueous chemistry

Element	Nuclide	$T_{1/2}$/s	Reaction	σ/nb	Chemistry	Apparatus
$_{104}$Rf	^{257}Rf	4	^{208}Pb (^{50}Ti, *n*)	10	S.E.	SISAK
	^{261a}Rf	78	^{248}Cm (^{18}O, 5*n*)	13	I.E., E.C.	ARCA,AIDA
$_{105}$Db	^{262}Db	34	^{249}Bk (^{18}O, 5*n*)	6	E.C. , I.E.	ARCA
			^{248}Cm (^{19}F, 5*n*)	1	I.E.	AIDA
$_{106}$Sg	^{265a}Sg	9	^{248}Cm (^{22}Ne, 5*n*)	0.24	I.E.	ARCA
$_{108}$Hs	^{269}Hs	9	^{248}Cm (^{26}Mg, 5*n*)	0.007	Adsorption	CALLISTO

S.E. : Solvent Extraction
I.E. : Ion Exchange
E.C. : Extraction Chromatography

1. Introduction

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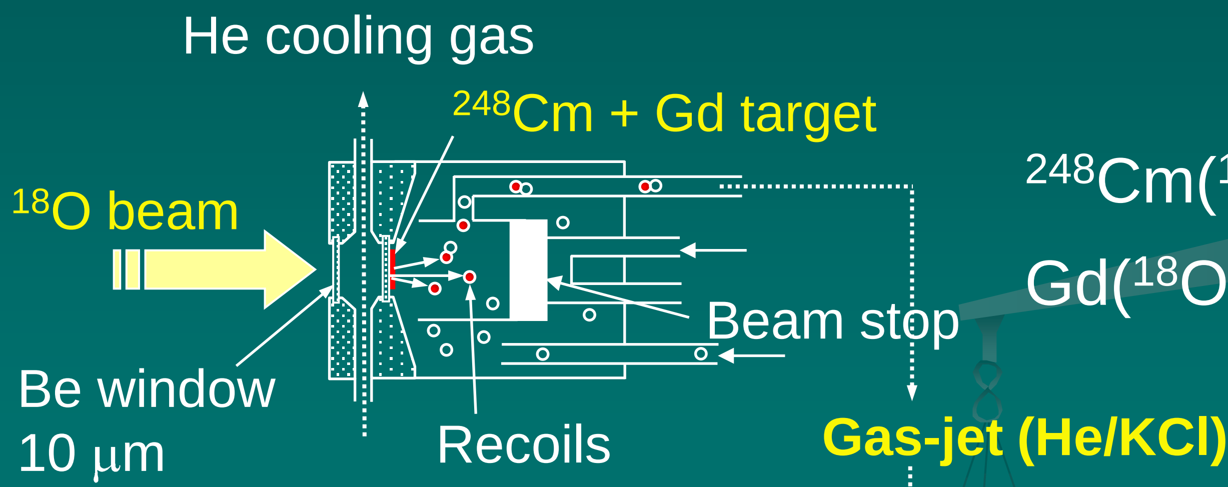
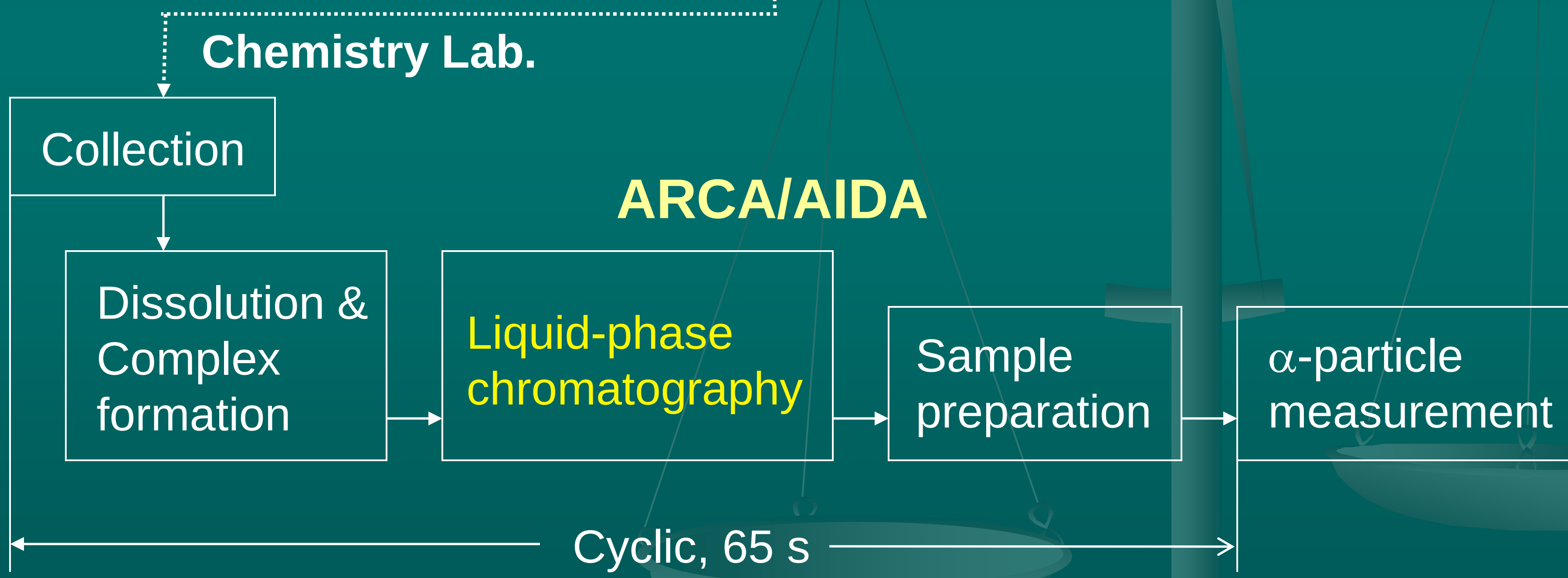
Schematic flow of the experiment

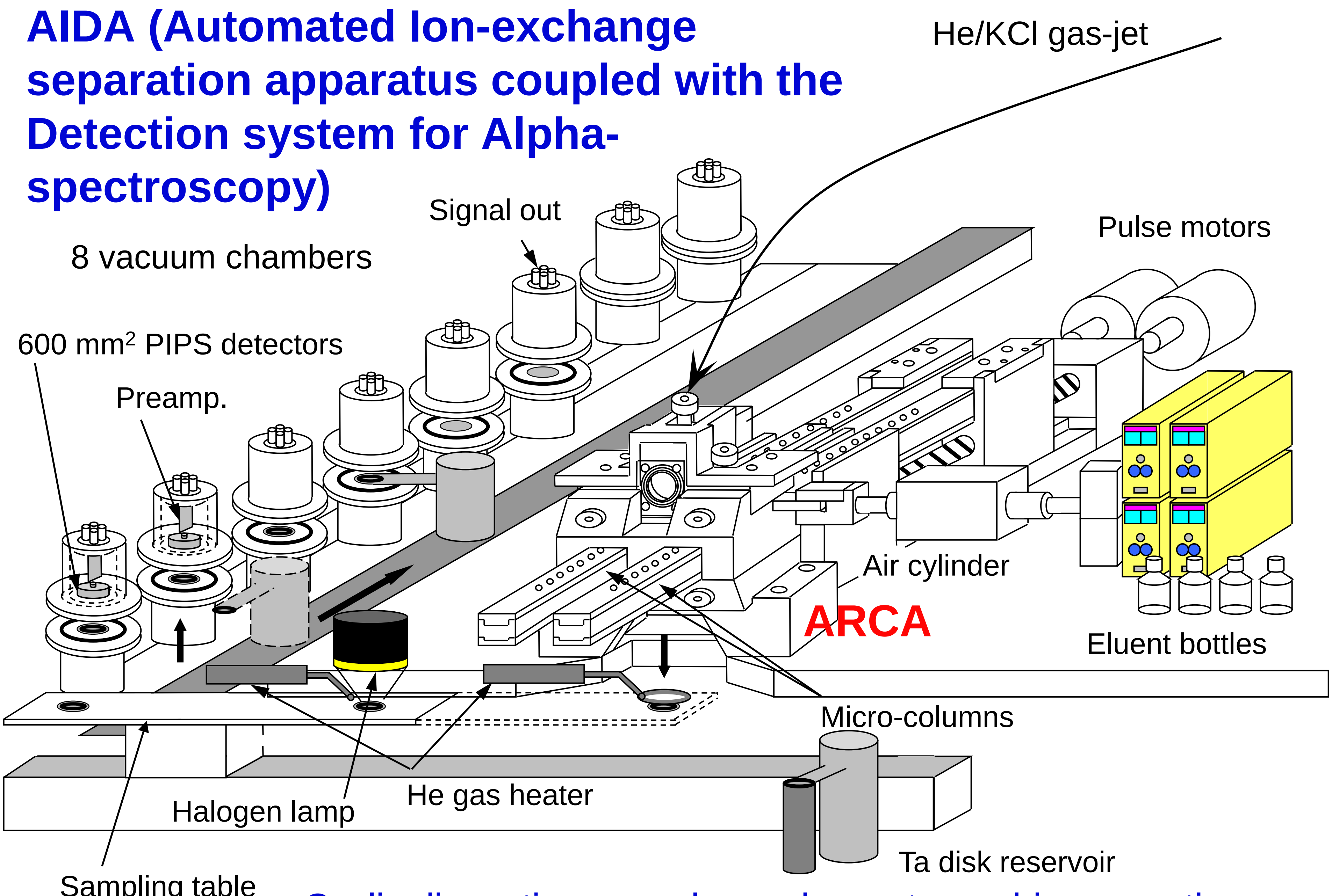


$^{248}Cm(^{18}O, 5n)^{261}Rf$ (78 s)

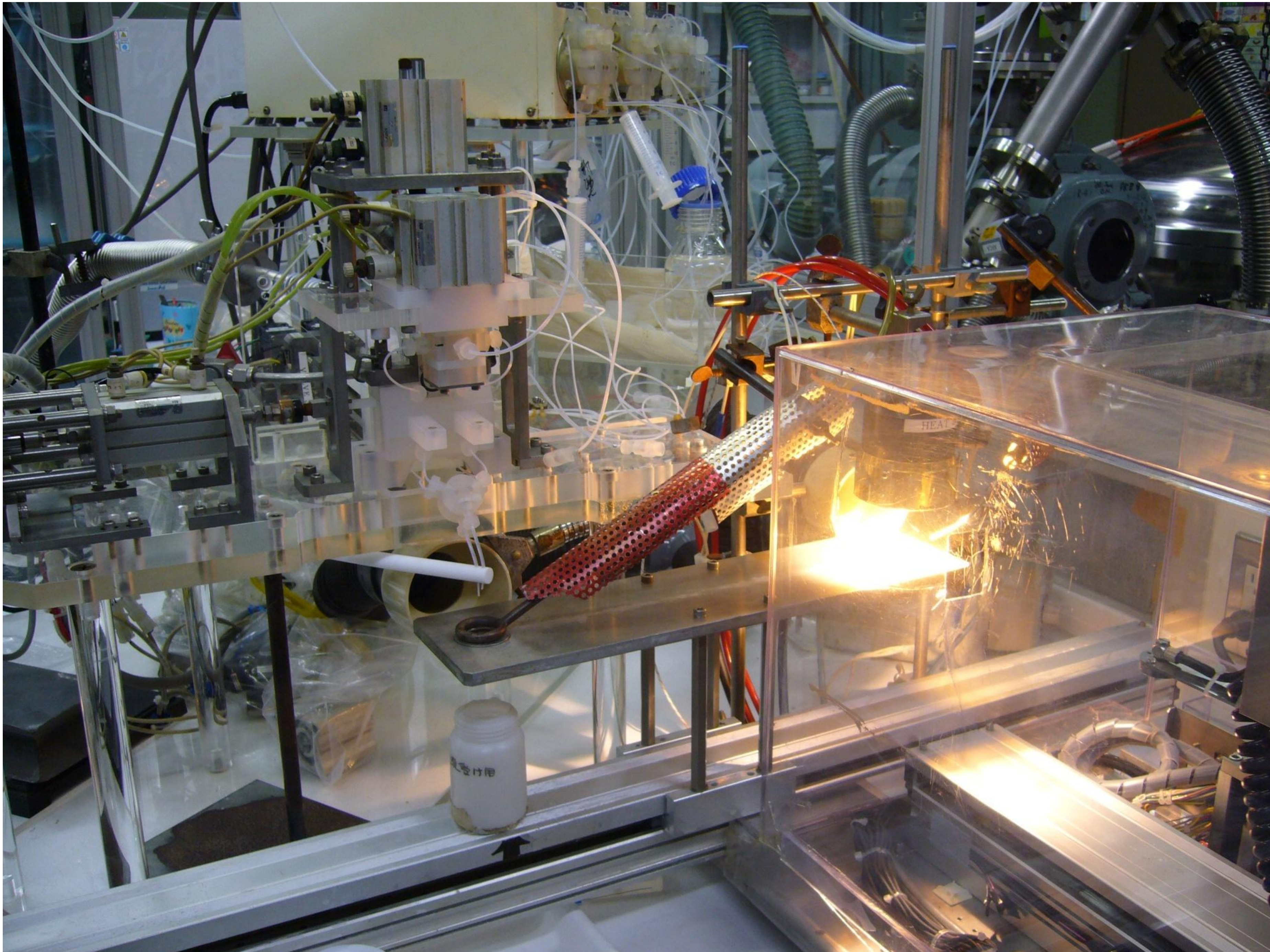
$Gd(^{18}O, xn)^{169}Hf$ (3.2 min)

