Anion-exchange experiment of **Db** with AIDA-II

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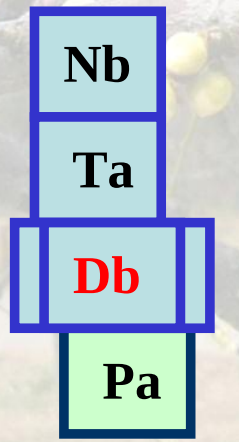

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CHE7

Contents

Introduction

Low production rates & Short half-lives

→ **one-atom-at-a-time chemistry**

Multistep process（Chromatography）

Comparison with the lighter homologues

	1												13	14	15	16	17	18
1	1 H	2																2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
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
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
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
6	55 Cs	56 Ba	Ln	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
7	87 Fr	88 Ra	An	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112	113	114	115	116	117	118

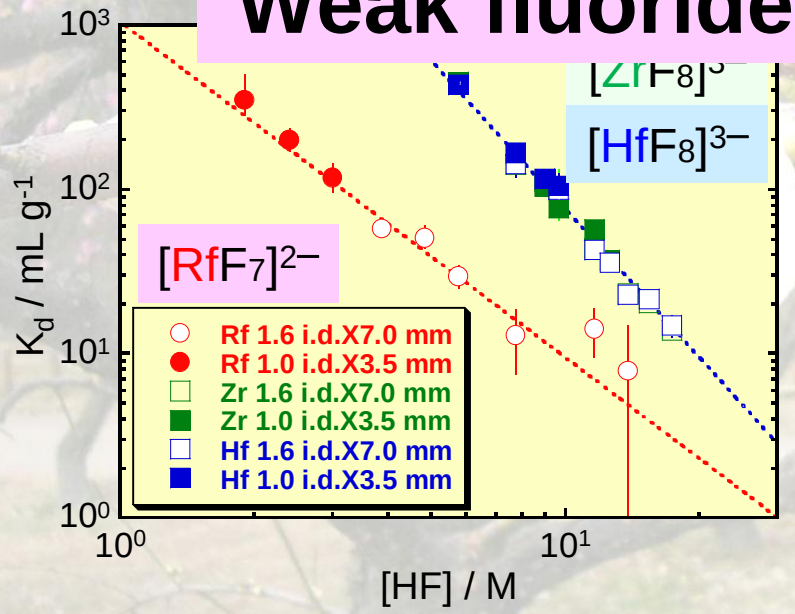
57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Fluoride complexation of Rf

Weak fluoride complexation of Rf

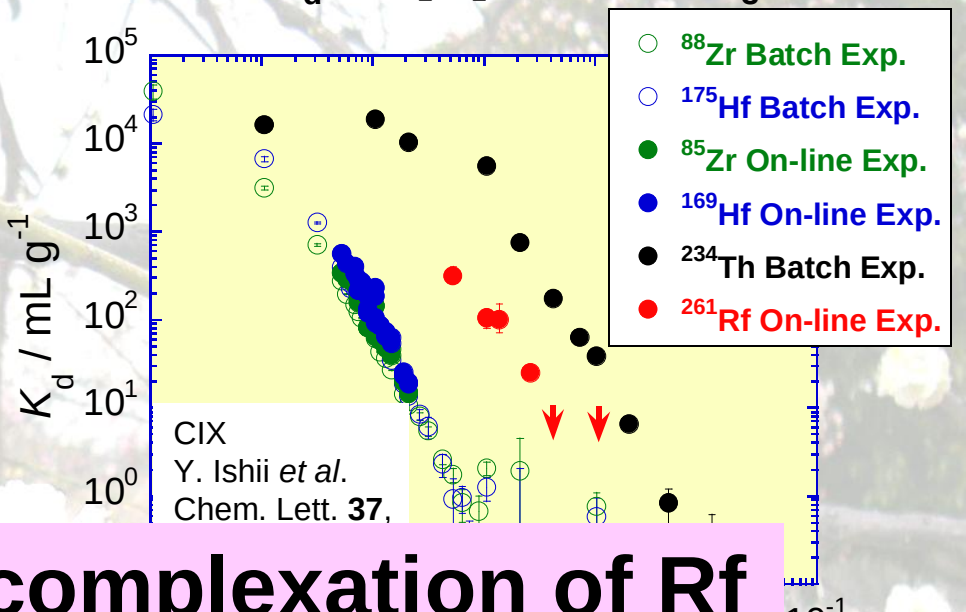
K_d vs. [HF]

