



Aqueous Chemistry of Rf and Db

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for

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collaboration

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Contents

1. Introduction – Aqueous chemistry of Rf at JAEA
2. Fluoro complex formation of Rf
Anion-exchange chromatography in HF and
in HF/HNO₃
Cation-exchange chromatography in HF/HNO₃
3. Fluoro complex formation of Db – AIX in HF
AIX in HF/HNO₃
with AIDA-II
→ Kasamatsu
4. Conclusions

JAEA Tandem Accelerator



1. Introduction

Systematic investigation on aqueous chemistry of Rf

Comparative study of Rf with the homologues Zr, Hf, and Th

1. Chloro complex formation: $[MCl_6]^{2-}$

Anion-exchange chromatography: $Rf \geq Zr > Hf$

EXAFS spectroscopy: $[RfCl_6]^{2-}$

2. TBP extraction (complex): $MCl_4(TBP)_2$

Reversed-phase chromatography: $Rf < Zr \approx Hf$

3. Nitrate complex formation

Anion-exchange chromatography: $Rf \approx Zr \approx Hf \neq Th$

4. Fluoro complex formation

5. Sulfate complex formation: in progress

2. Fluoro complex formation of Rf

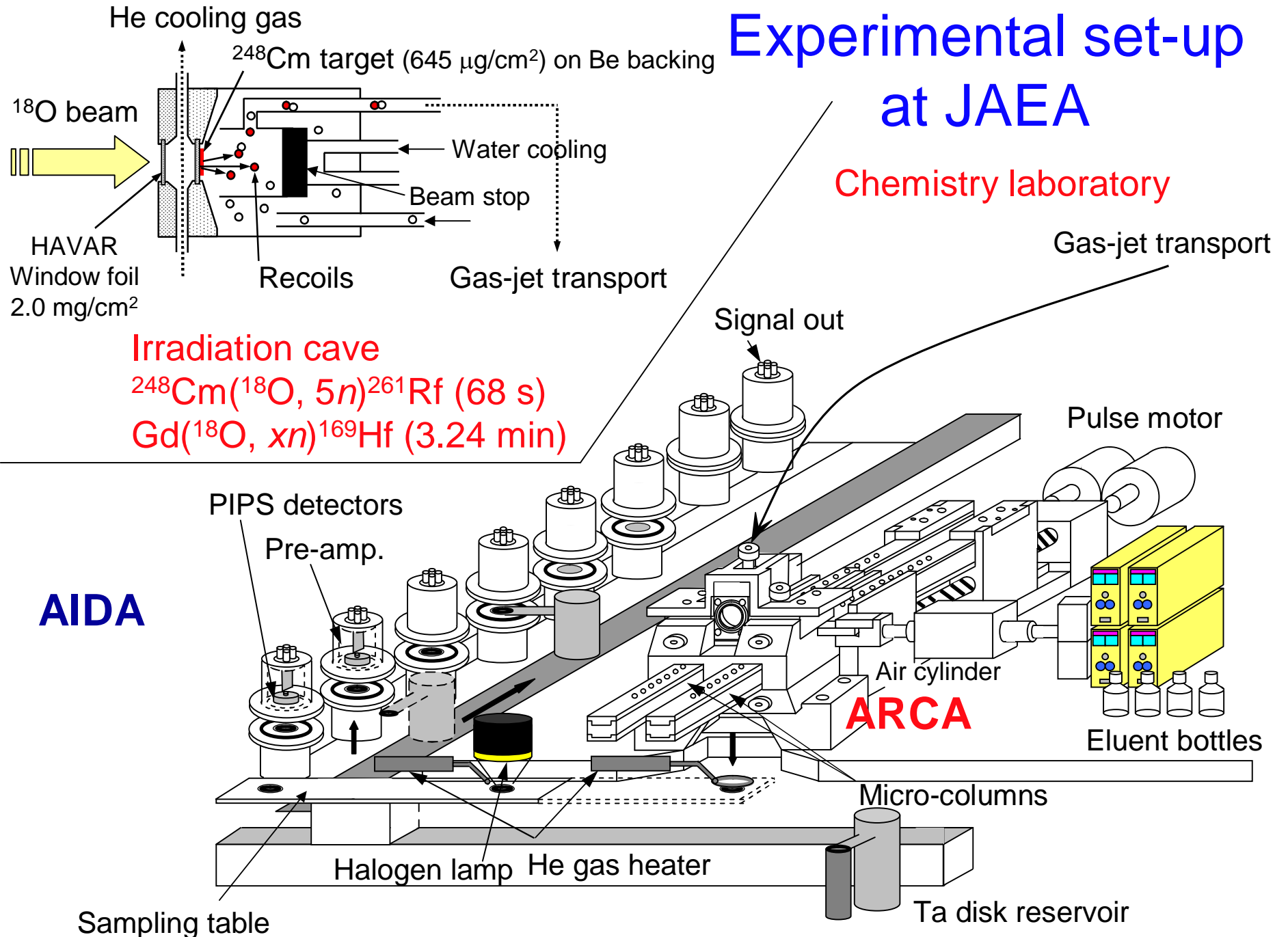
- Anion-exchange chromatography in HF and HF/HNO₃
- Cation-exchange chromatography in HF/HNO₃