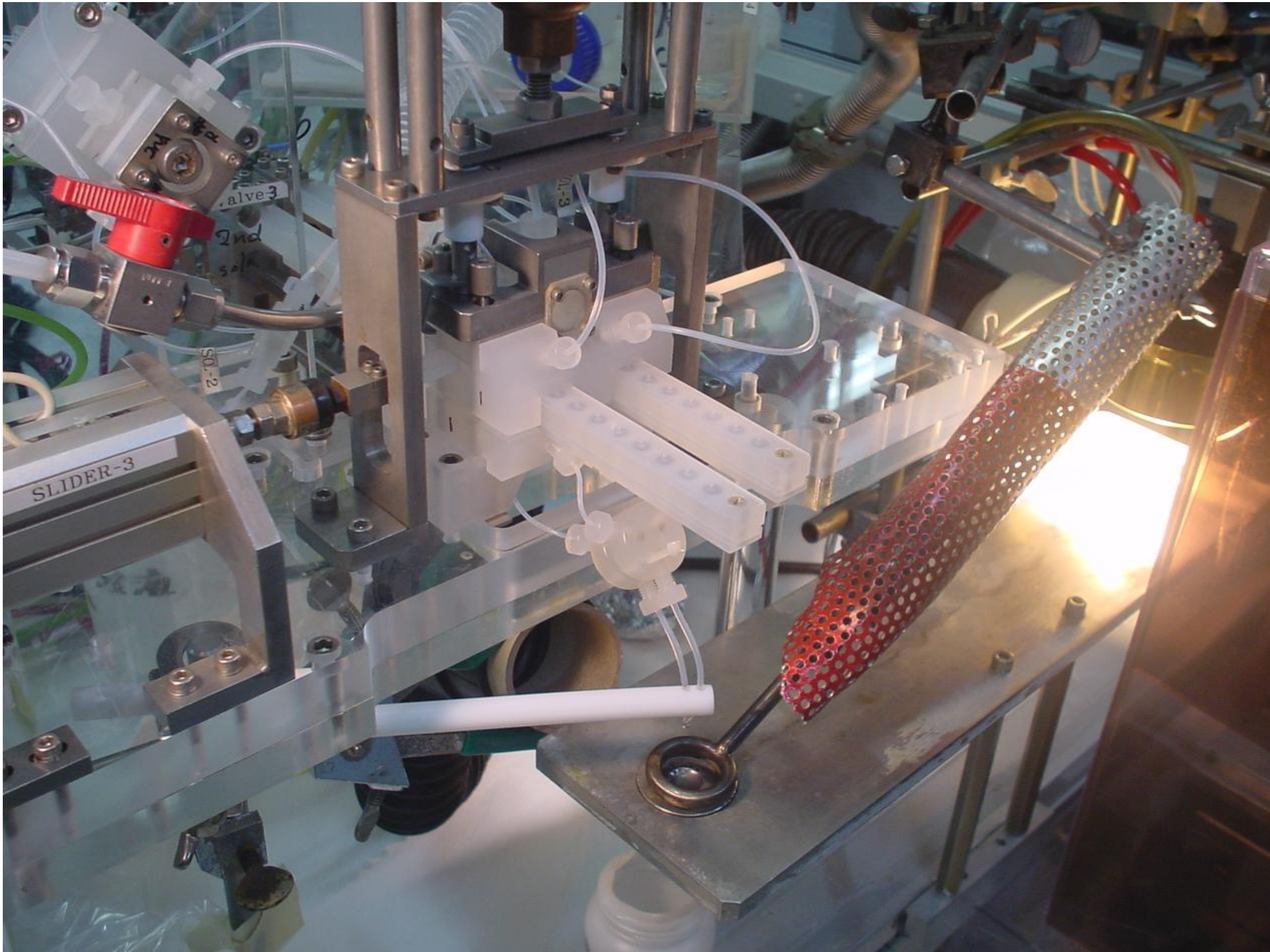


AIDA (Automated Ion-exchange separation apparatus coupled with the Detection system for Alpha-spectroscopy)



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


HEAT


SLIDER-3

Anion-exchange procedure in HF with AIDA

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

3. 200 μL of 4.0 M HCl at 1.0 mL/min

AIX column: MCI GEL CA08Y resin (25 μm)
1.6 mm i.d. × 7.0 mm (1.0 mm i.d. × 3.5 mm)

1st fraction (A_1) **2nd fraction (A_2) ⇒ α-spectrometry**

Adsorption probability (%) = 100 A_2 / (A_1 + A_2)

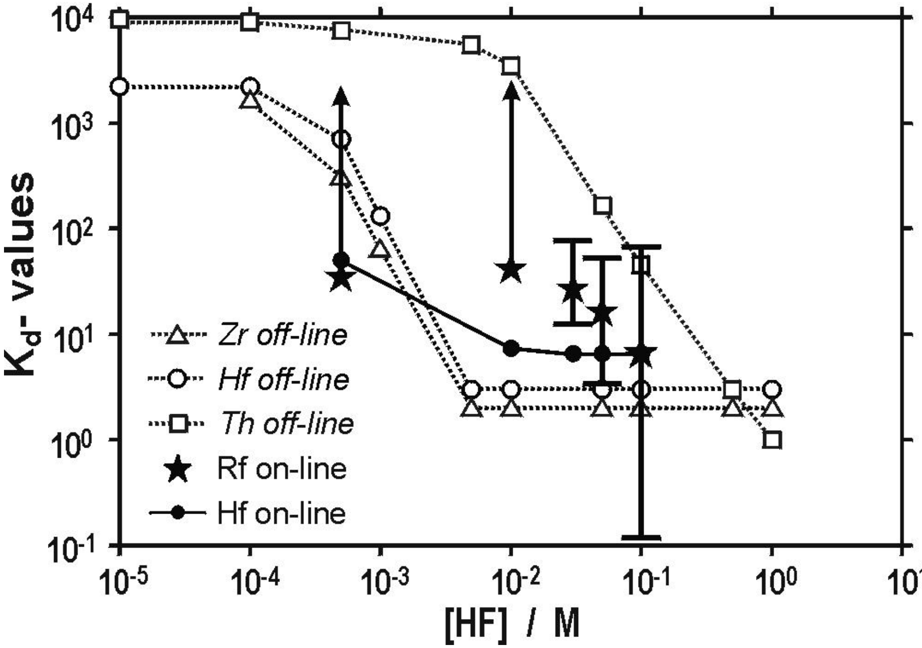
^{169}Hf : elution behavior and chemical yields (~ 60%)

^{85}Zr and ^{169}Hf from Ge/Gd target: Ge/Gd(^{18}O, x*n*)

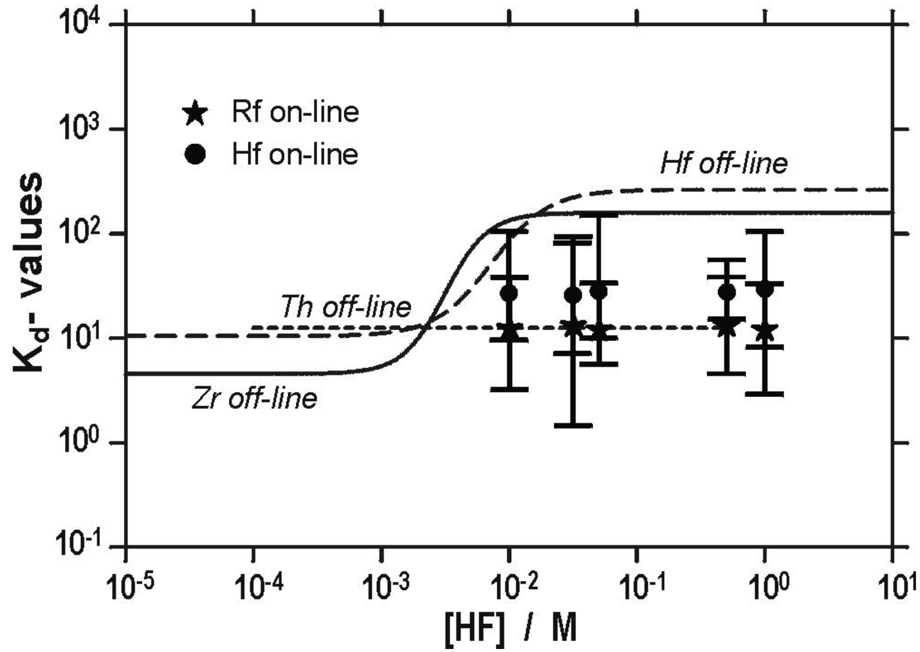
2-1. Fluorido complex formation of Rf

Sorption of Zr, Hf, Rf and Th on ion-exchange resin in 0.1 M HNO_3 at various HF concentrations.