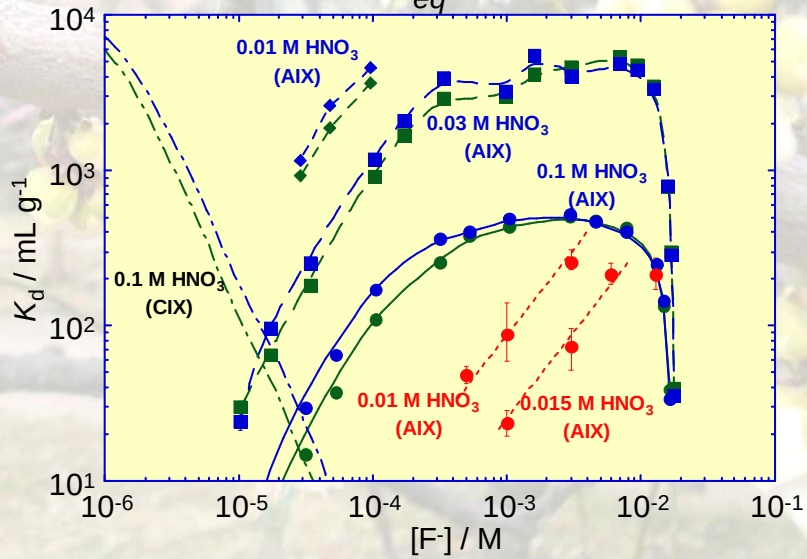
AIX



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

K_d vs. [F$^-$] in HF/HNO$_3$





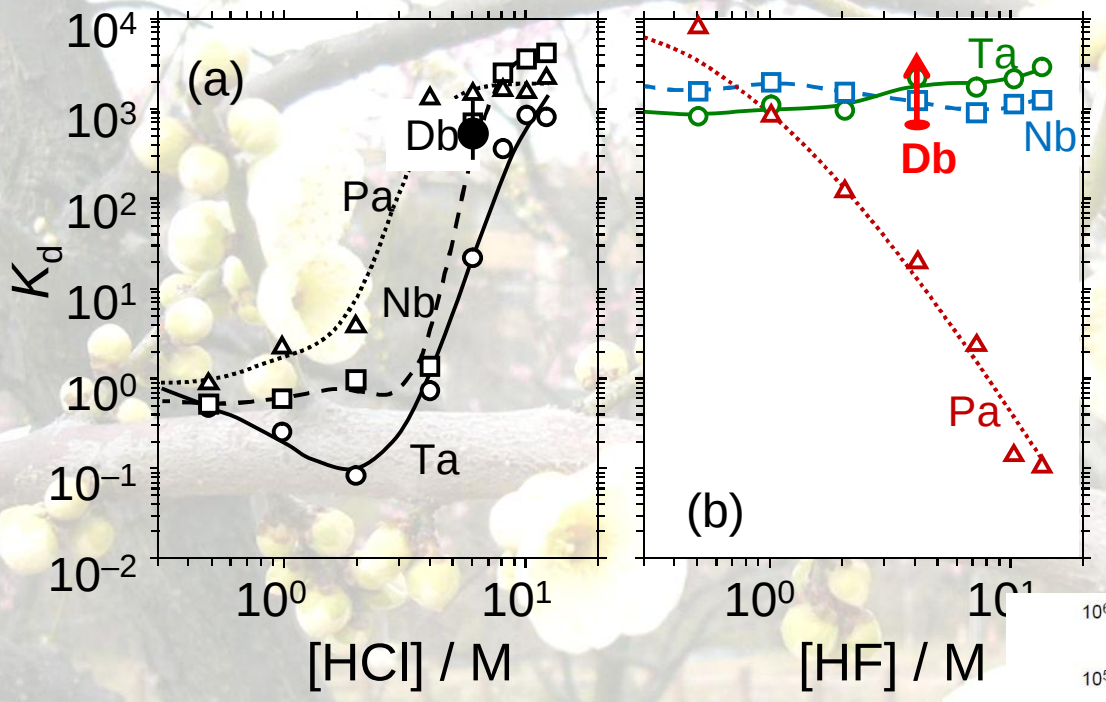
AIX

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

Solution chemistry of Db
（Fluoride complexation）

^{262}Db $T_{1/2}$ = 34s

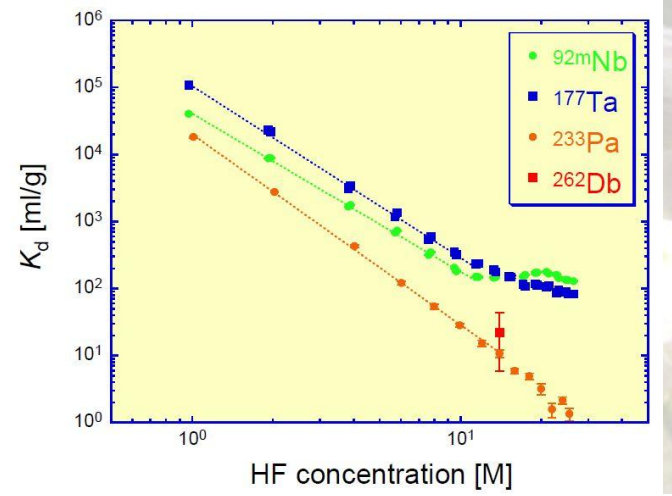
Aliphatic amines – HCl, HF



W. Paulus *et al*. Radiochim. Acta **84**, 69 (1999).

Our previous work: anion-exchange of Db in 13.9 M HF→ **Nb = Ta > Db ≧ Pa**

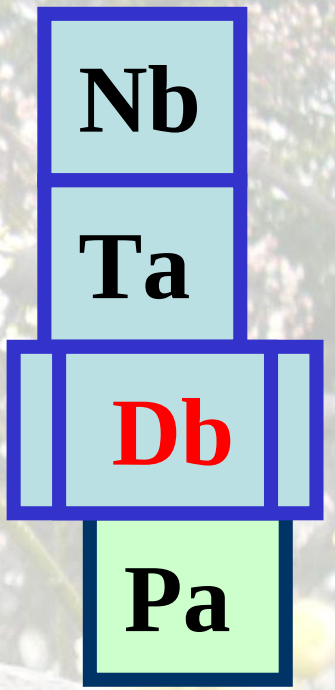
K. Tsukada *et al*. Radiochim. Acta **97**, 83 (2009).



Purpose

Observation of the fluoride complexation of **Db** in diluted fluoride ion concentration solution.

Systematic study on **Db**
as a function of concentration of the ligand ion and that of the counter ion



Chemical Properties of Db

Fluoride complexation, Relativistic effects, ・・・

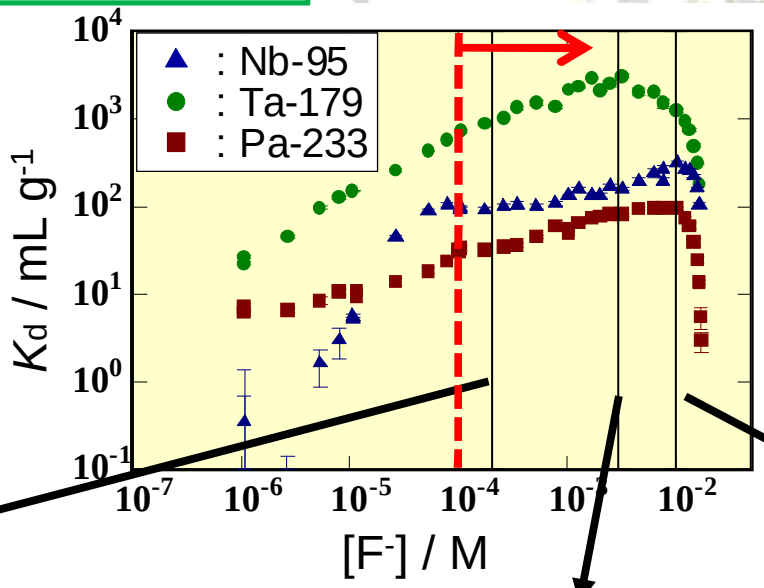
Present work

Anion-exchange chromatography of Nb, Ta, Pa, and **Db** in **HF/HNO_3** solutions

with the newly developed rapid ion-exchange and alpha detection apparatus **AIDA-II !!**