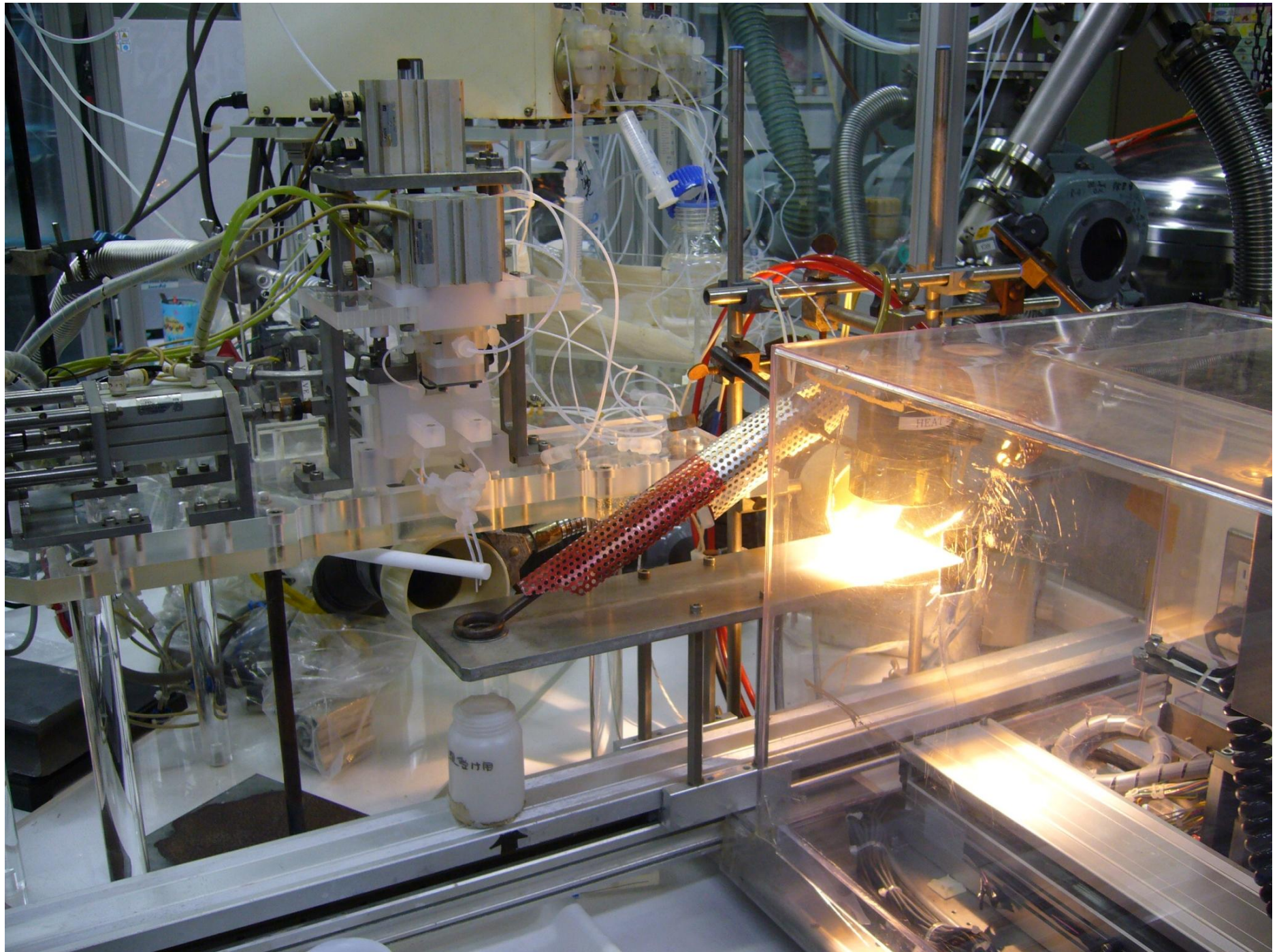
$^{248}\text{Cm}(^{18}\text{O}, 5n)^{261}\text{Rf}$
 $\sigma = 13 \text{ nb}$

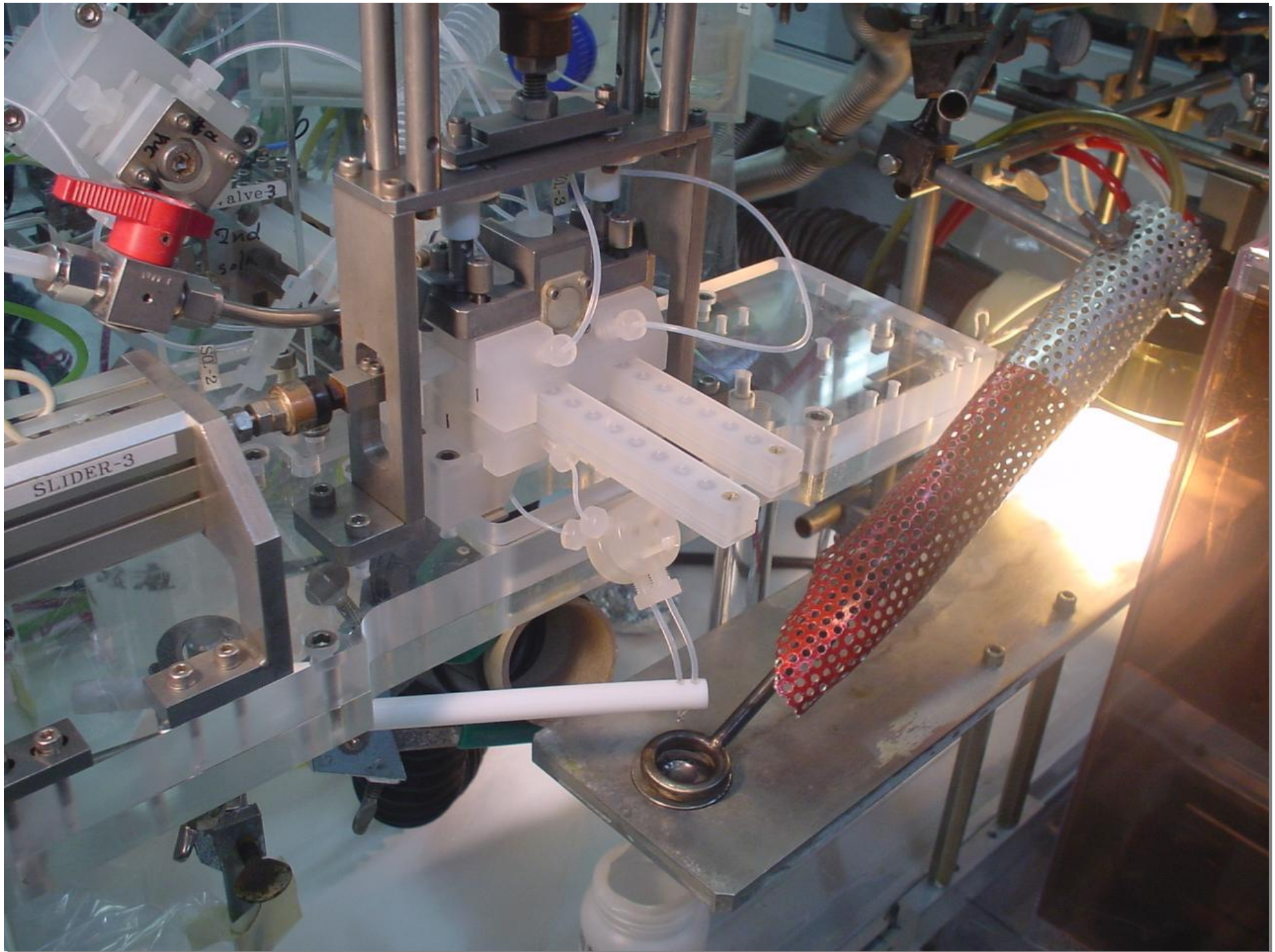
1																	18
1	2											13	14	15	16	17	2
H	Li											B	C	N	O	F	He
3	4											5	6	7	8	9	10
Li	Be											13	14	15	16	17	18
11	12											13	14	15	16	17	18
Na	Mg											Al	Si	P	S	Cl	Ar
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
87	88	89	104	105	106	107	108	109	110	111	112	113	114	115	116		118
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	112	113	114	115	116		118
Lanthanides	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71		
	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
Actinides	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103		
	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr		