Cation-exchange

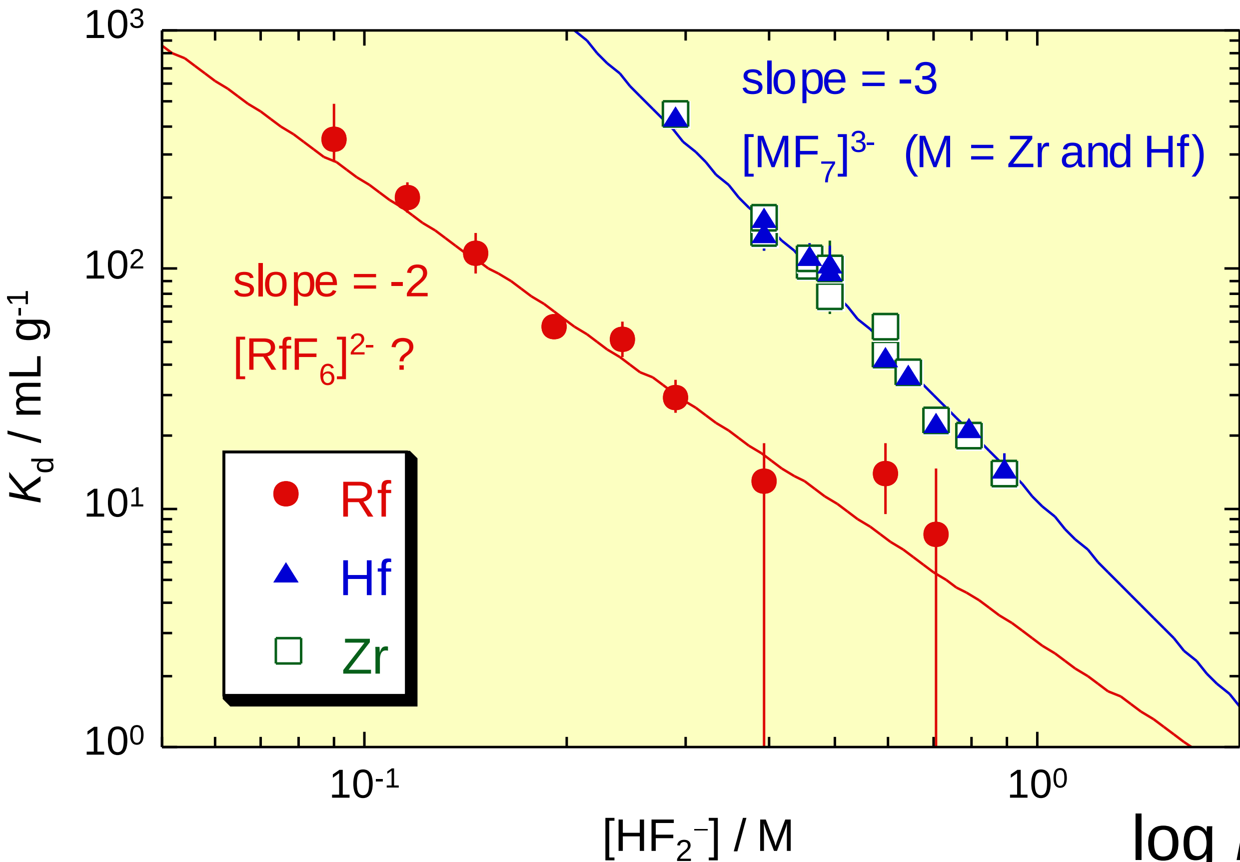


Anion-exchange



E. Strub *et al*., Radiochim. Acta **88**, 265 (2000).

Anion-exchange behavior of Rf in HF



$HF \rightleftarrows H^+ + F^-$

$HF + F^- \rightleftarrows$ **HF_2^-**

4226 cycles of anion-exchange experiments ⇒ 266 α events form ^{261}Rf and ^{257}No, 25 α–α time correlations

$$\log K_d = C - n \cdot \log[HF_2^-]$$

K_ds linearly decrease with $[HF_2^-]$.

⇒displacement of the metal fluorido complexes from the binding sites of the resin by the counter anion HF_2^-

$R_n\text{-}MF_{4+n} + n \cdot HF_2^- \rightleftarrows n \cdot R\text{-}HF_2 + MF_{4+n}^{n-}$ (M=Rf, Zr, and Hf), R: resin

H. Haba *et al*., J. Am. Chem. Soc. **126**, 5219 (2004).

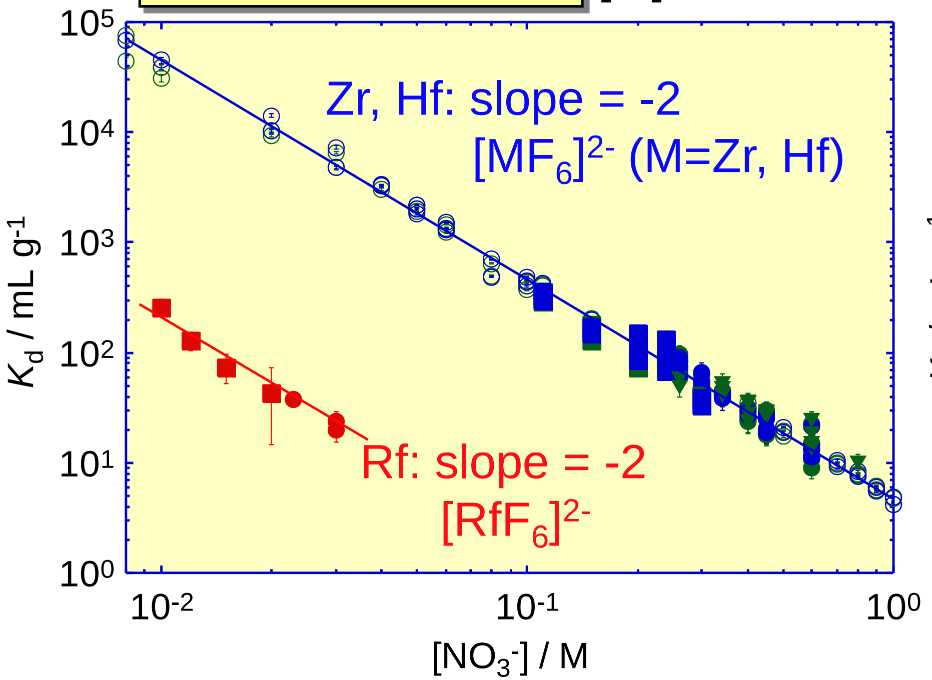
Anion-exchange behavior of Rf in HF/HNO_3

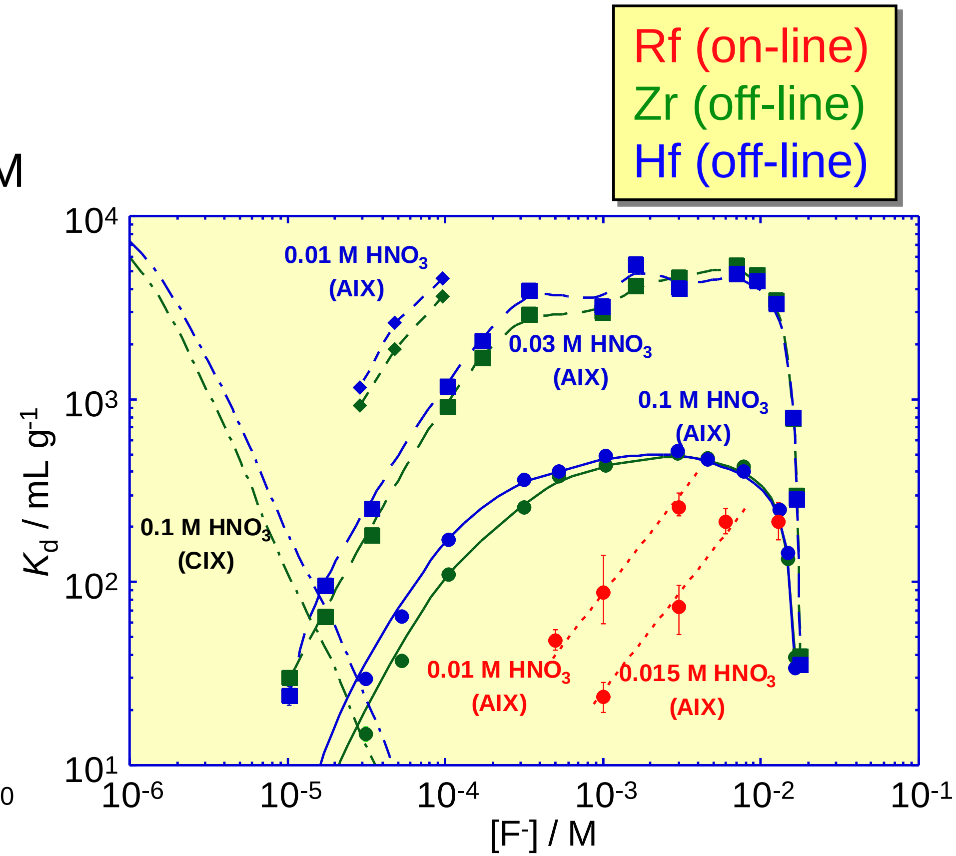
$HF \rightleftarrows H^+ + F^-$

$(HF + F^- \rightleftarrows HF_2^-)$

$HNO_3 \rightleftarrows H^+ +$ **NO_3^-**

$[F^-] = 3 \times 10^{-3}$ M





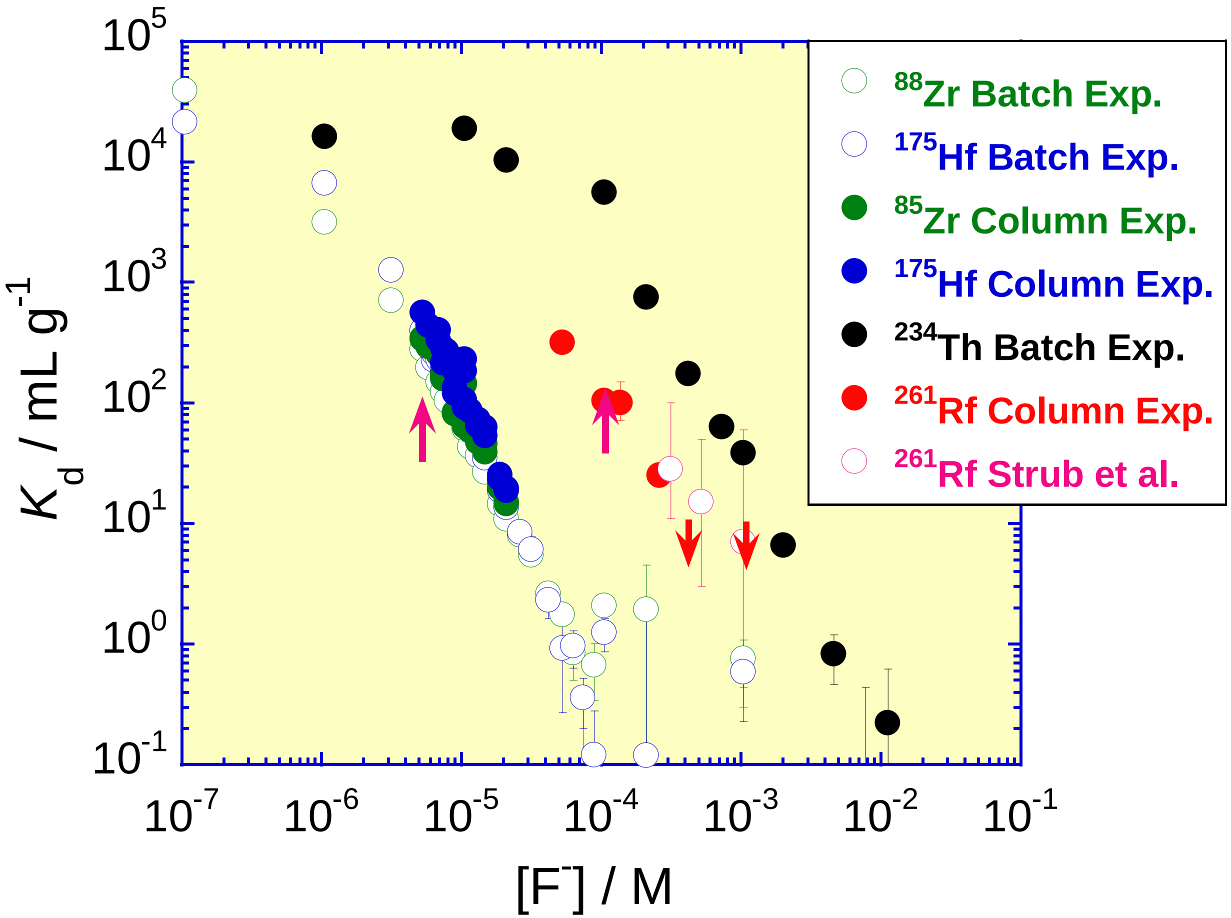
$R_n\text{-}MF_{4+n} + n \cdot NO_3^- \rightleftarrows n \cdot R\text{-}NO_3 + MF_{4+n}^{n-}$

Formation of $[MF_6]^{2-}$: Zr ≈ Hf > Rf

***n* = -2** ⇒ $[MF_6]^{2-}$

A. Toyoshima *et al*., Radiochim. Acta **96**, 125 (2008).

Cation-exchange behavior of Rf in HF/0.1 M HNO_3



$$M^{4+} + F^- \rightleftarrows MF^{3+}$$
$$MF^{3+} + F^- \rightleftarrows MF_2^{2+}$$
$$MF_2^{2+} + F^- \rightleftarrows MF_3^{+}$$
$$MF_3^{+} + F^- \rightleftarrows MF_4$$
(M= Rf, Zr, Hf and Th)

The fluorido 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.