Batch experiment

Variations of the K_d values as functions of $[F^-]$ and $[NO_3^-]$

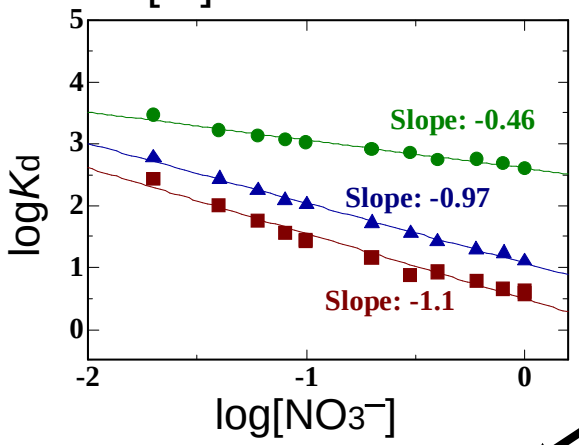


In HF/HNO_3

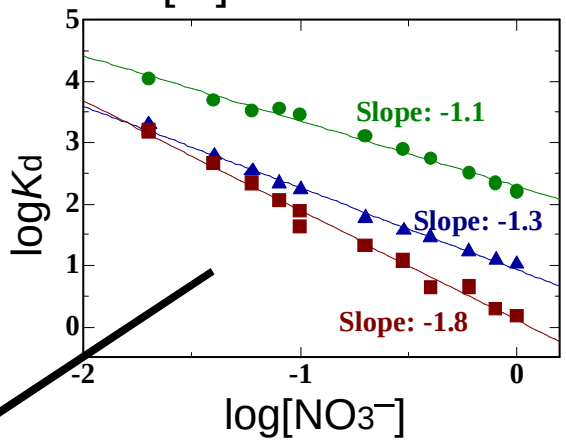
$[HNO_3]$ = 0.1 M

Y. Kasamatsu et al., J. Nucl. Radiochem. Sci. **8**, 69 (2007).

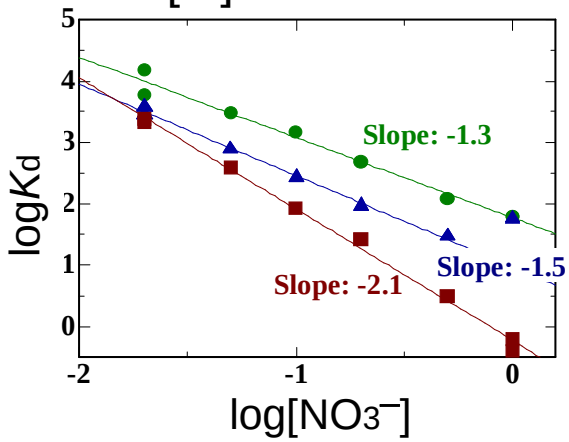
[F-] = 0.0002 M



[F-] = 0.003 M



[F-] = 0.01 M



TaF_6^-, $NbOF_4^-$, PaF_7^{2-}, $PaOF_5^{2-}$, ,,,

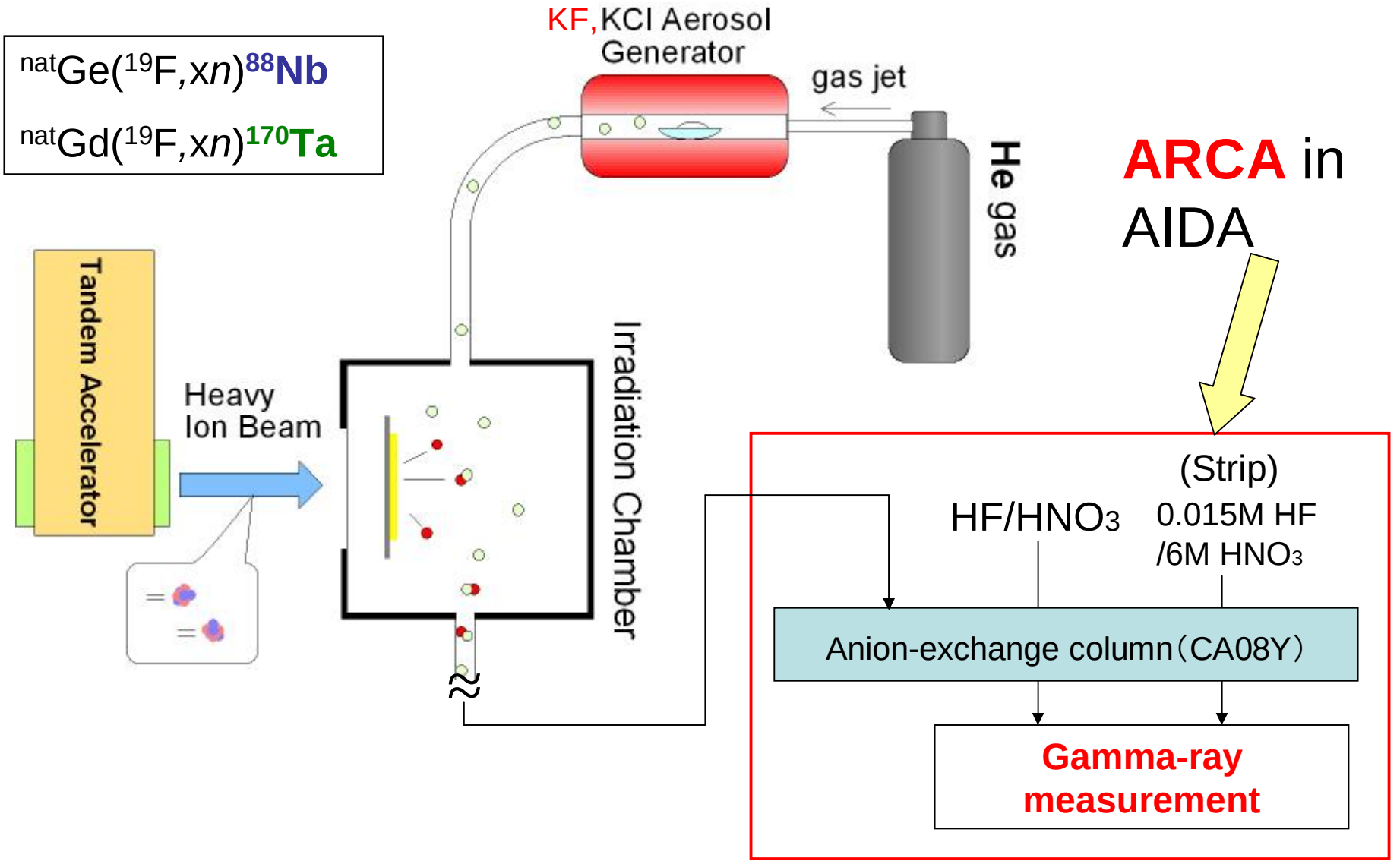
DbF_7^{2-}?, DbF_6^-? or $DbOF_5^{2-}$?, $DbOF_4^-$? or …?

Y. Kasamatsu et al., J. Radioanal. Nucl. Chem. **279**, 371 (2009).

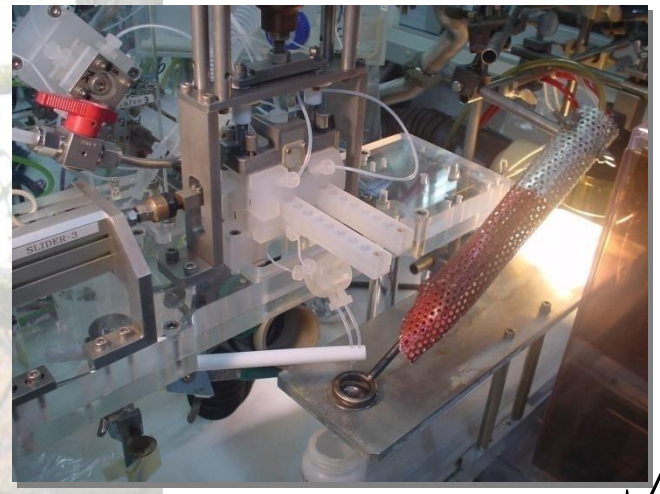
On-line Experiment (Nb, Ta)

$^{nat}Ge(^{19}F,xn)^{88}Nb$

$^{nat}Gd(^{19}F,xn)^{170}Ta$



ARCA



He/KCl gas-jet

Schädel *et al.* Radiochim. Acta **48**, 171 (1989).