Experimental set-up at JAEA

Chemistry laboratory







Anion-exchange procedure in HF with AIDA

1. Collection of ^{261}Rf and ^{169}Hf for 125 s
2. Dissolution with 250 μL of HF solution and feed onto the column at 740 $\mu\text{L}/\text{min}$

3. 200 μL of 4.0 M HCl at 1.0 mL/min

AIX column: MCI GEL CA08Y resin (20 μm)
1.6 mm i.d. \times 7.0 mm (1.0 mm i.d. \times 3.5 mm)

Fraction 1 (A_1)

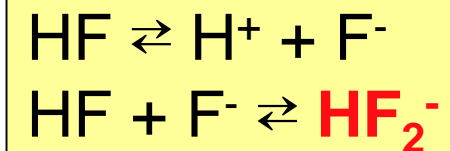
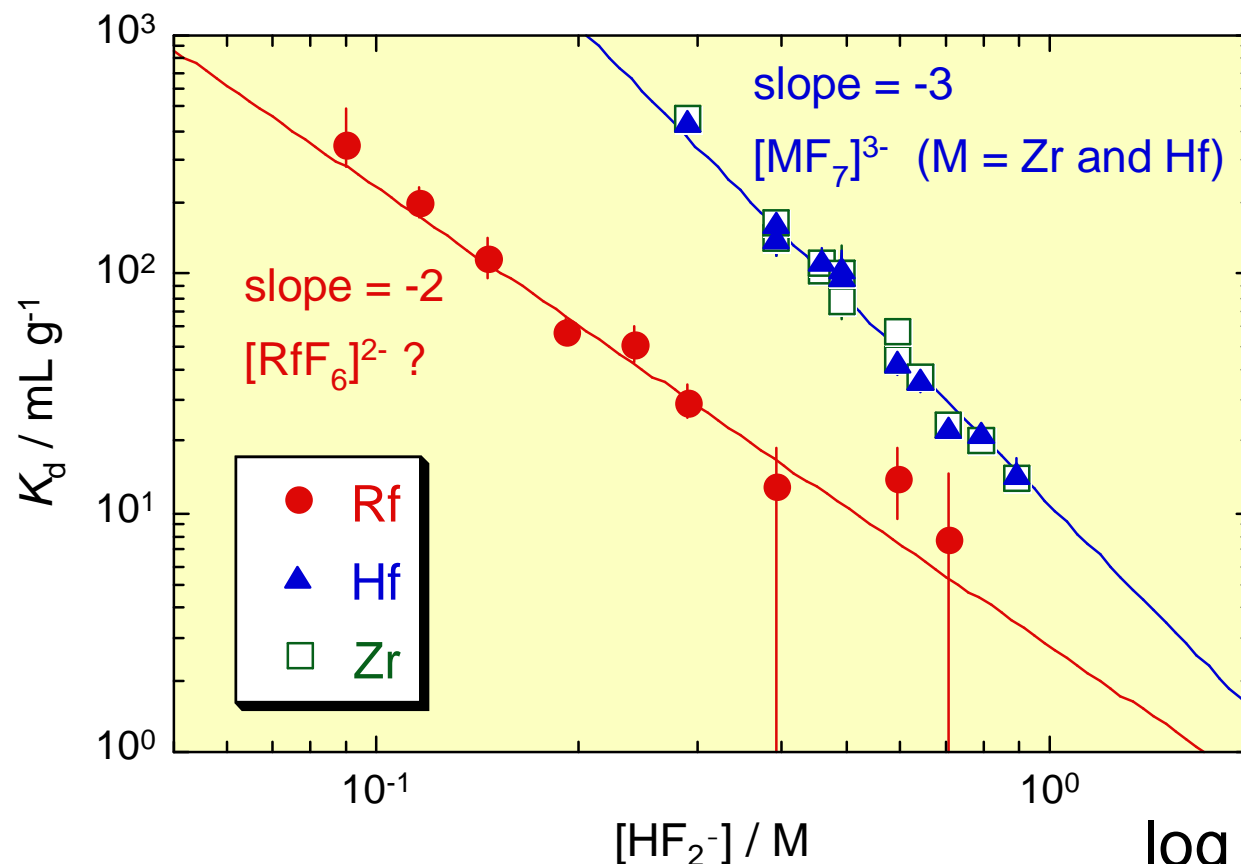
Fraction 2 (A_2) \rightarrow α -spectrometry