Y. Ishii *et al*., Bull. Chem. Soc. Jpn., in press.

Fluorido complex formation of Rf

1. We clarified that Rf is present as the hexafluorido complex, $[RfF_6]^{2-}$ in $[F^-] = 3 \times 10^{-3}$ M.

2. The sequence of the fluorido complex formation was clearly demonstrated: $Zr \approx Hf > Rf > Th$.

3. The present result is absolutely consistent with the theoretical calculation by Pershina .

Aqueous chemistry of Rf

Systematic investigation on aqueous chemistry of Rf
through the comparative study with the homologues Zr and Hf

1. Chlorido complex formation: $[MCl_6]^{2-}$
   Anion-exchange chromatography: Rf ≥ Zr > Hf
2. TBP and TOPO extraction (complex): $MCl_4(TBP)_2$
   Reversed-phase chromatography: Rf < Zr ≈ Hf
3. Nitrate complex formation
   Anion-exchange chromatography: Rf ≈ Zr ≈ Hf
4. Fluorido complex formation
   Anion- & cation-exchange chromatography: Rf < Zr ≈ Hf
5. Sulfate complex formation
   Cation-exchange chromatography: Rf < Zr < Hf

Comparative study with the homologues

1. Reaction kinetics:
   Ion-exchange reaction processes of Rf and the homologues taking place in the column experiments with AIDA have to reach equilibrium.
   ⇒ K_d

2. Chemical forms of Rf in solution should be clarified.
   different species → different adsorption

⇒ Fluorido complex formation

2-2. Fluorido complex formation of Db

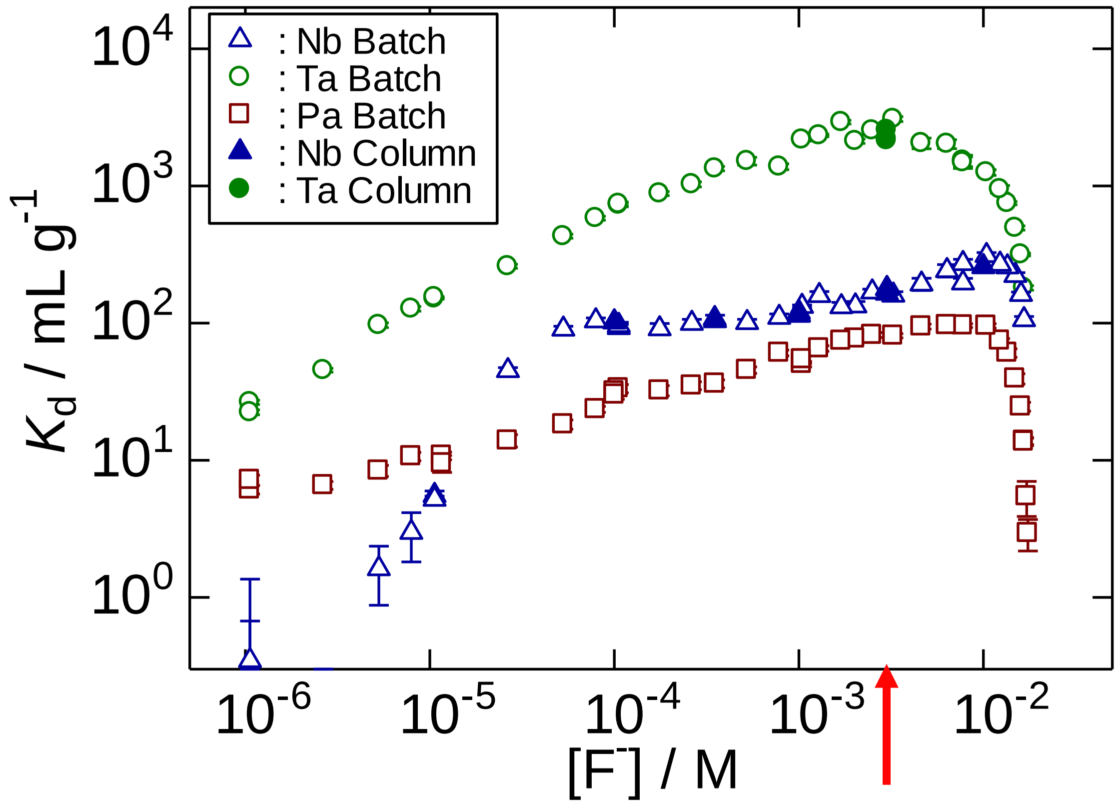
Anion-exchange chromatography
in 0.31 M HF/0.10 M HNO_3 ($[F^-] = 3 \times 10^{-3}$ M)

$^{248}\mathrm{Cm}(^{19}\mathrm{F}, 5n)^{262}\mathrm{Db}$ ($T_{1/2}$ = 34 s)

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
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
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
55 Cs	56 Ba	57 La	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
87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 113	114 114	115 115	116 116	117 117	118 118

Lanthanides	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
Actinides	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

Anion-exchange behavior of the group-5 elements in HF/0.10 M HNO_3



$[TaF_6]^-$

$[NbOF_4]^-$

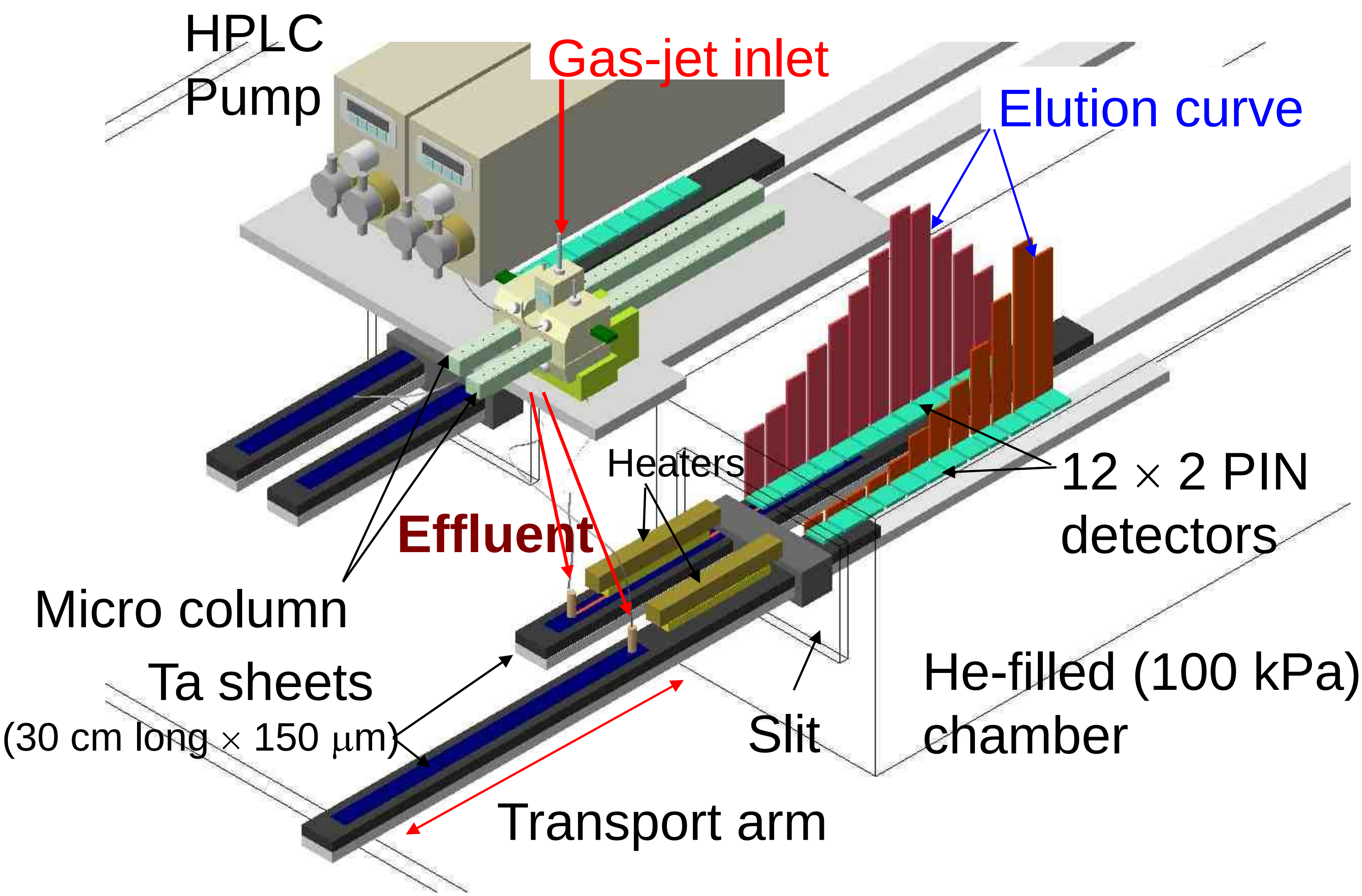
$[PaOF_5]^{2-}$
or
$[PaF_7]^{2-}$

in [F^-] ≤ 0.01 M

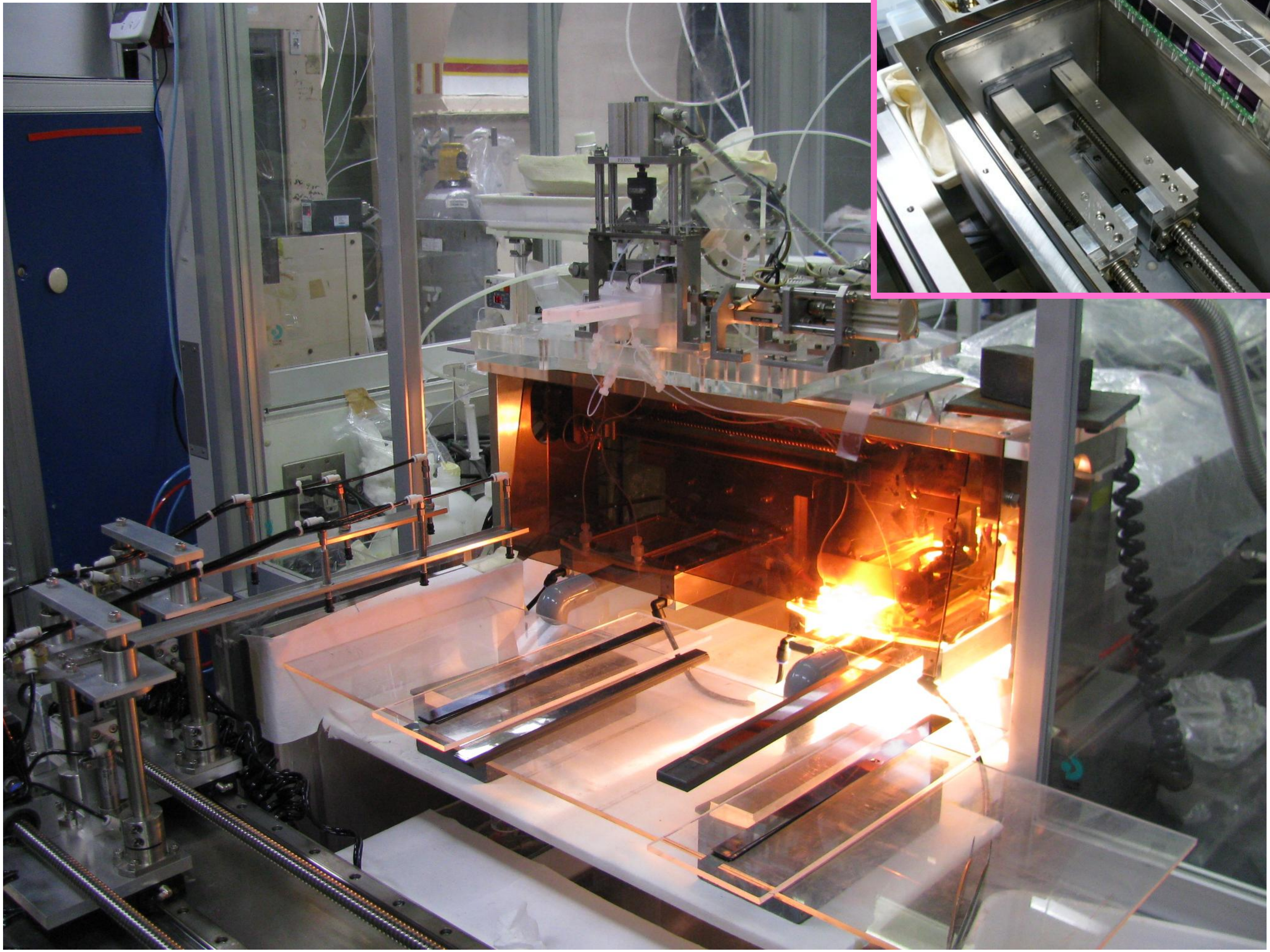
Y. Kasamatsu *et al*., J. Nucl. Radiochem. Sci. **8**, 69 (2007).
Y. Kasamatsu *et al*., J. Radioanal. Nucl. Chem. **279**, 371 (2009).