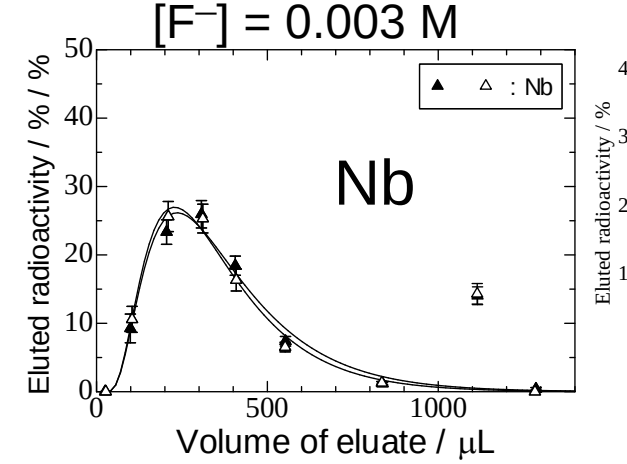
Pulse motors

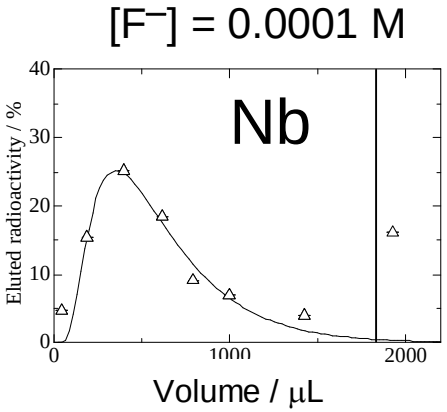
Air cylinder

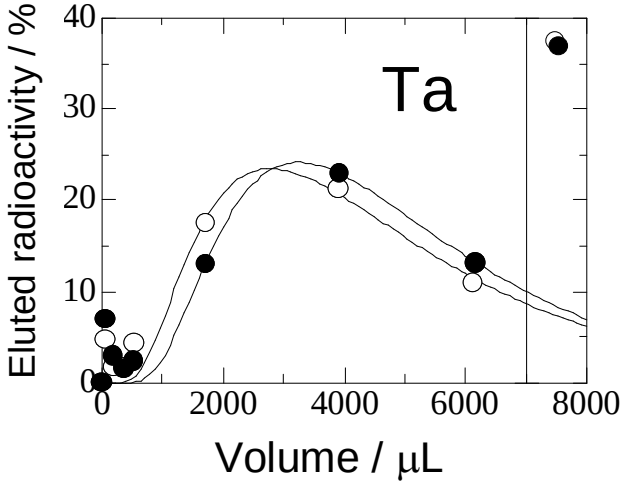
Eluent bottles

Micro-columns ϕ1 mm × 3.5 mm

Elution curves of Nb and Ta

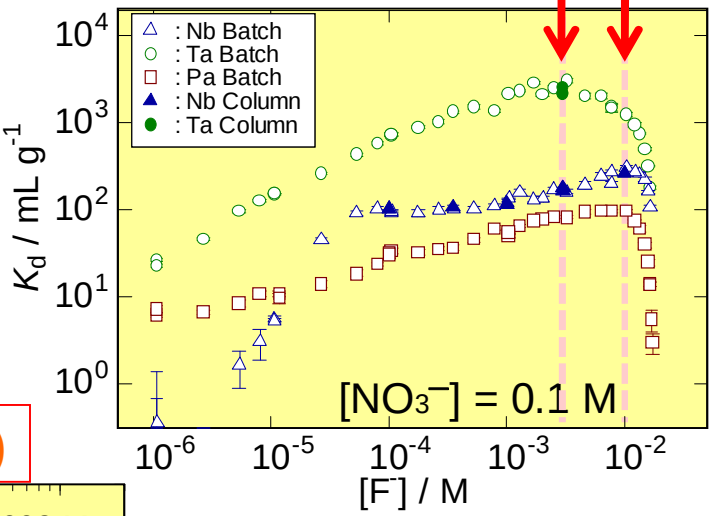




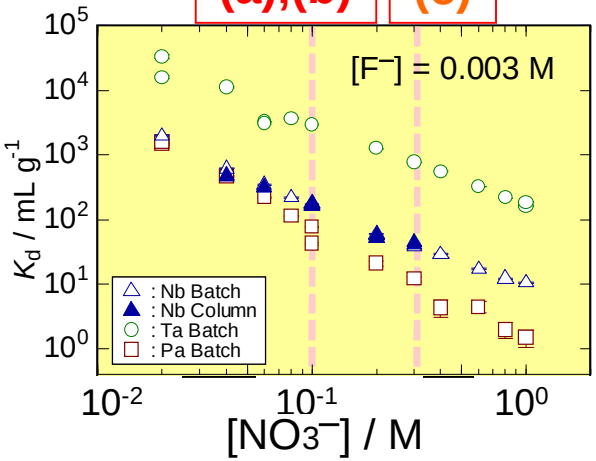


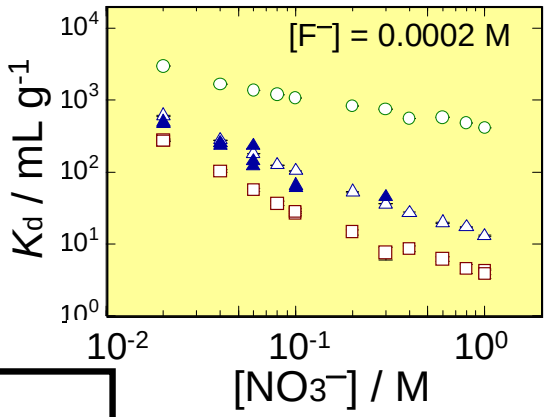
(a), (c)

(b)



(a),(b) (c)





K_d by column method = K_d by batch method

⇨ Fast kinetics (equilibrated)

For Db experiment

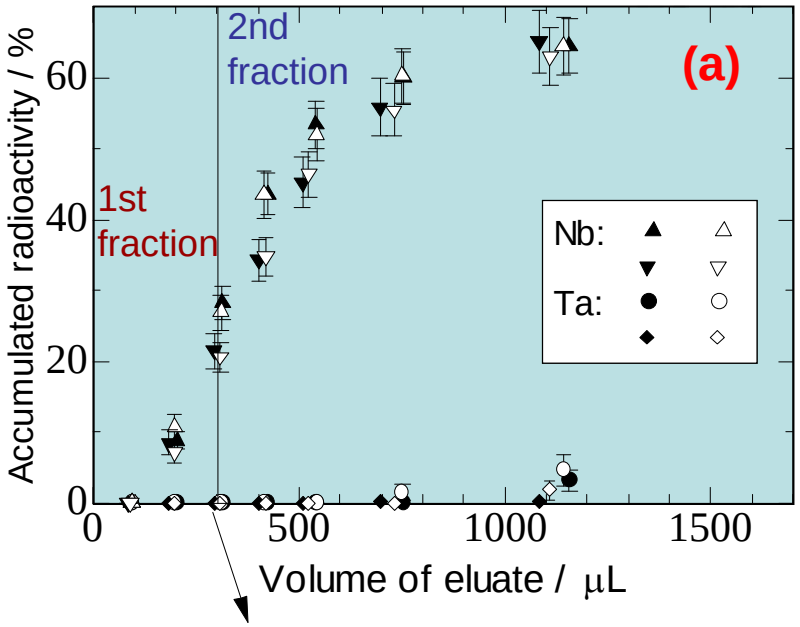
(c) 0.89 M HF/0.30 M HNO_3 (Eluent)
$[F^-]$ = 0.003 M

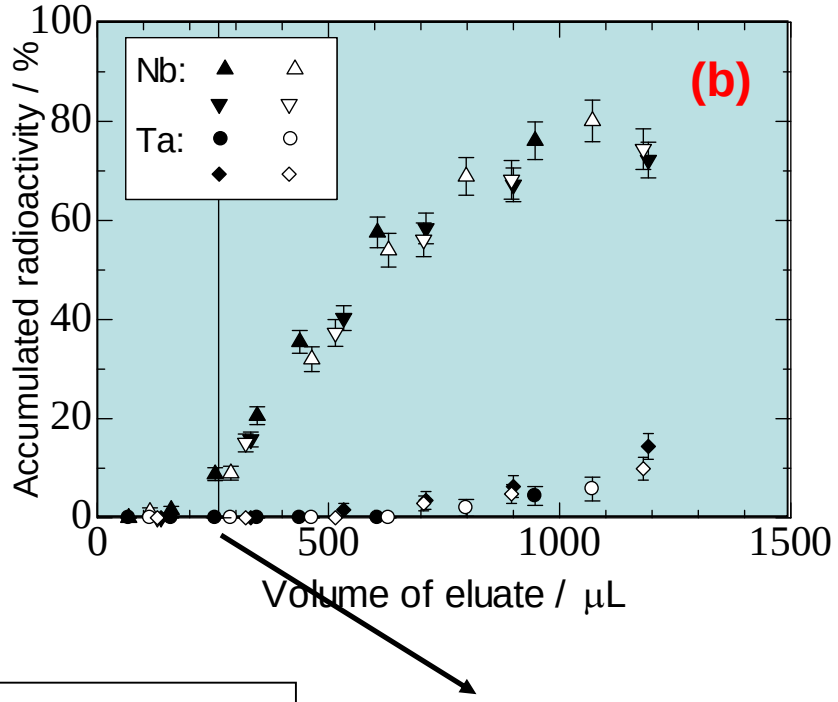
Cumrative elution curves of Nb and Ta

(a) 0.31 M HF/0.10 M HNO_3 (Eluent)
$[F^-]$ = 0.003 M

(b) 1.7 M HF/0.10 M HNO_3 (Eluent)
$[F^-]$ = 0.01 M

2^{nd} solution: 0.015 M HF/6.0 M HNO_3 (For Strip)