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

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

Anion-exchange experiments with ^{85}Zr and ^{169}Hf
from the Ge/Gd target: $\text{Ge}(^{18}\text{O}, xn)^{85}\text{Zr}$, $\text{Gd}(^{18}\text{O}, xn)^{169}\text{Hf}$

Anion-exchange behavior of Rf in HF



4226 cycles of anion-exchange experiments
 \Rightarrow 266 α events from ^{261}Rf and ^{257}No , 25 α - α time correlations

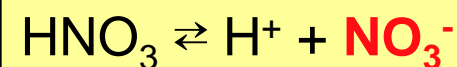
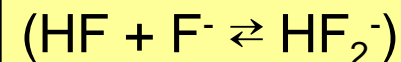
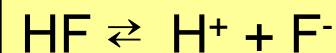
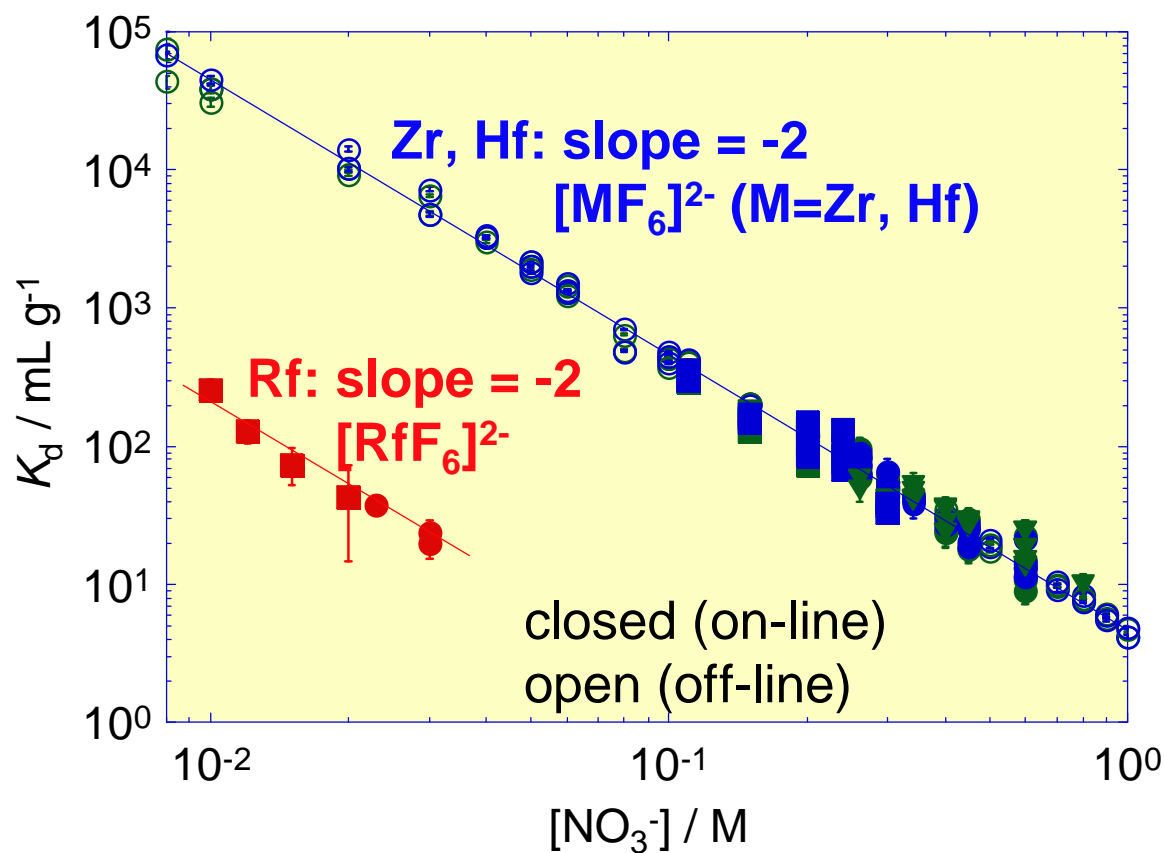
$$\log K_d = C - n \cdot \log[\text{HF}_2^-]$$

K_d s linearly decrease with $[\text{HF}_2^-]$.

\Rightarrow displacement of the metal fluoro complexes from the binding sites of the resin by the counter anion HF_2^-