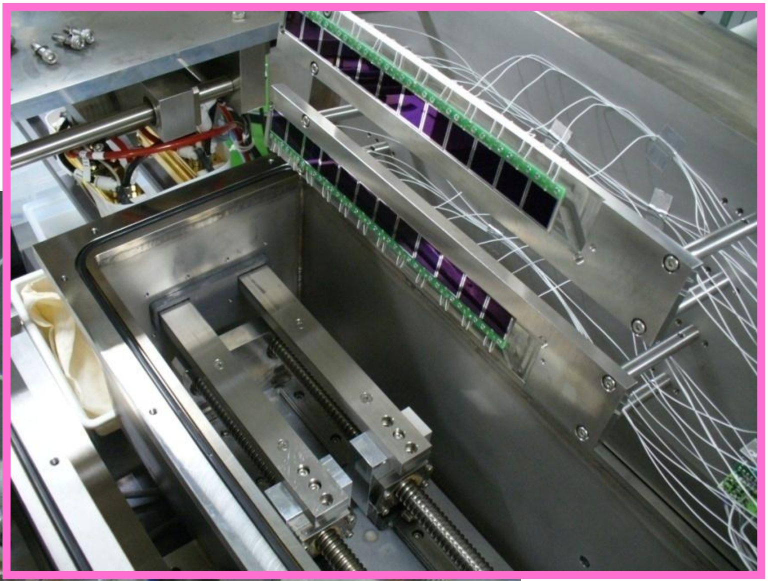
AIDA-II Time for sample preparation

	1st	2nd
AIDA:	65 s,	80 s
AIDA-II:	15 s,	35 s



AIDA-II

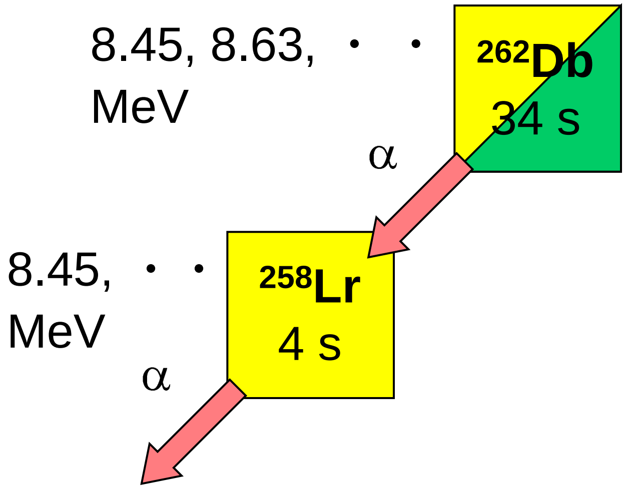


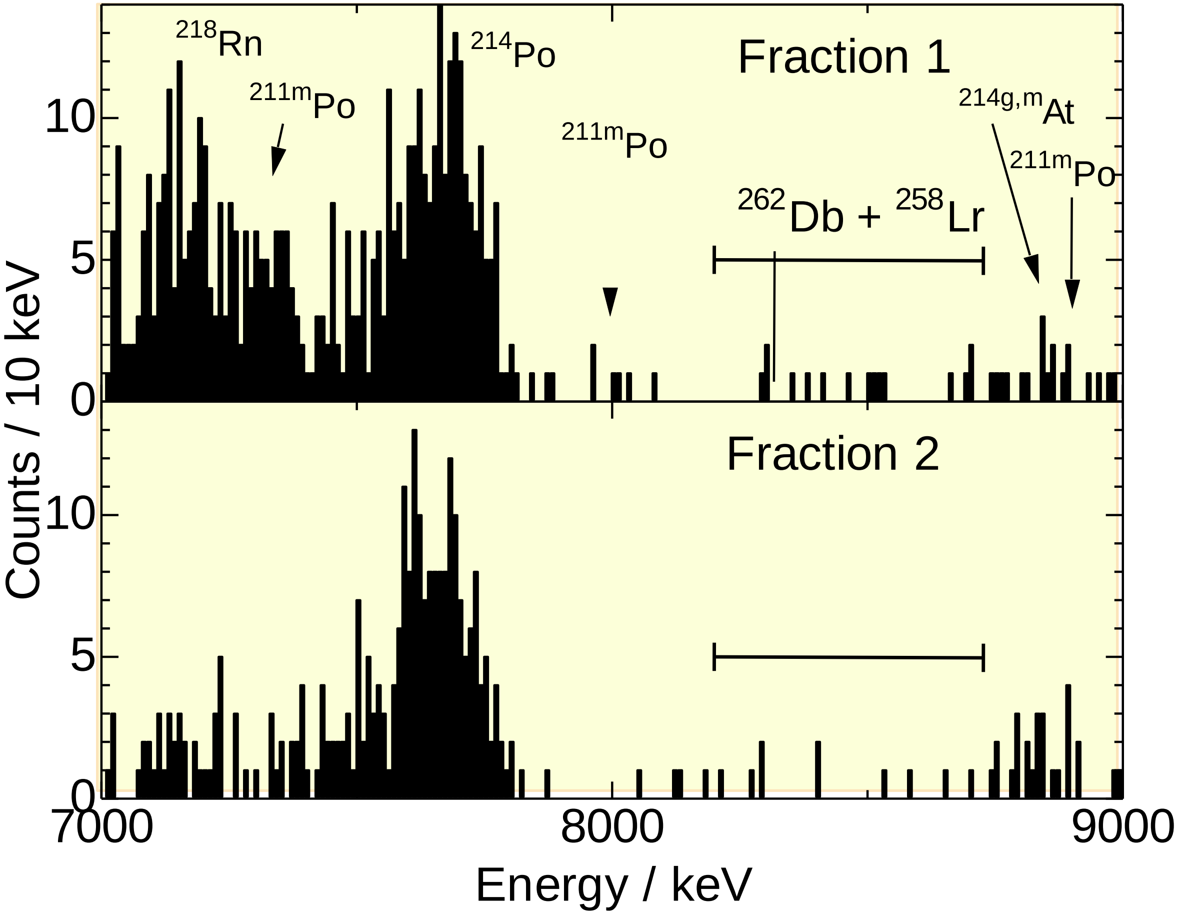


α-particle spectra

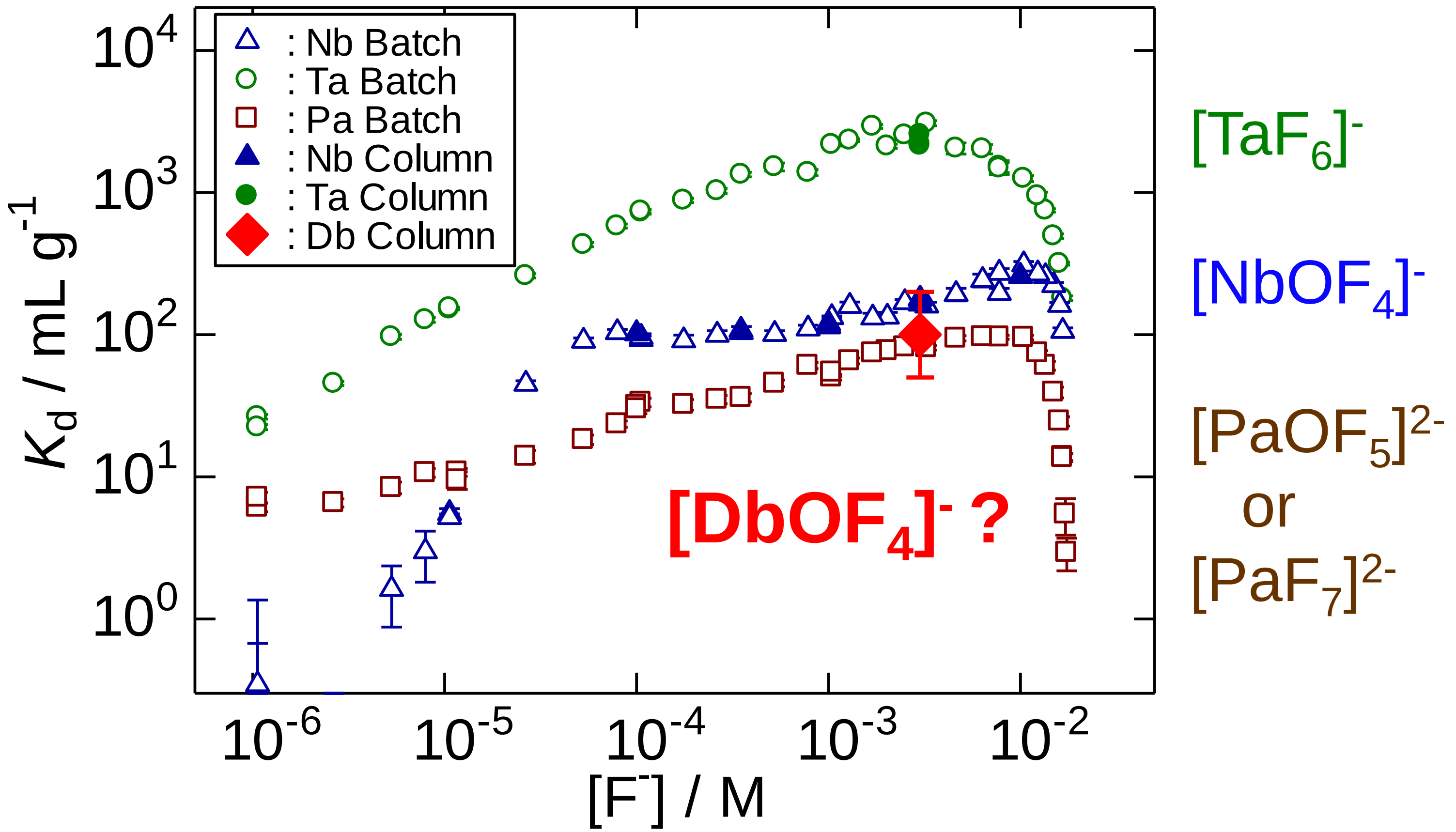
1222 cycles of the anion-exchange experiments

1st frac.: 0.31 M HF/0.10 M HNO_3 ([F^-] = 0.003 M): 9.7 events
2nd frac.: 0.015 M HF/6.0 M HNO_3 : 7.6 events