Condition for Db
1st : **300** μL
2nd : 290 μL

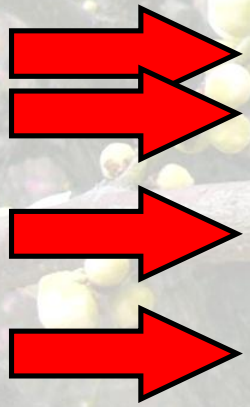
%ads
Nb : 76%
Ta : >99%

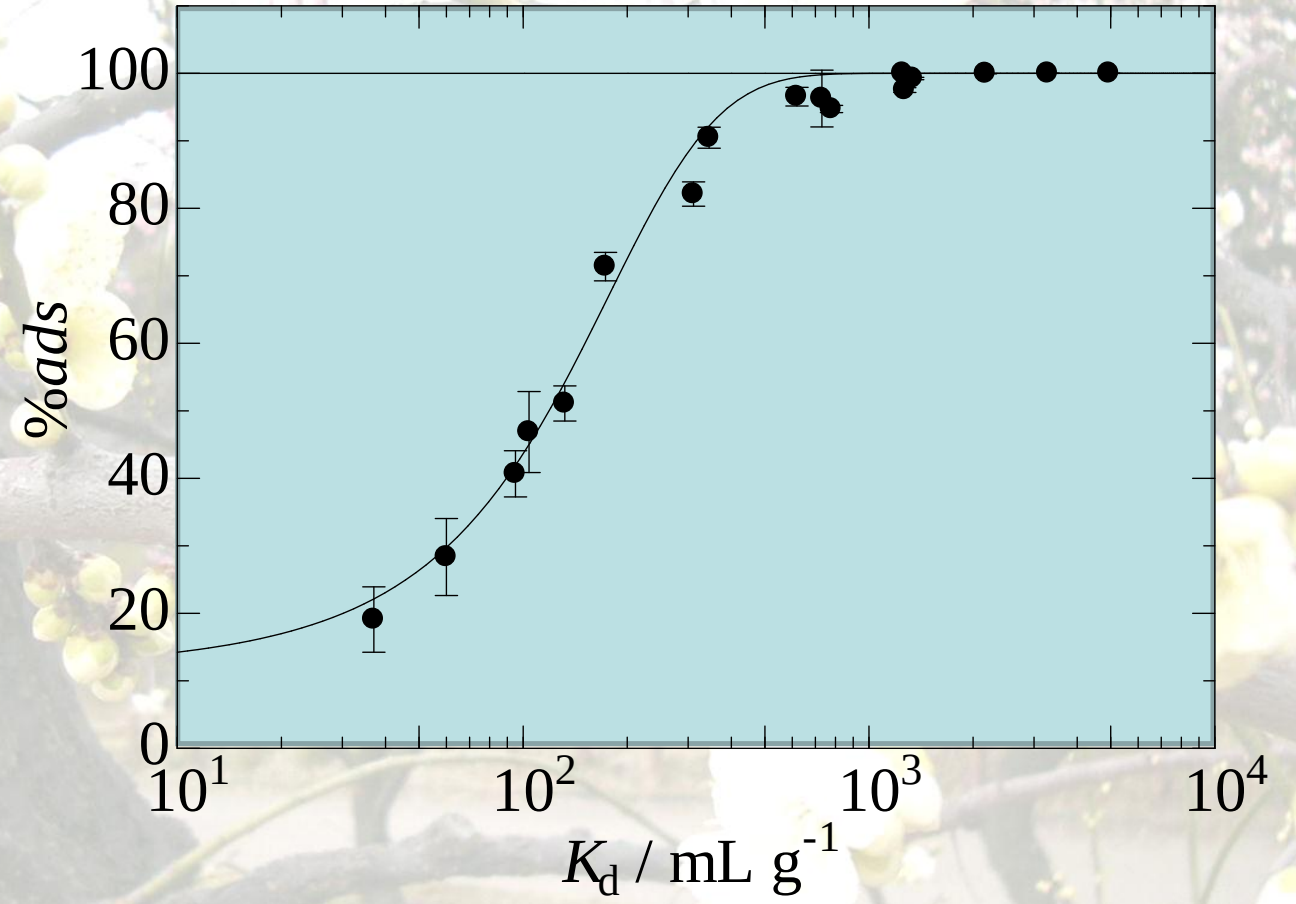
$$\%ads = \frac{100 \times A_2}{A_1 + A_2}$$

Nb : 90%
Ta : >99%

Estimation of the K_d value of Db

Db??

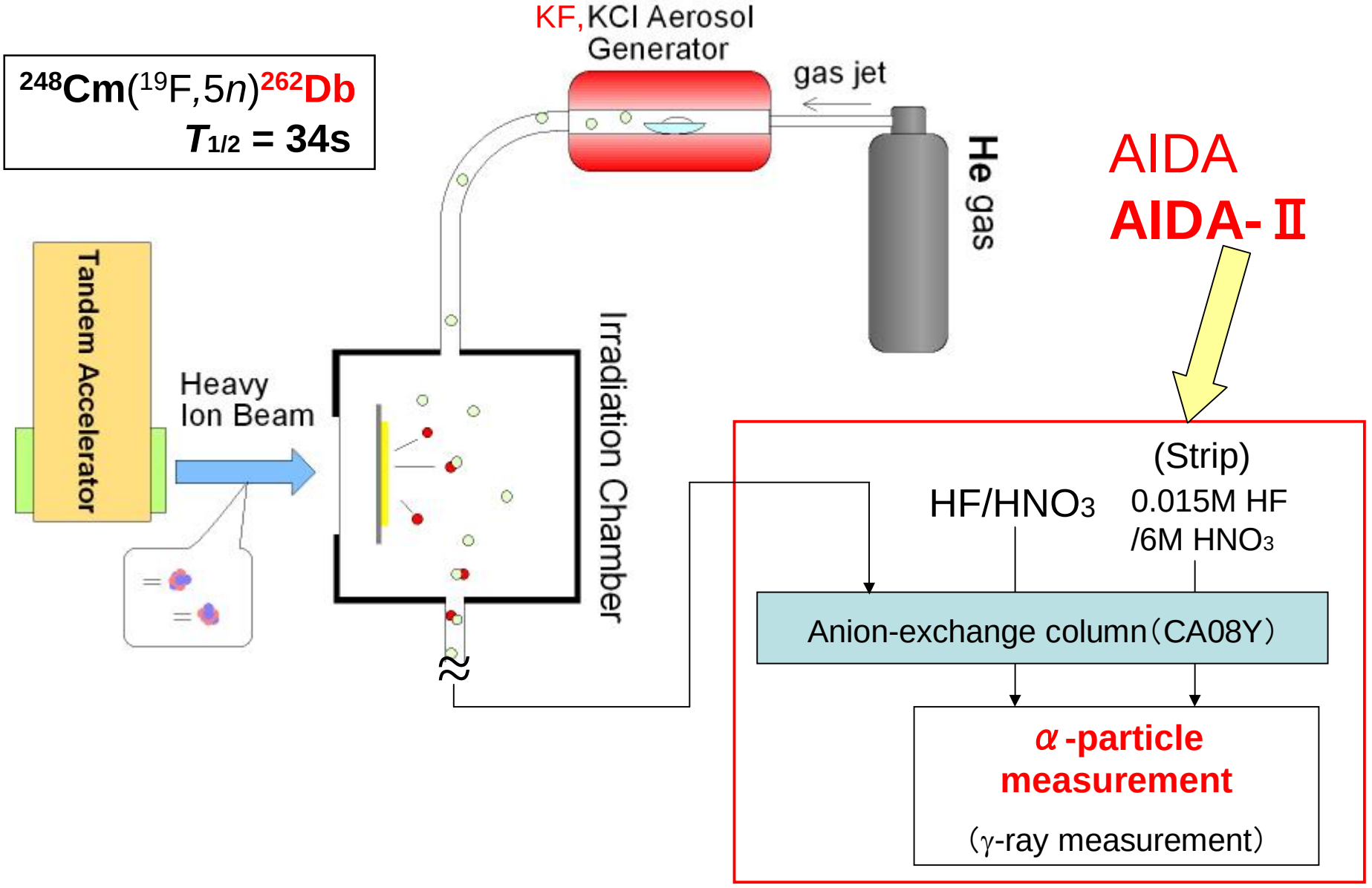




On-line experiment (Db)