Anion-exchange behavior of Rf in HF/HNO₃



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

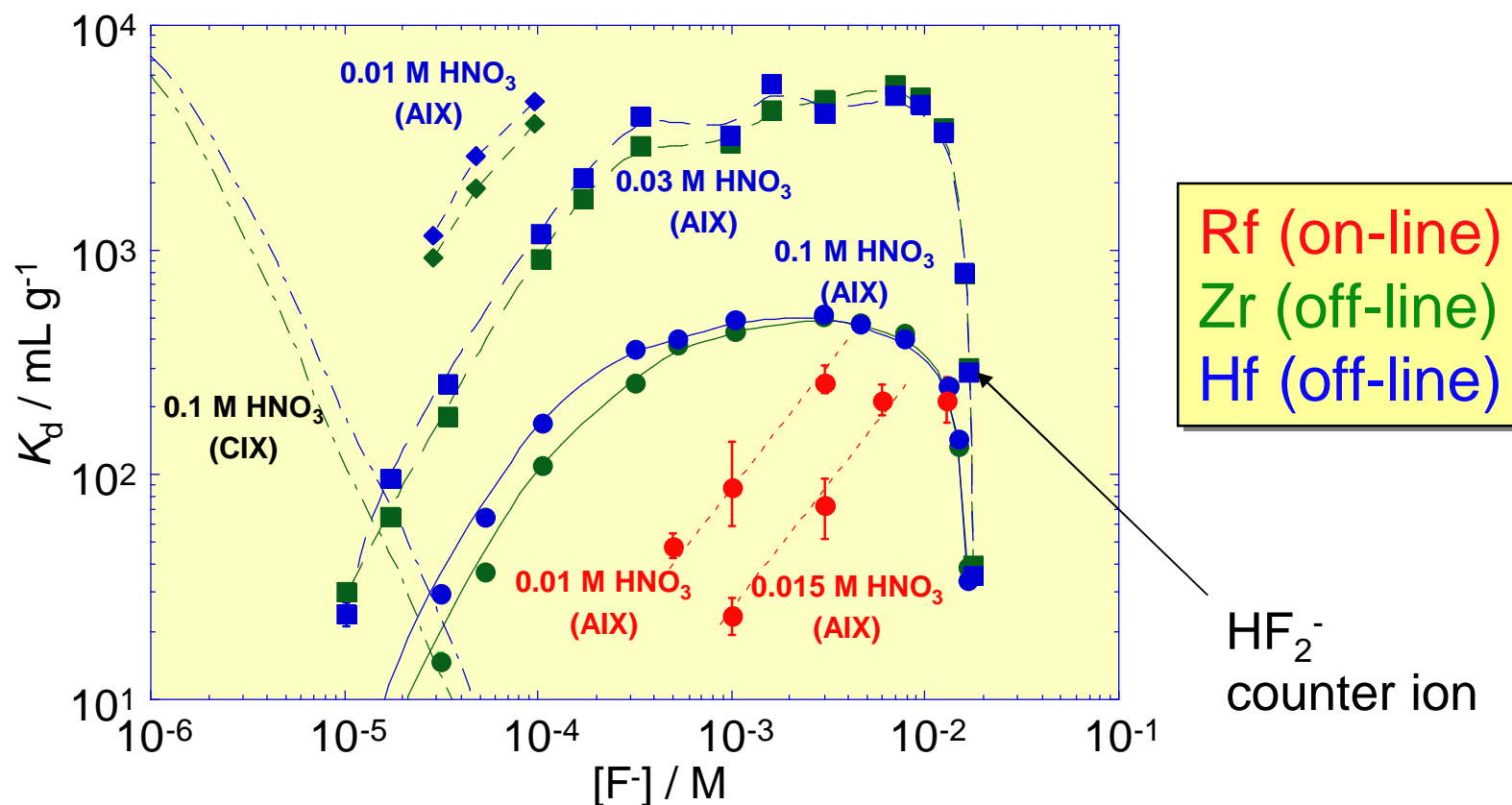
3788 cycles of anion-exchange experiments
 \Rightarrow 334 α events from ²⁶¹Rf and ²⁵⁷No, 46 α - α correlations

K_d s linearly decrease with $[\text{NO}_3^-]$.

\Rightarrow displacement of the metal fluoro complexes from the binding sites of the resin by the counter anion NO_3^-



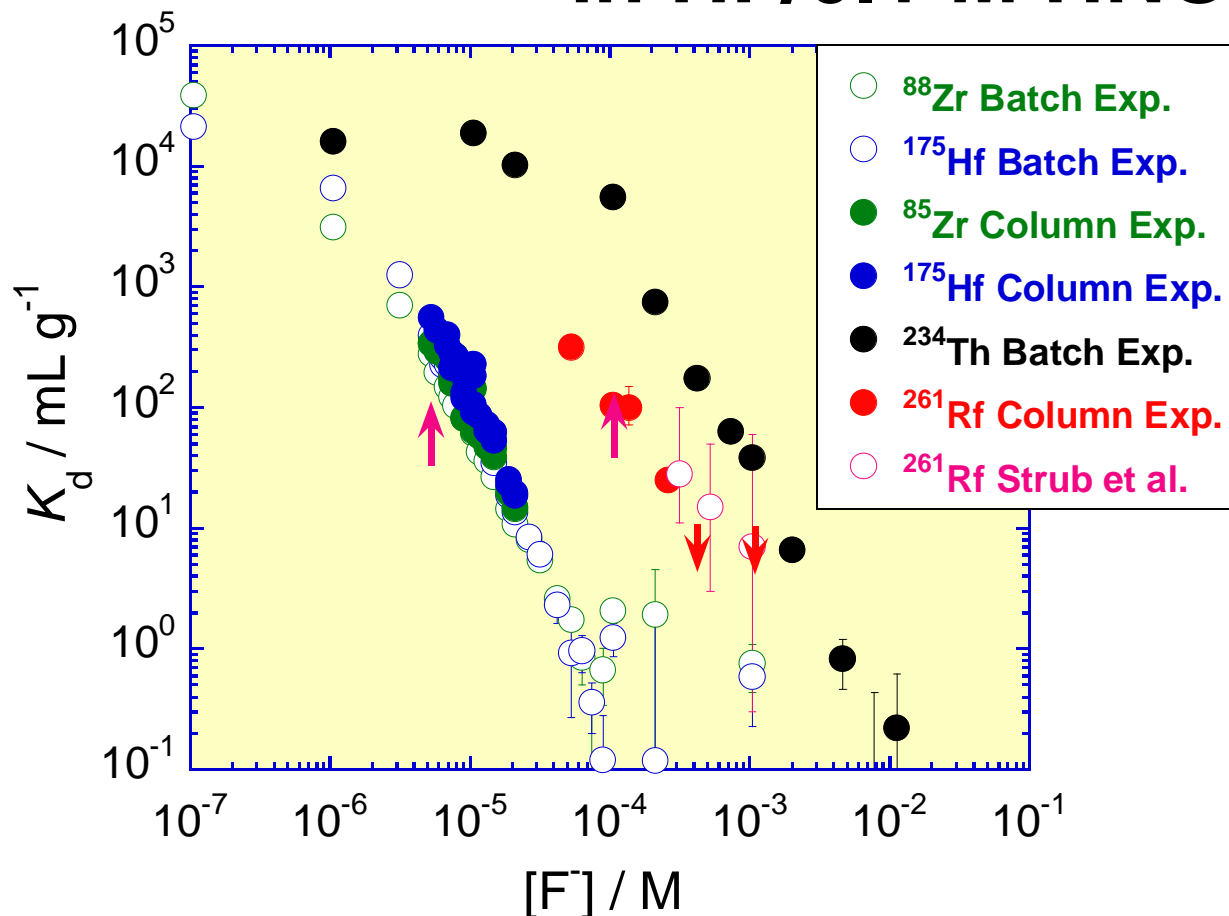
Anion-exchange behavior of Rf in HF/HNO₃



There is about two-orders of magnitude difference in the fluoride ion concentration of Rf and the homologues for the formation of $[MF_6]^{2-}$.