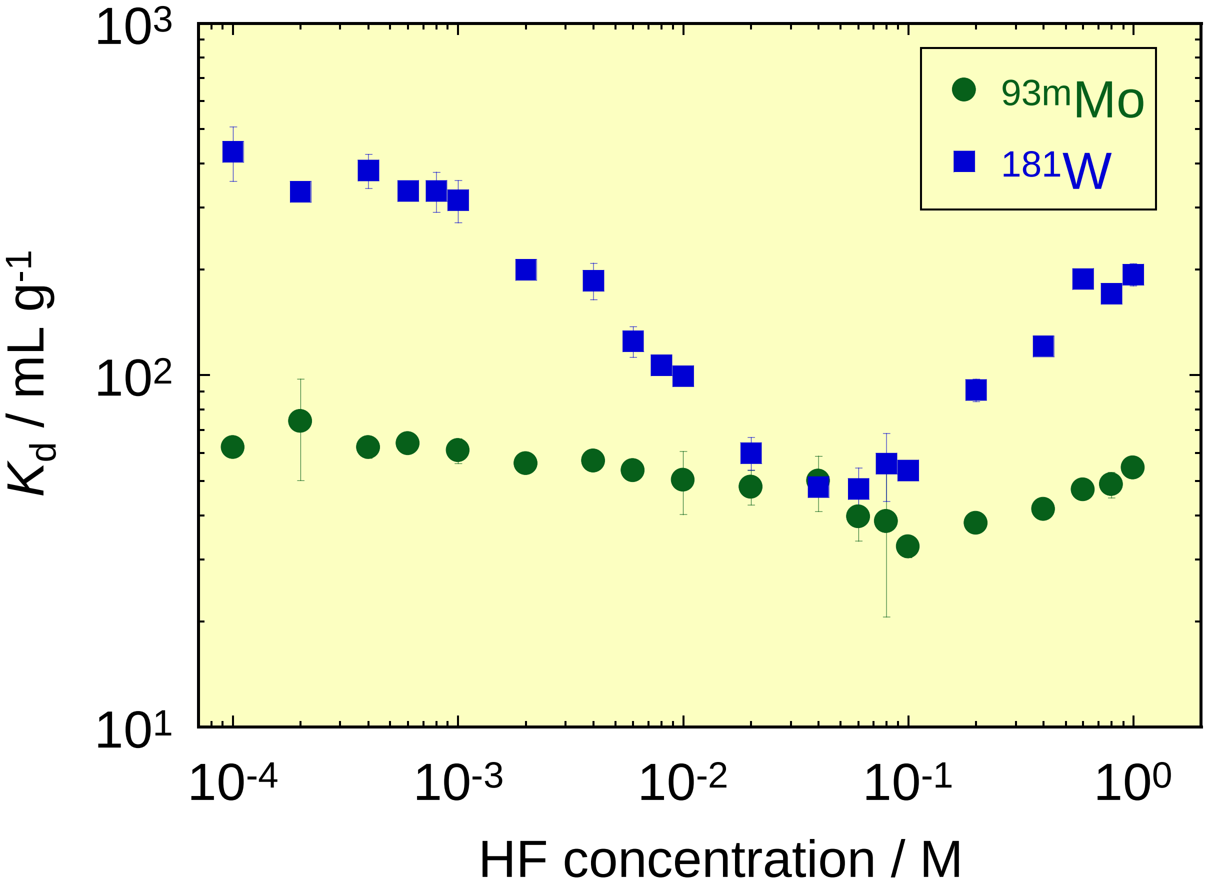
Anion-exchange behavior of Db and its lighter homologues



Y. Kasamatsu *et al*., Chem. Lett. **38**, 1084 (2009).

2-(3). Fluorido complex formation of Sg

Anion-exchange behavior of Mo and W
in 10^{-4} - 1 M HF/0.1 M HNO_3 at 70 ^{o}C



X. H. Liang *et al*., to be submitted.

3. Electrochemistry of the heaviest elements with single atoms

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

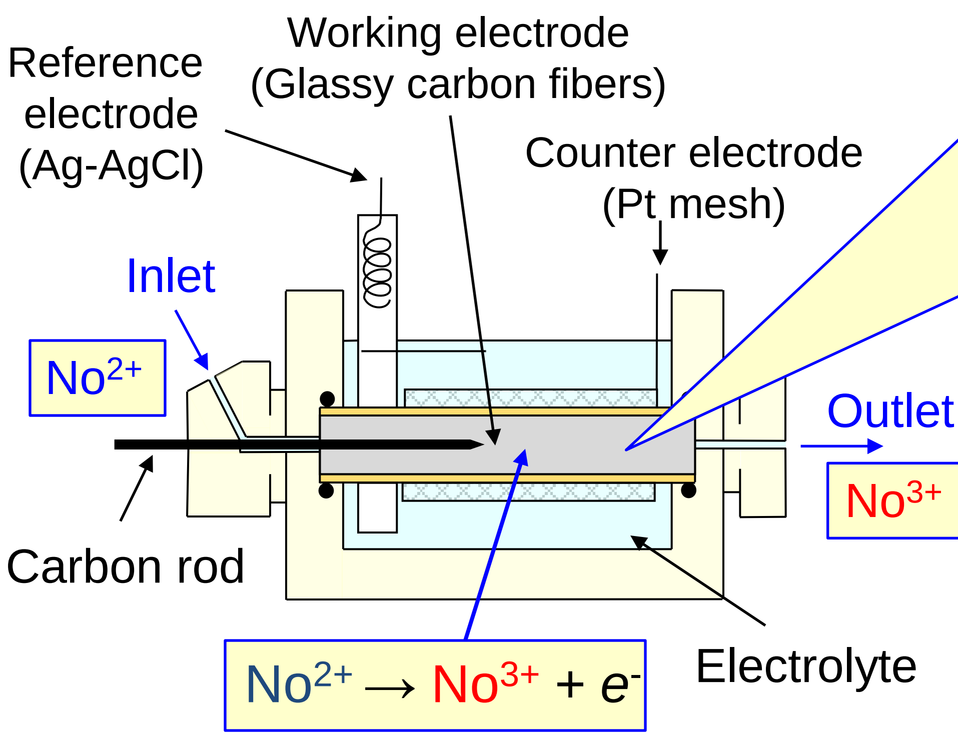
$^{248}Cm(^{12}C, 5n)^{255}No$ (3.1 min)

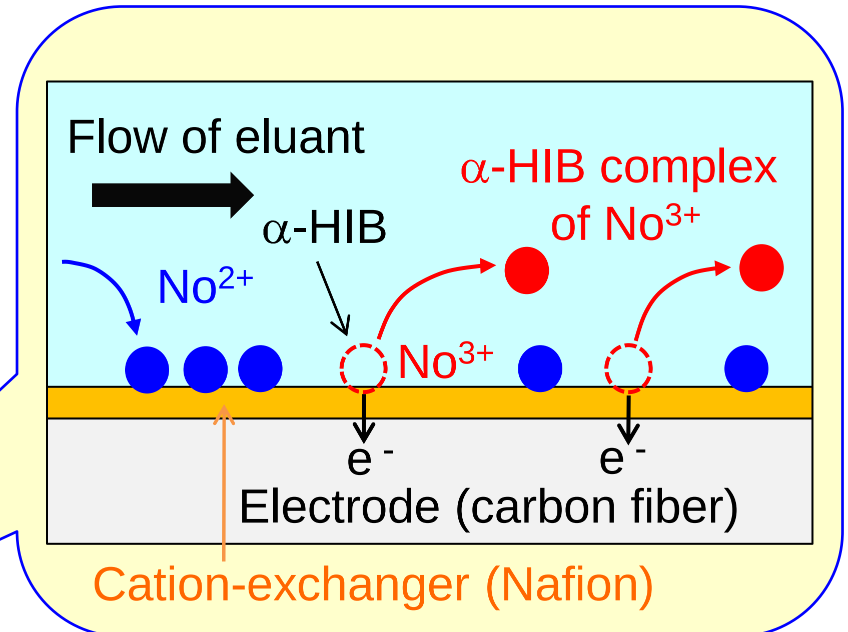
$^{248}Cm(^{11}B, 4n)^{255}Md$ (27 min)

JAEA Tandem Accelerator

Electrochemistry apparatus

Flow electrolytic column with cation-exchanger





Oxidation of No^{2+}

Complex formation of No^{3+}
with α-HIB

A. Toyoshima *et al*., Radiochim. Acta **96**, 323-326 (2008).

Experimental procedure: Oxidation of No

JAEA tandem accelerator

$^{248}Cm(^{12}C, 5n)^{255}No$

gas-jet transport

2) 0.1 M α-HIB (pH3.9)

1) Collection for 10 min

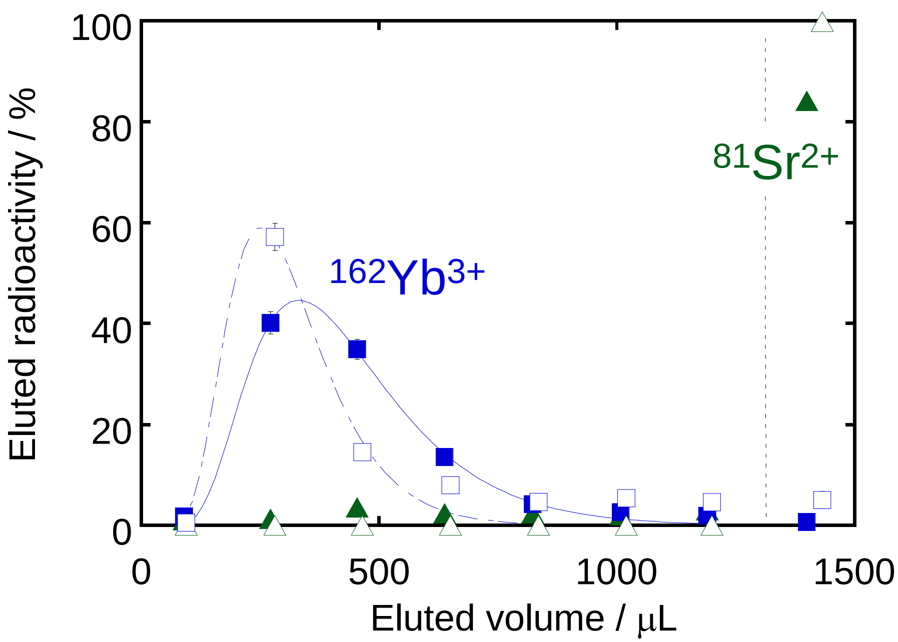
collection and dissolution

$Gd(^{12}C, xn)^{162}Yb^{3+}$ (18.9 min)

$Ge(^{12}C, xn)^{81}Sr^{2+}$ (22.2 min)

3) 3.0 M HCl

Flow electrolytic-column (500 μL)
(chemically modified electrode)
Applied potentials : 0.2 - 1.2 V

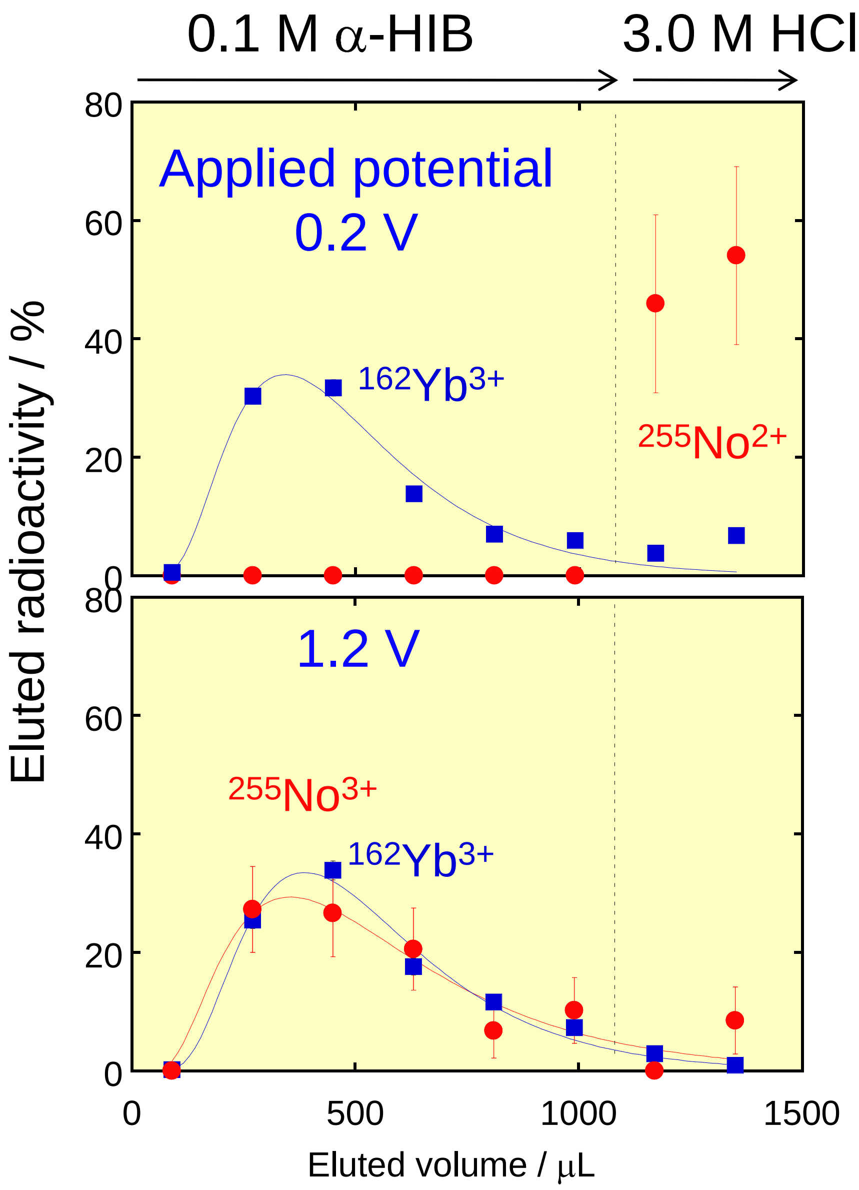


No^{3+} (Yb^{3+}) No^{2+} (Sr^{2+})