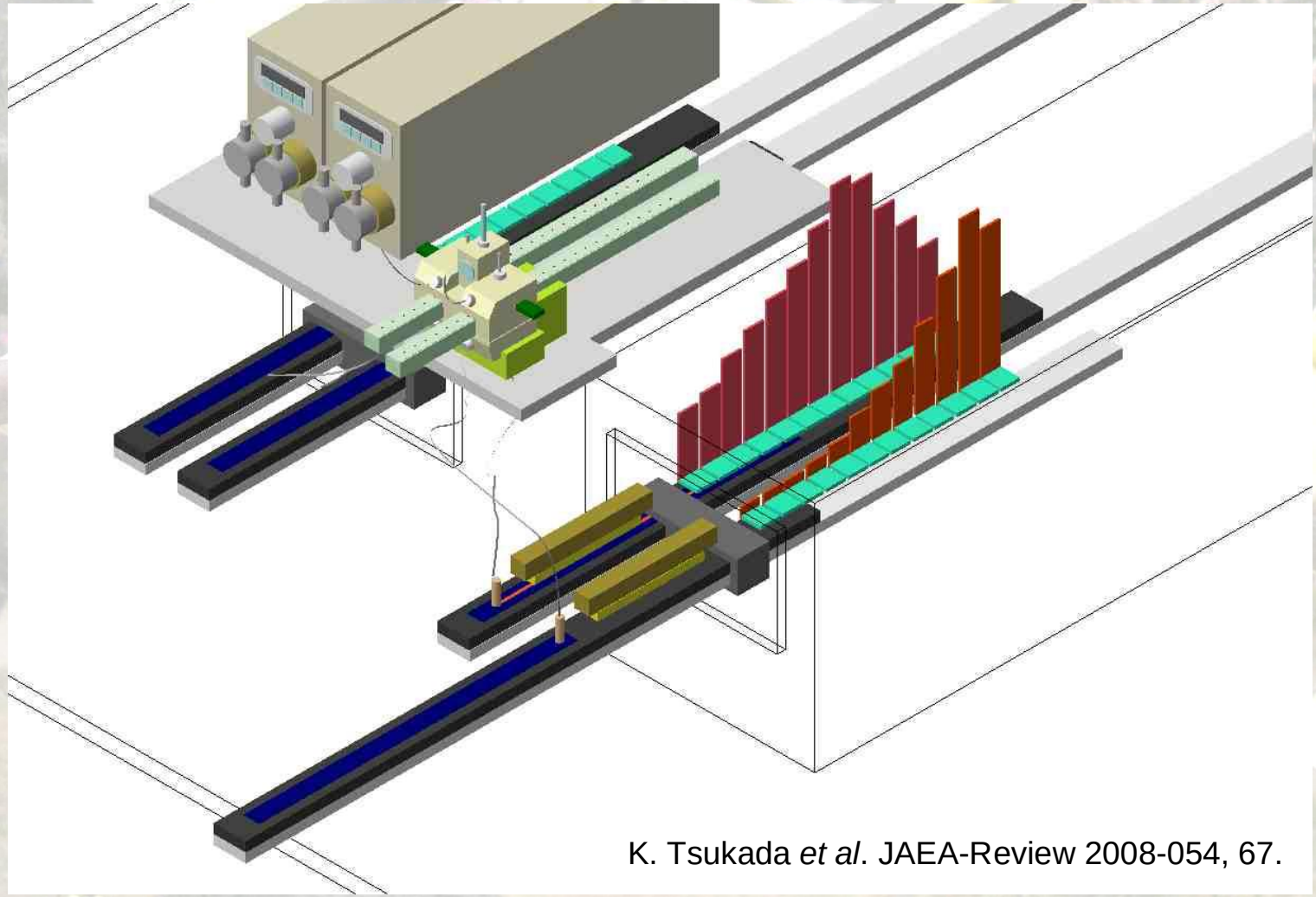
$^{248}Cm(^{19}F,5n)^{262}Db$

$T_{1/2}$ = 34s



AIDA-Ⅱ

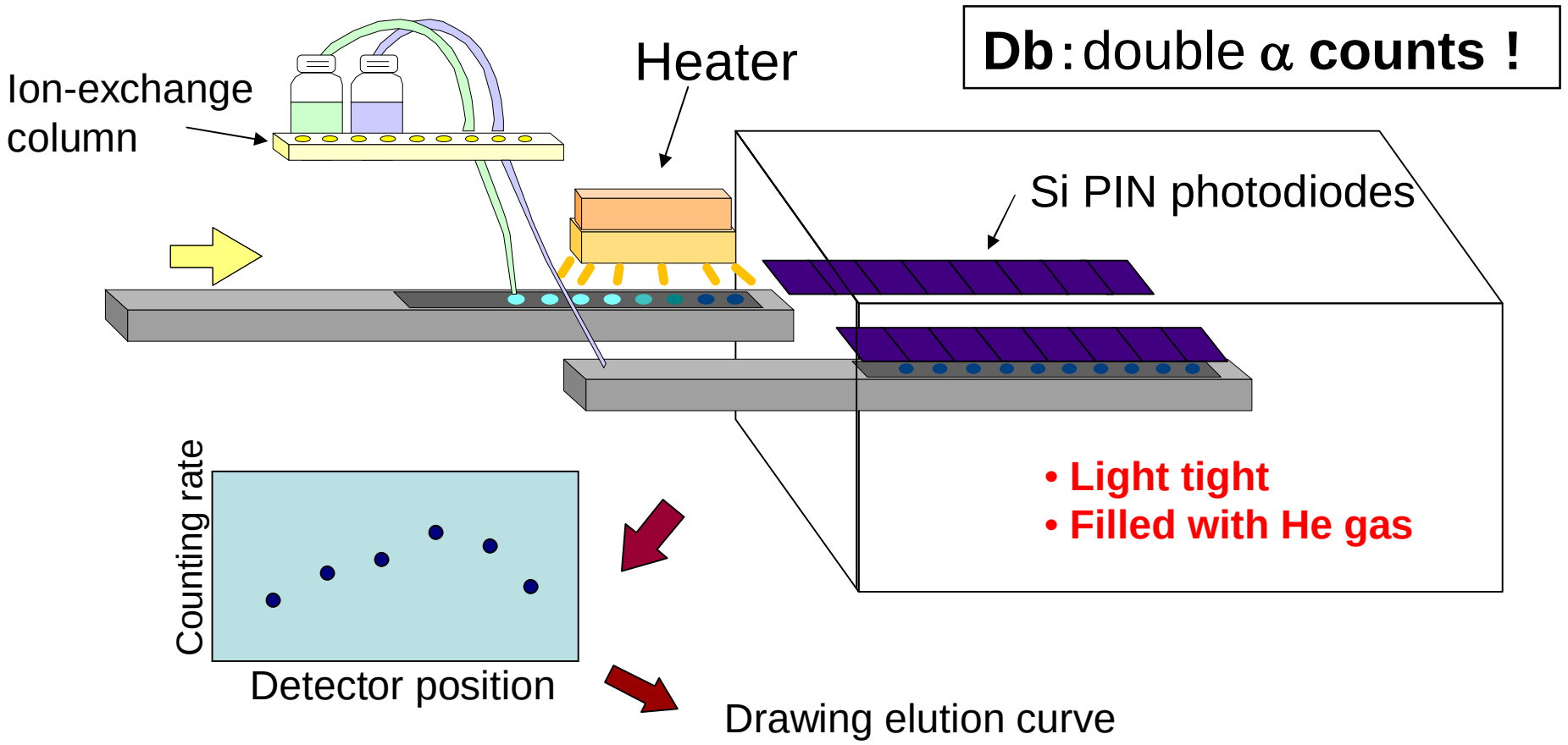
ARCA part is the same as that in the Nb and Ta experiment (AIDA).
Equipment of the alpha-particle detection was improved.