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

Cation-exchange behavior of Rf in HF/0.1 M HNO₃



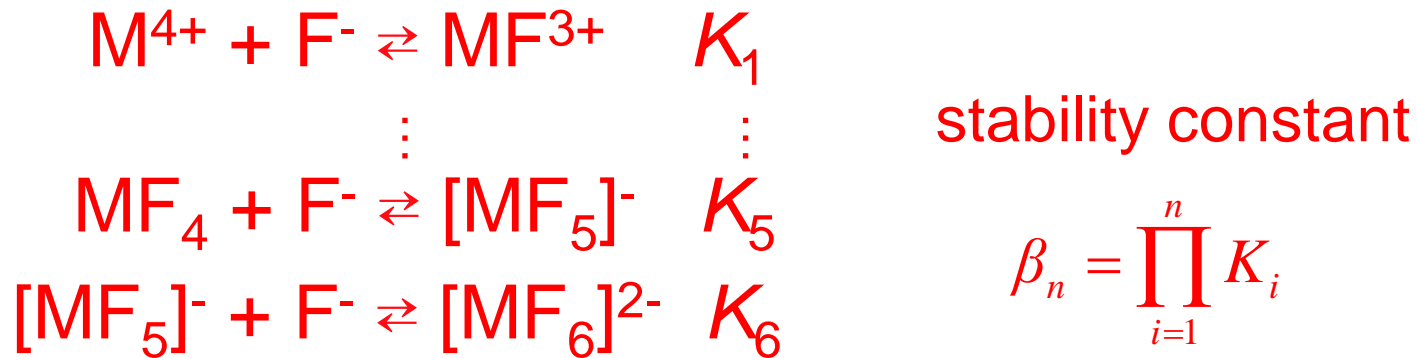
Y. Ishii et al.,
Chem. Lett. **37**, 288 (2008).

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

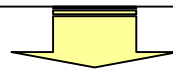
The strength of the coordination of the fluoride ions to Rf is significantly weaker than that to Zr and Hf. \Rightarrow consistent with the anion-exchange study

Formation of anionic fluoro complexes

Consecutive formation reactions of Zr^{4+} and Hf^{4+} (M^{4+})



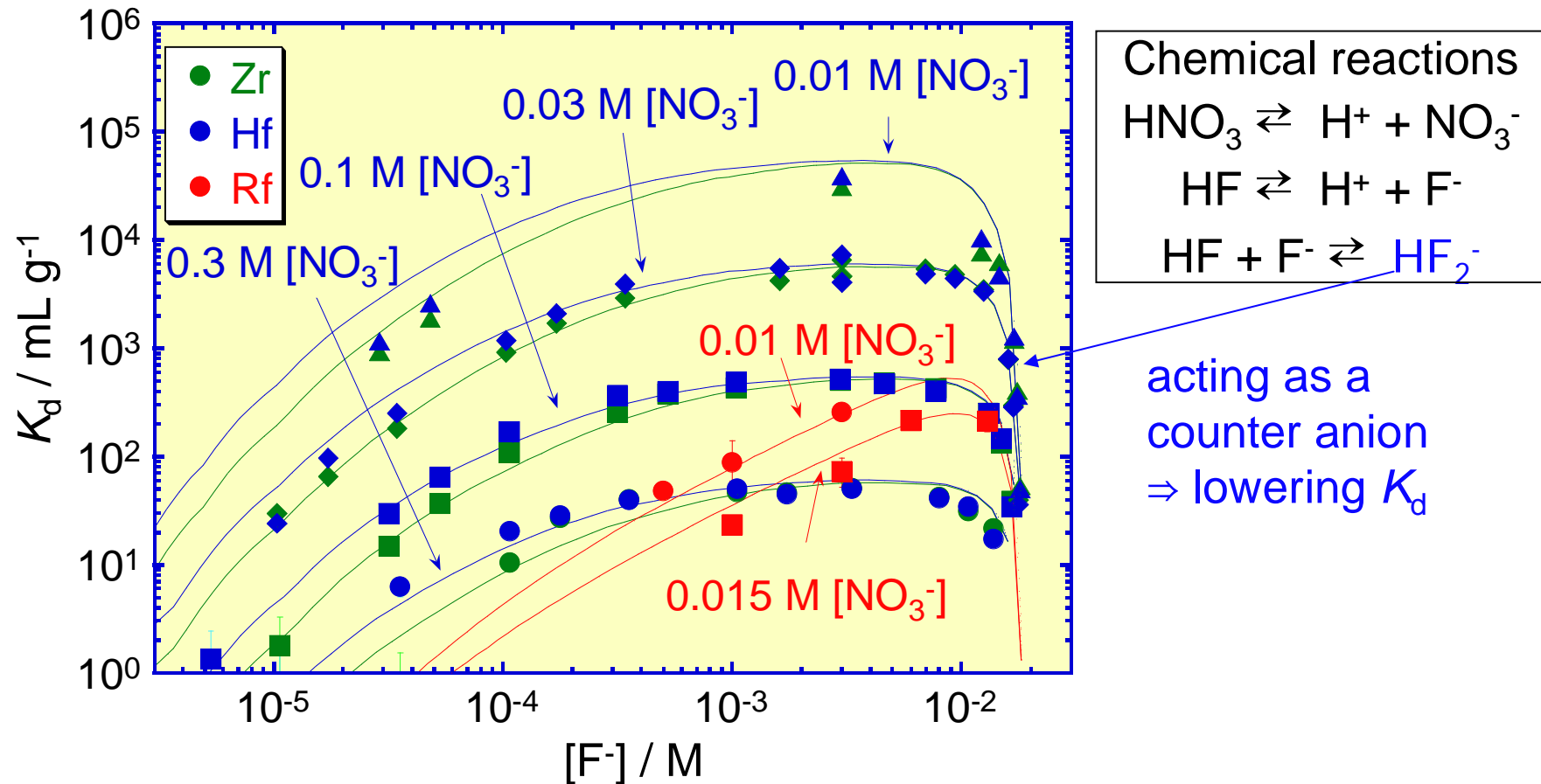
Anion-exchange reactions between $[MF_6]^{2-}$ and NO_3^-