(6 fractions) (2 fractions)

α-source preparation and
α-particle measurements

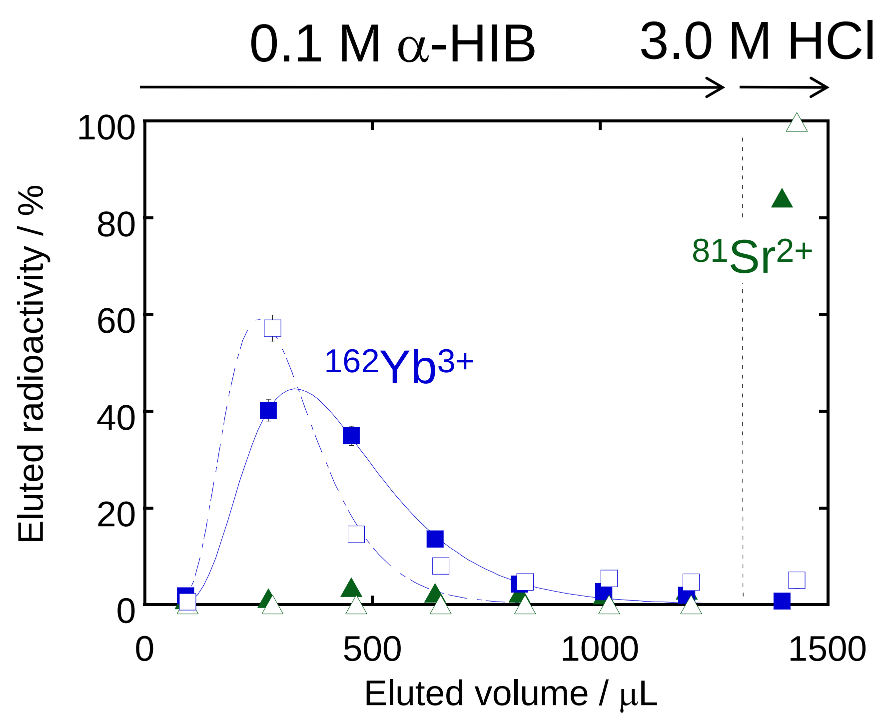
Oxidation of No^{2+}



$$No^{3+} + e^{-} \rightleftarrows No^{2+}$$

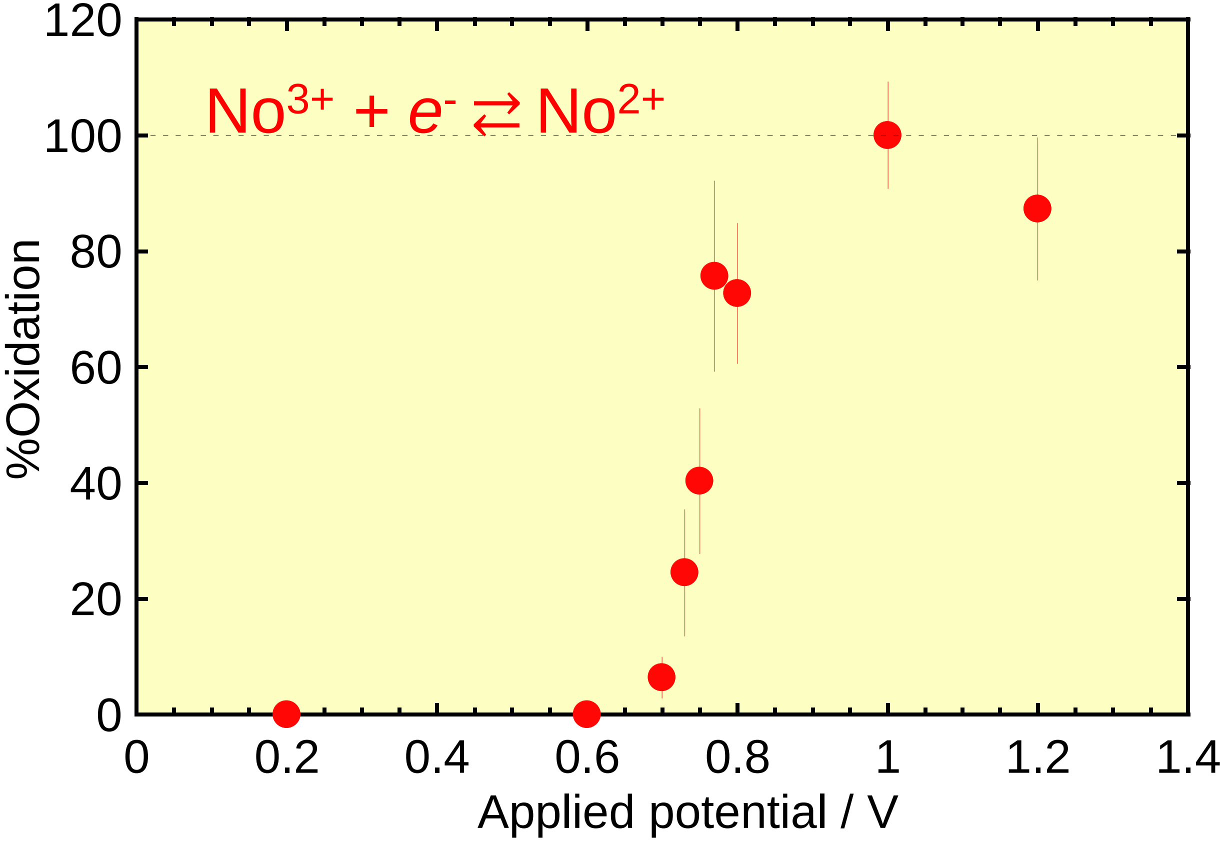
the number of ^{255}No atoms
≈ 100 atoms (10^{-21} M)

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



Variation of oxidation rates

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



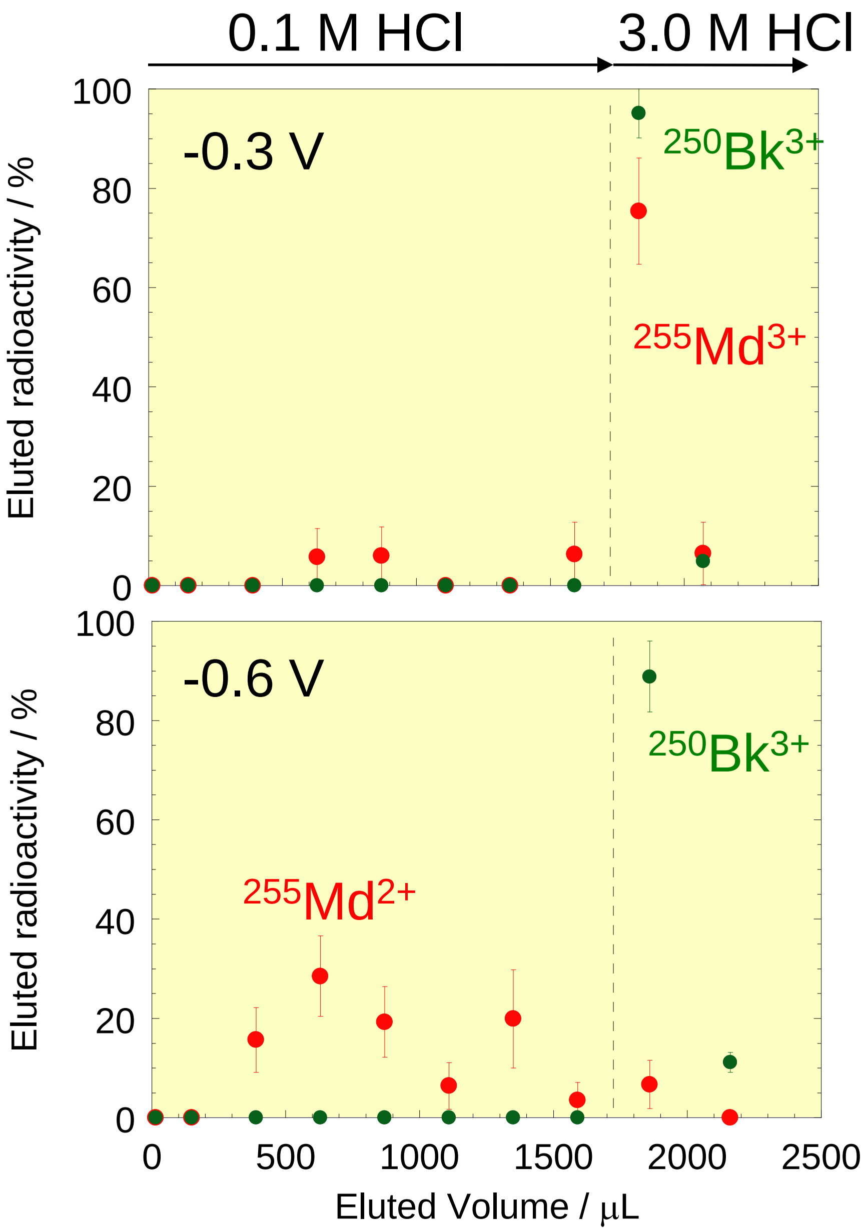
$$E = E_0 + \frac{RT}{nF} \ln \frac{[No^{3+}]}{[No^{2+}]}$$

$E = E_0$
at $[No^{3+}] = [No^{2+}]$

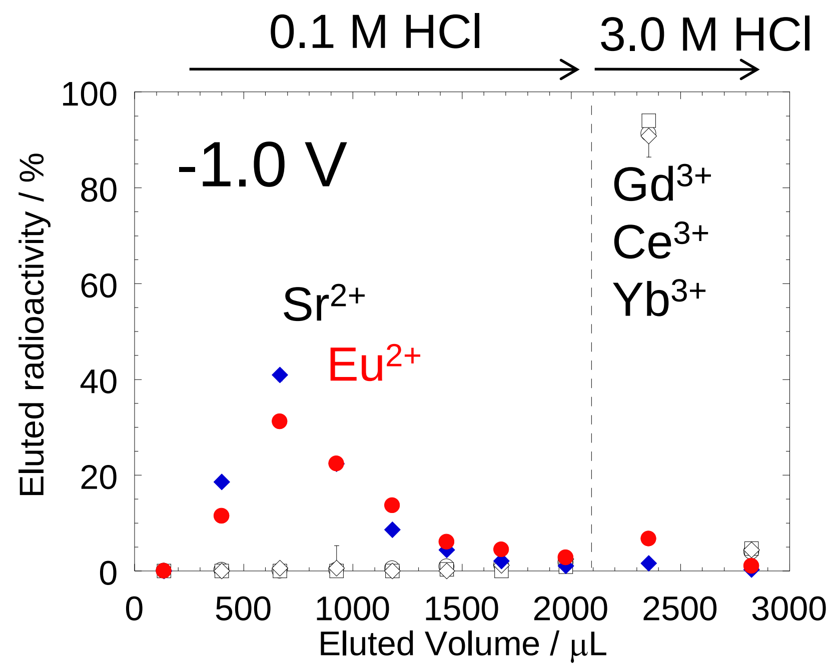
$E_0 \approx 0.75$ V

A. Toyoshima *et al*., J. Am. Chem. Soc. **131**, 9180 (2009).

Reduction of Md^{3+}



Elution behavior of Sr^{2+}, Eu^{2+}, Gd^{3+}, Ce^{3+}, and Yb^{3+} measured in a separate off-line experiment