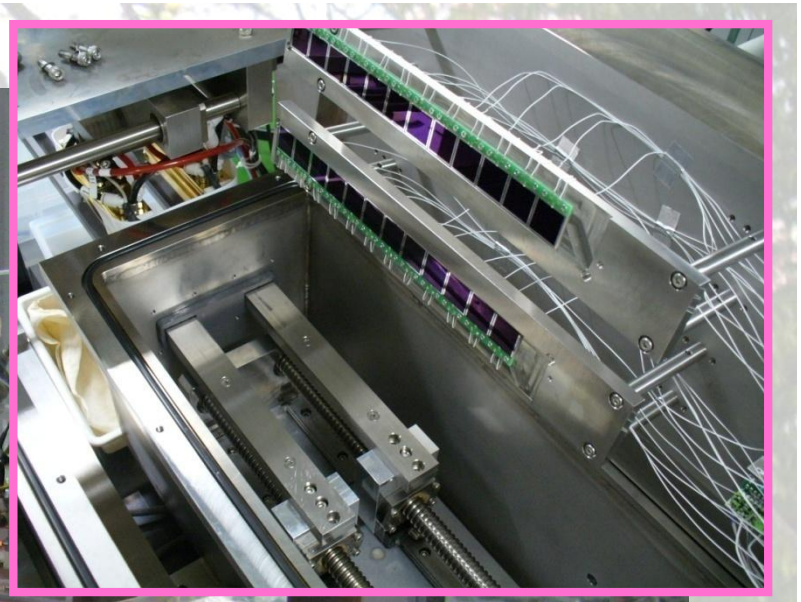
K. Tsukada *et al*. JAEA-Review 2008-054, 67.

AIDA-Ⅱ

- Rapid evaporation
- Increasing elution volume



Photos



Conditions of Db experiments

Beam: $^{19}F^{7+}$ 103 MeV on target, 270 - **440** pnA

Target: ^{248}Cm 560 or **1400** μg/cm^2 containing Gd

1st solution: (a) 0.31 M HF/0.10 M HNO_3: [F^-] = 0.003 M (1222 cycles)

(b) 1.7 M HF/0.10 M HNO_3: [F^-] = 0.01 M (985 cycles)

(c) 0.89 M HF/0.3 M HNO_3: [F^-] = 0.003 M (3160 cycles)

2nd solution: 0.015 M HF/6.0 M HNO_3 (Stripping)

Elution speed: 1.2 mL/min for 1st solution

0.8-1.0 mL/min for 2nd solution

Column: S size (1.0 mmϕ × 3.5 mm)

AIDA-Ⅱ operation (a, b)

Cycle time: 83, 84 s

Measurement duration: 75.0 s

Cooling time 1st : 14-30 s

2nd : 38-57 (-62) s

AIDA-Ⅰ (c)

Cycle time: ~73 s

Measurement duration: 1st : 233 s

2nd : 215 s

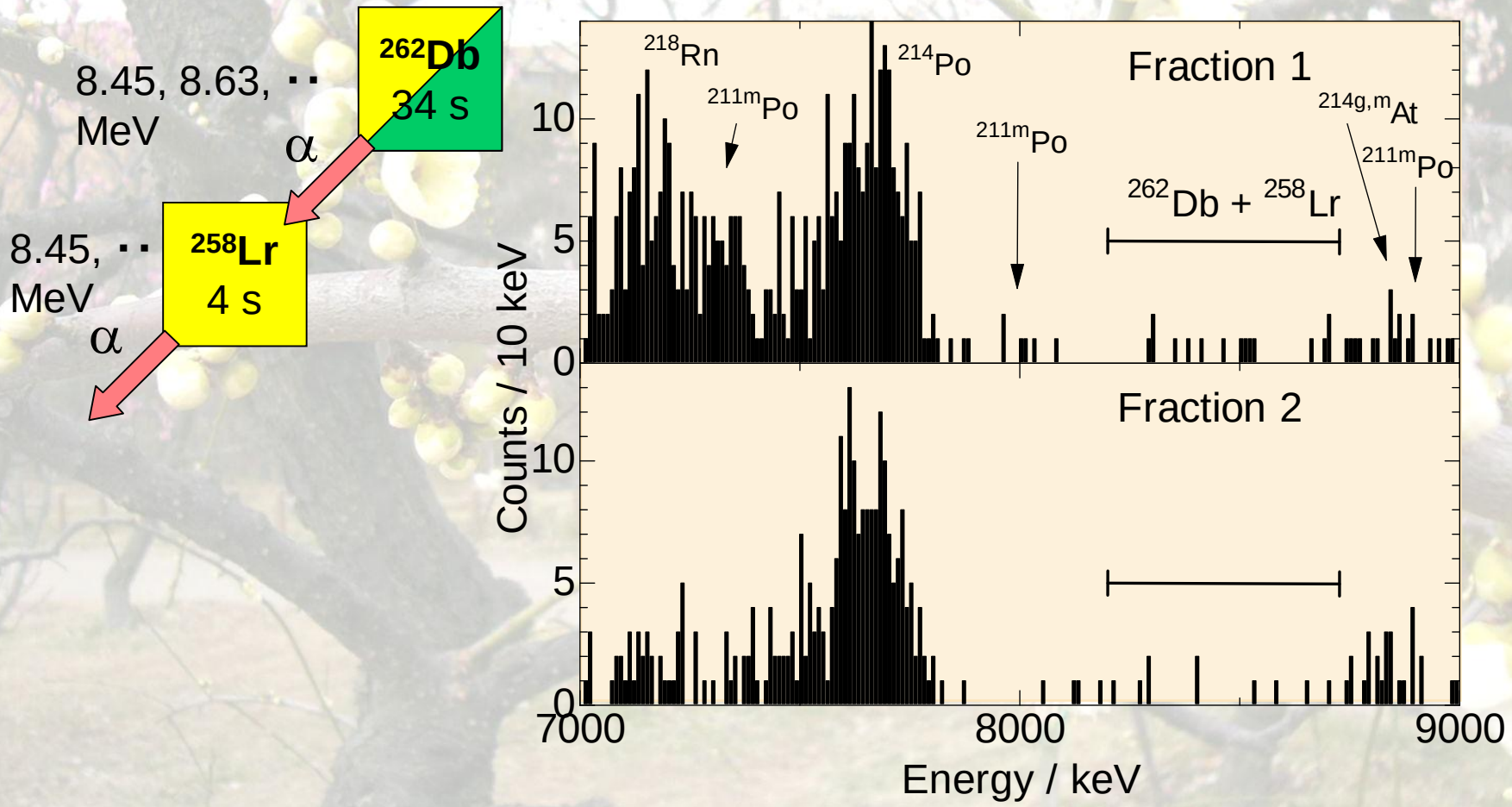
Cooling time: 1st : 48 s

2nd : 66 s

Results and discussion

Average chemical yield (Ta) : ~60%

α-particle spectra of ^{262}Db and ^{258}Lr **(a)**



(a) Db-Lr alpha counts (8.1-8.7 MeV)