$$\log K_d = \log D_2 - 2 \log \frac{[NO_3^-]}{[R-NO_3]} + \log \frac{\beta_6 [F^-]^6}{1 + \sum_{n=1}^6 \beta_n [F^-]^n}$$

β_n of Zr and Hf : literature values

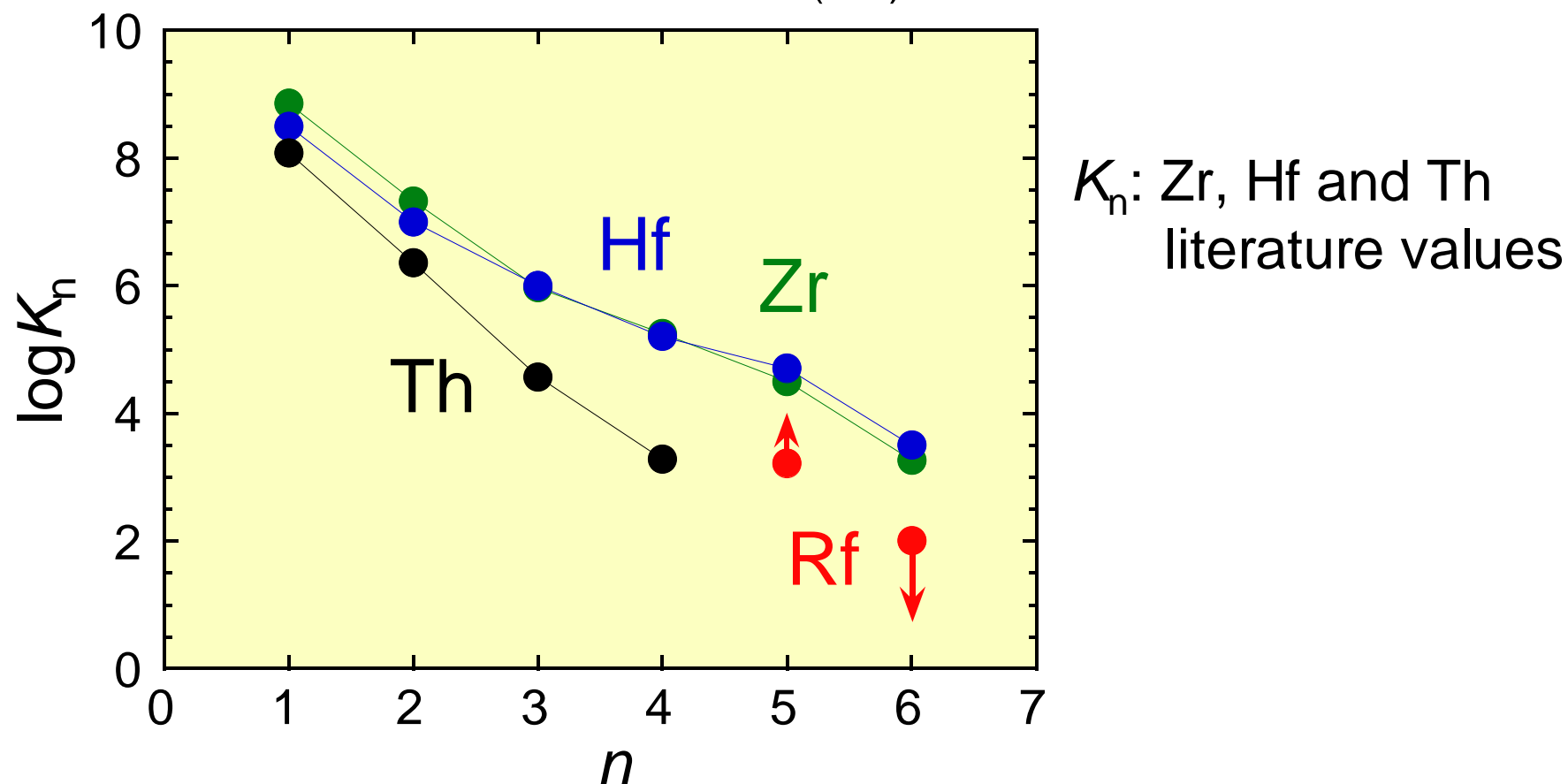
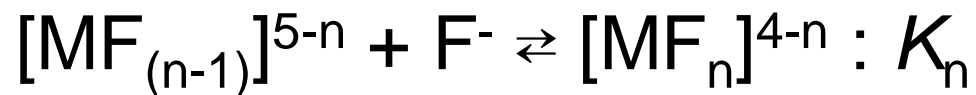
Results of the calculation (solid lines)



The data of Zr and Hf are well reproduced by the calculations.

To reproduce the data of Rf, we carried out the same calculations by using the consecutive formation constants as parameters: K_5 and K_6 .
 \Rightarrow well reproduced

Consecutive formation constants of Rf



The K_6 value of Rf should be at least more than one-order of magnitude smaller than those of Zr and Hf.