Reduction of Md^{3+} to Md^{2+}

A. Toyoshima *et al.*, to be submitted.

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

4. Perspective on aqueous chemistry

1. Sg: Production of ^{265}Sg ($T_{1/2} \approx$ 15 s) at RIKEN
   → Presentation by Hiro Haba
   Fluorido complex formation with AIDA-II
   Solvent extraction with SISAK+GARIS at RIKEN
   Reduction of Sg^{6+} with electrochemistry

2. Electrochemical approach
   Ionic radius of No^{3+}

3. Hs: Electrodeposition by the Mainz group

4. Development of new apparatuses:
   MicroSISAK, Electrodeposition, Electrochemical chromatography

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

Univ. Tsukuba – K. Sueki

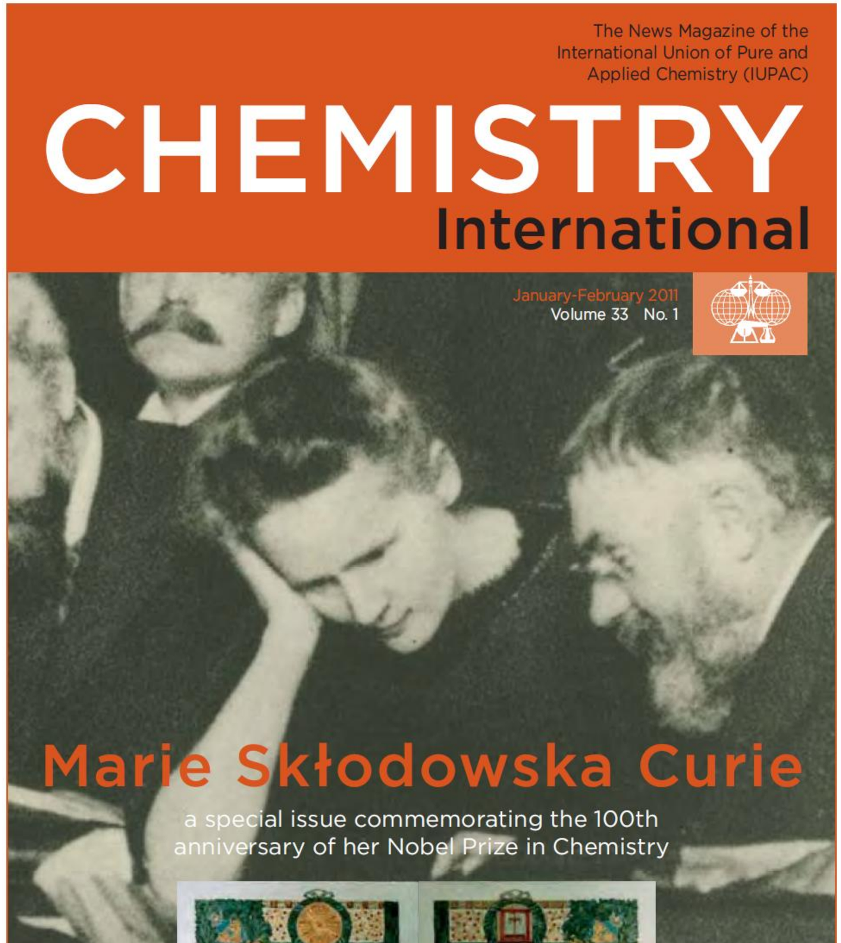
Kanazawa Univ. – W. Sato and A. Yokoyama

GSI - Ch. E. Düllmann and V. Pershina

Univ. Mainz - J. V. Kratz

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

Thank you for your attention!

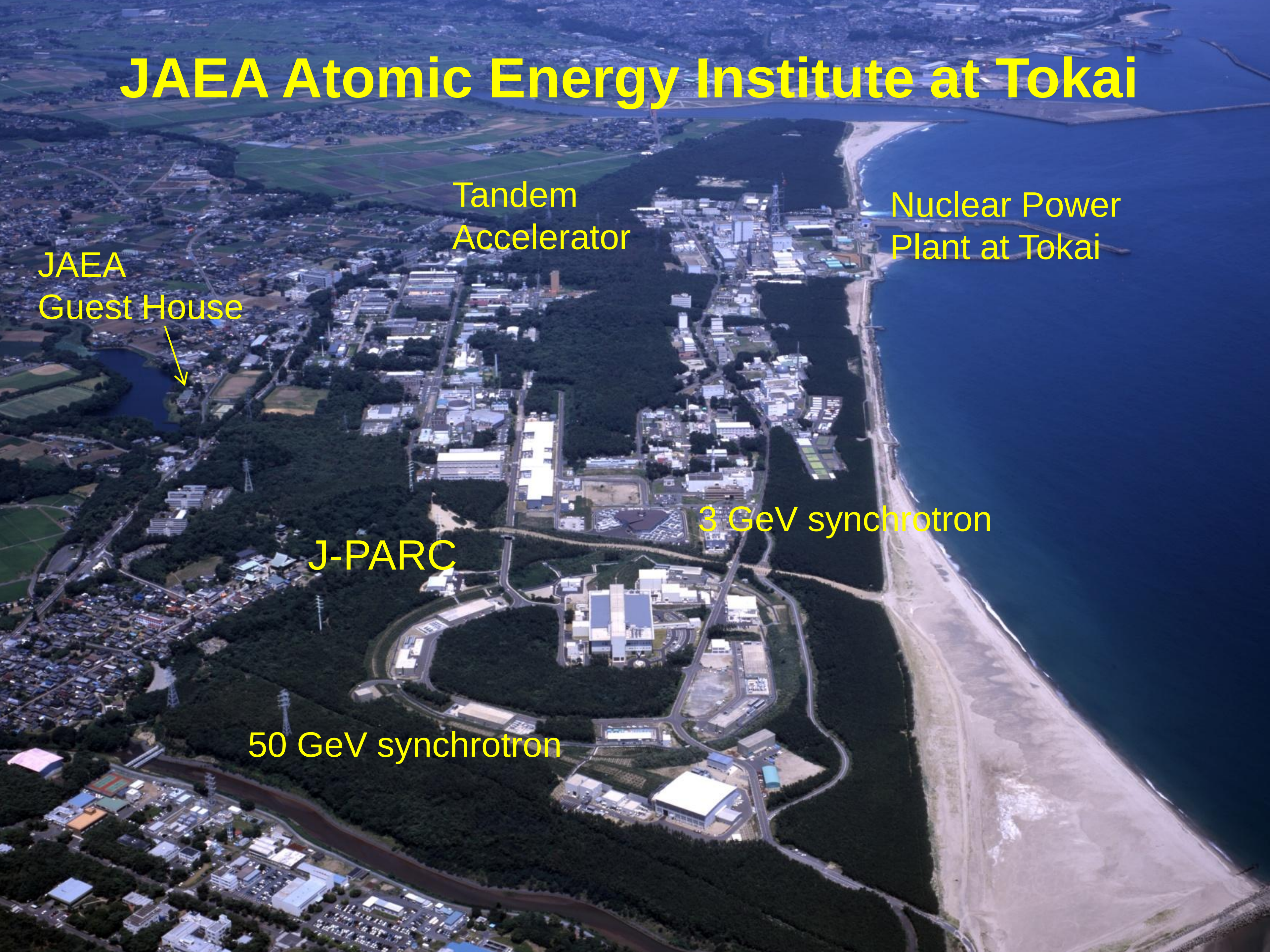


Thank you for your cooperation

Fukushima Daiichi

Tsunami

JAEA Atomic Energy Institute at Tokai



JAEA Guest House

Highway around the Mito area

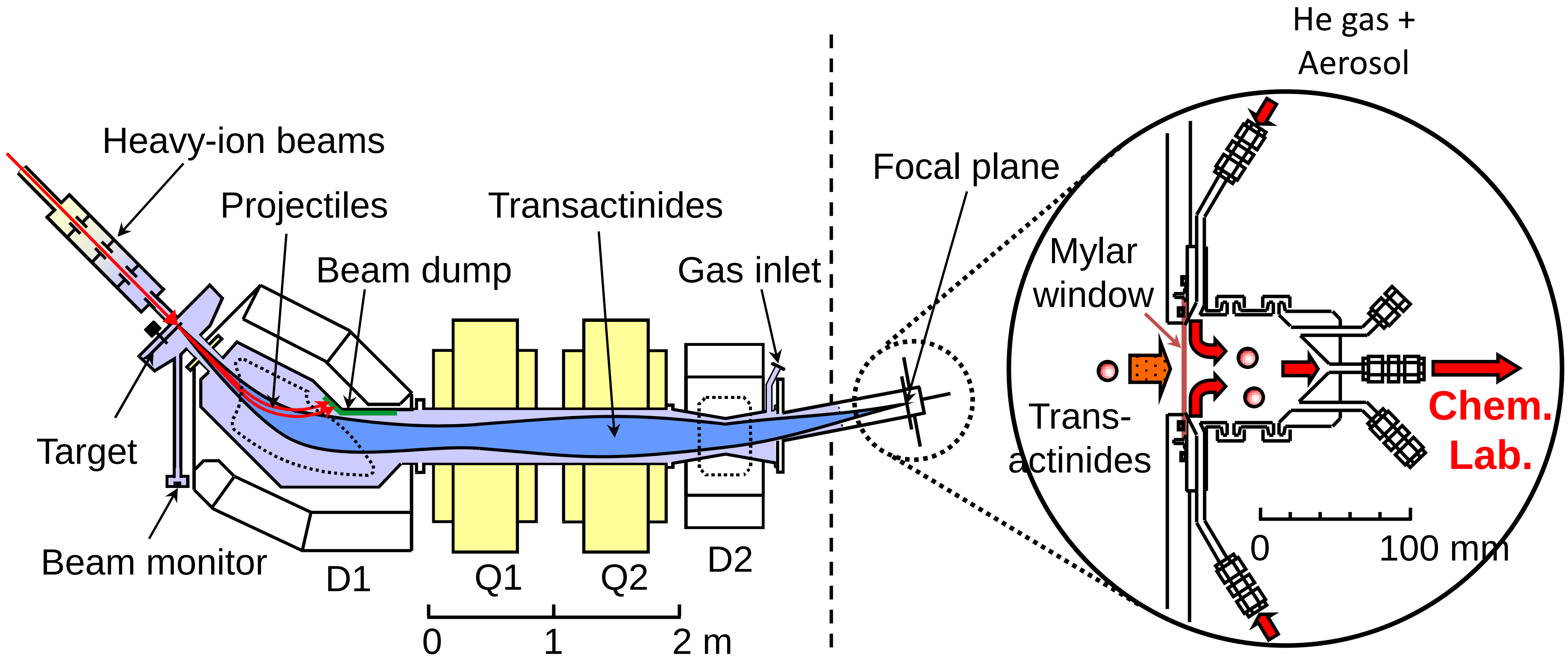
16:30 on March 11

3月11日 16:30頃

3月17日 17:00頃

17:00 on March 17

RIKEN-GARIS + Gas-jet System



H. Haba *et al*. Chem. Lett. **38**, 426 (2009).

Contraction of ionic radius