Line1 : 5

Line2 : 8

Line3 : 9

Line4 : 4

Total : **26** counts (BGD 8.8)

1st soln. : 2nd soln

9.7 : 7.6

Decay correction

4.4 : 5.6

%ads: 56^{+16}_{-13}%

Correlation

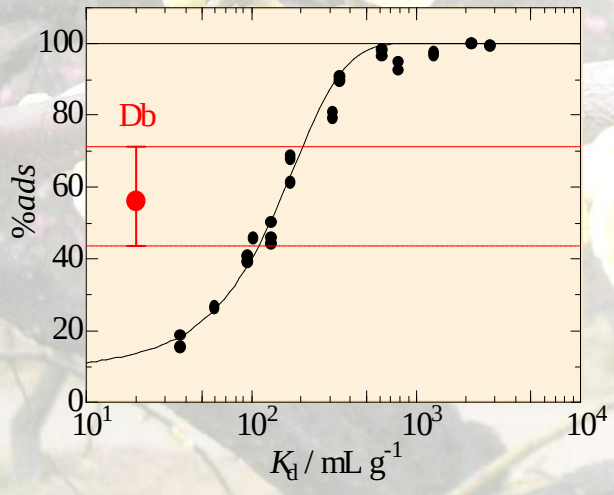
1 chain / 17 singles

(Calc. 1 / 7)

Cross section

~1.3 nb

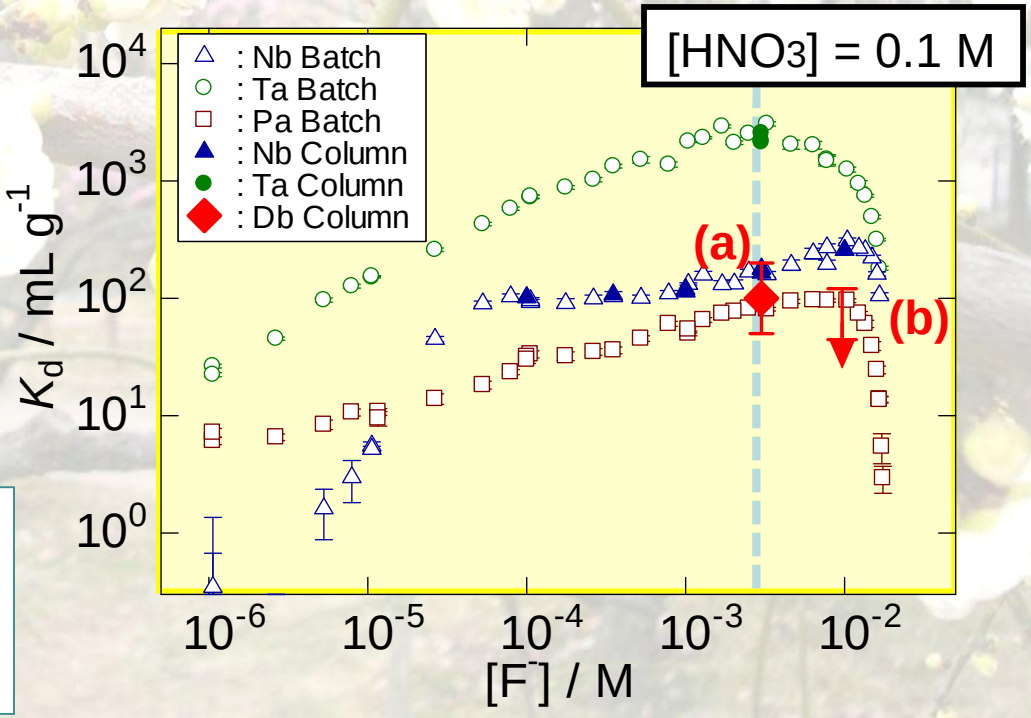
(Ref. 1.5 ± 0.4 nb)



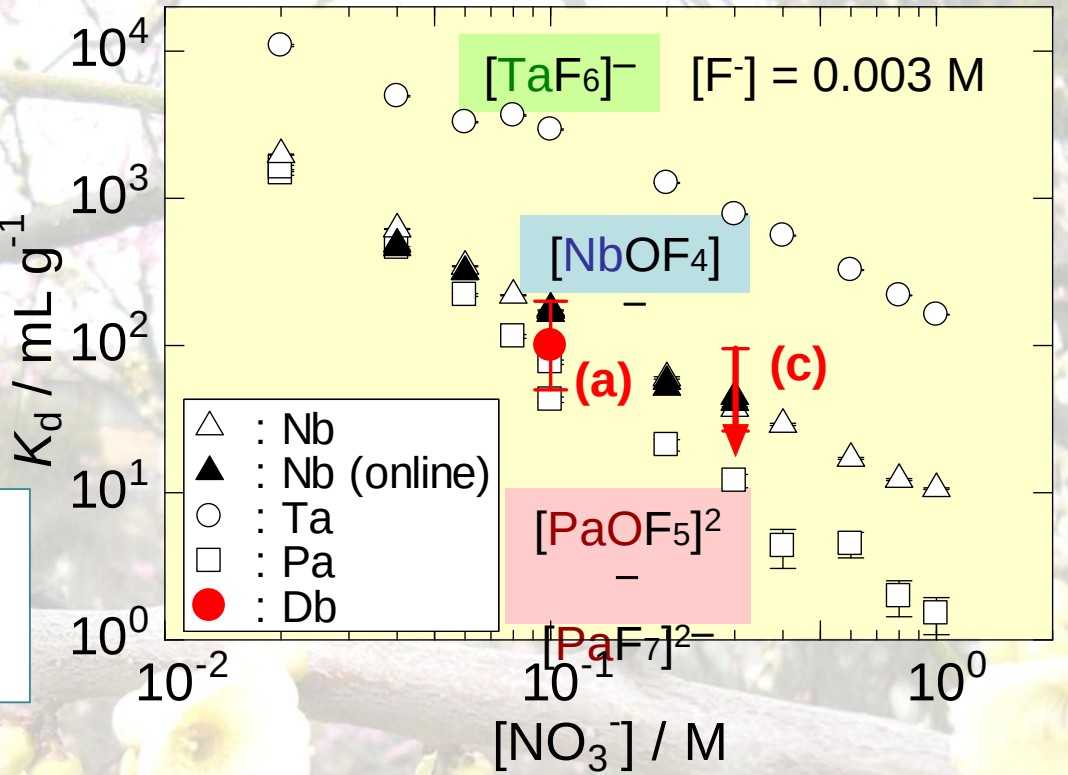
(b) 1st 2nd

9 : 1

%ads: 0 $^{+50}$ (3σ)



Variations of the K_d values as functions of $[NO_3^-]$



(c) 1st 2nd
8 : 3
%ads: 17^{+63}% **(3σ)**

Adsorption on the resin in the HF/HNO_3 solutions at $[F^-]$ = 0.003 M.

Ta >> Nb ≥ Db ≥ Pa

$DbOF_4^-$?, $DbOF_5^{2-}$?, (DbF_7^{2-} ?), DbF_6^- ?

Summary

- Anion-exchange behavior of **Nb**, **Ta**, **Pa**, and **Db** in HF/HNO_3 solutions was investigated.
- By employing new apparatus **AIDA-II** and improving the irradiation setup (beam current, thickness of the target), we were able to obtain enough α counts of ^{262}Db to determine the *K*d value of the anion-exchange reaction.
- It was found that the adsorption of **Db** on the anion-exchange resin was clearly weaker than that of **Ta** and similar to that of **Nb** and **Pa**.


Thank you very much!