Summary of the fluoro complex formation of Rf

1. We clarified that Rf is present as the hexafluoro complex in dilute HF: $[\text{RfF}_6]^{2-}$.
2. The sequence of the fluoride complexation strength was clearly demonstrated: $\text{Zr} \approx \text{Hf} > \text{Rf} > \text{Th}$.
3. A weaker fluoro complex formation of Rf as compared to the formation of Zr and Hf would be reasonable if the size of the Rf^{4+} ion is larger than those of Zr^{4+} and Hf^{4+} as expected:
 Zr^{4+} (72 pm) \approx Hf^{4+} (71 pm) $<$ Rf^{4+} (78 pm) $<$ Th^{4+} (94 pm).
(prediction)

3. Anion-exchange behavior of Db in HF



$$\sigma = 1.3 \text{ nb}$$

1 H																	18 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
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
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	112 112	113 113	114 114	115 115	116 116		118 118

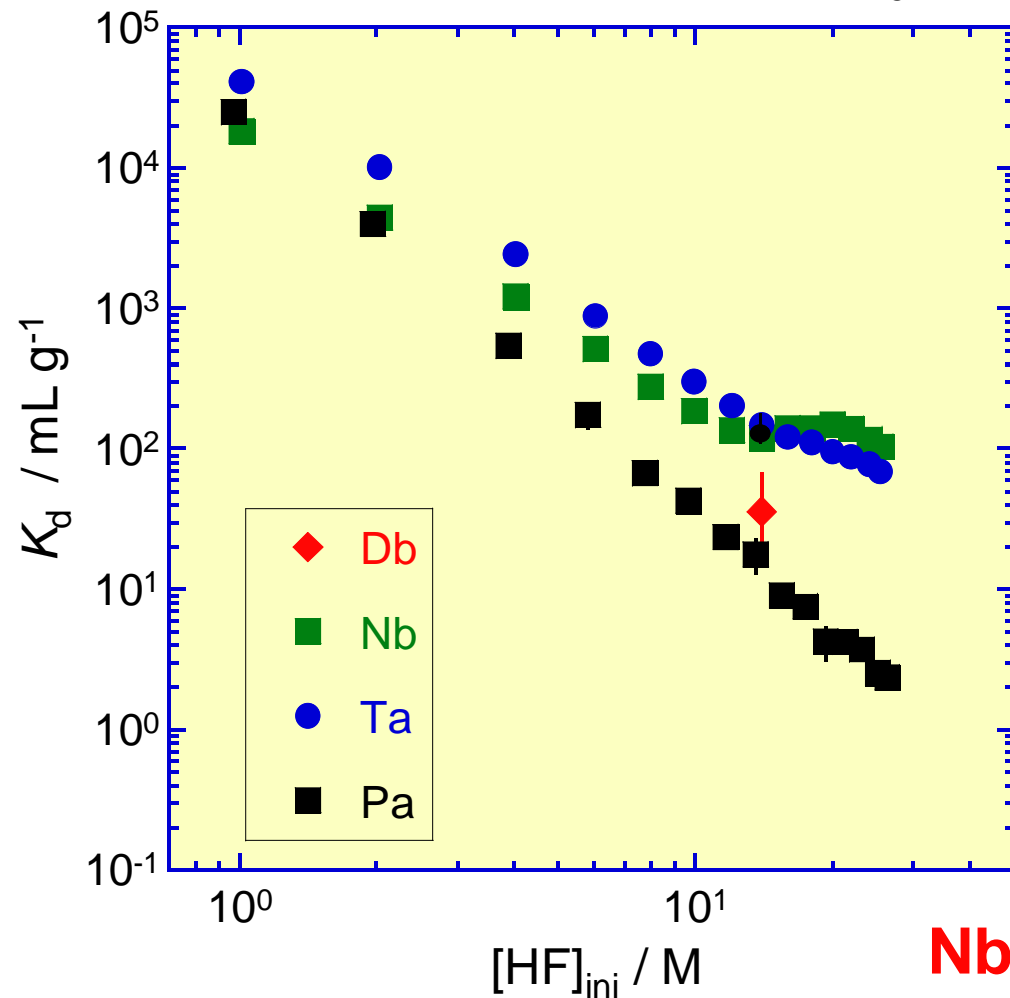
Lanthanides	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
Actinides	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Anion-exchange behavior of Db in 14 M HF

1702 cycles of anion-exchange experiments

⇒ 1st effluent of 14 M HF: 6 α events

⇒ 2nd effluent of 6 M HNO₃/0.015 M HF: 4 α events



Off-line with radiotracers
 ^{92m}Nb (10.15 d)
 ^{177}Ta (56.6 h)
 ^{233}Pa (27.0 d)

On-line
 $^{248}\text{Cm}(^{19}\text{F}, 5n)^{262}\text{Db}$
 $\text{Gd}(^{19}\text{F}, xn)^{170}\text{Ta}$

Nb \approx Ta > Db \geq Pa in 14 M HF



4. Conclusions

The formation of the hexafluoro complex of Rf was clarified, and the formation of Rf was significantly weaker than that of the lighter homologues, Zr and Hf.

Adsorption of Db on the anion-exchange resin was evidently smaller than that of the homologues, Nb and Ta, in 14 M HF.

→The fluoro complex formation of Rf and Db is remarkably different from that of the homologues.

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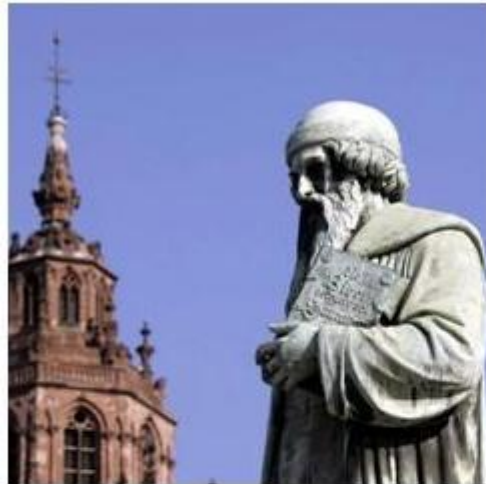
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M. Schädel

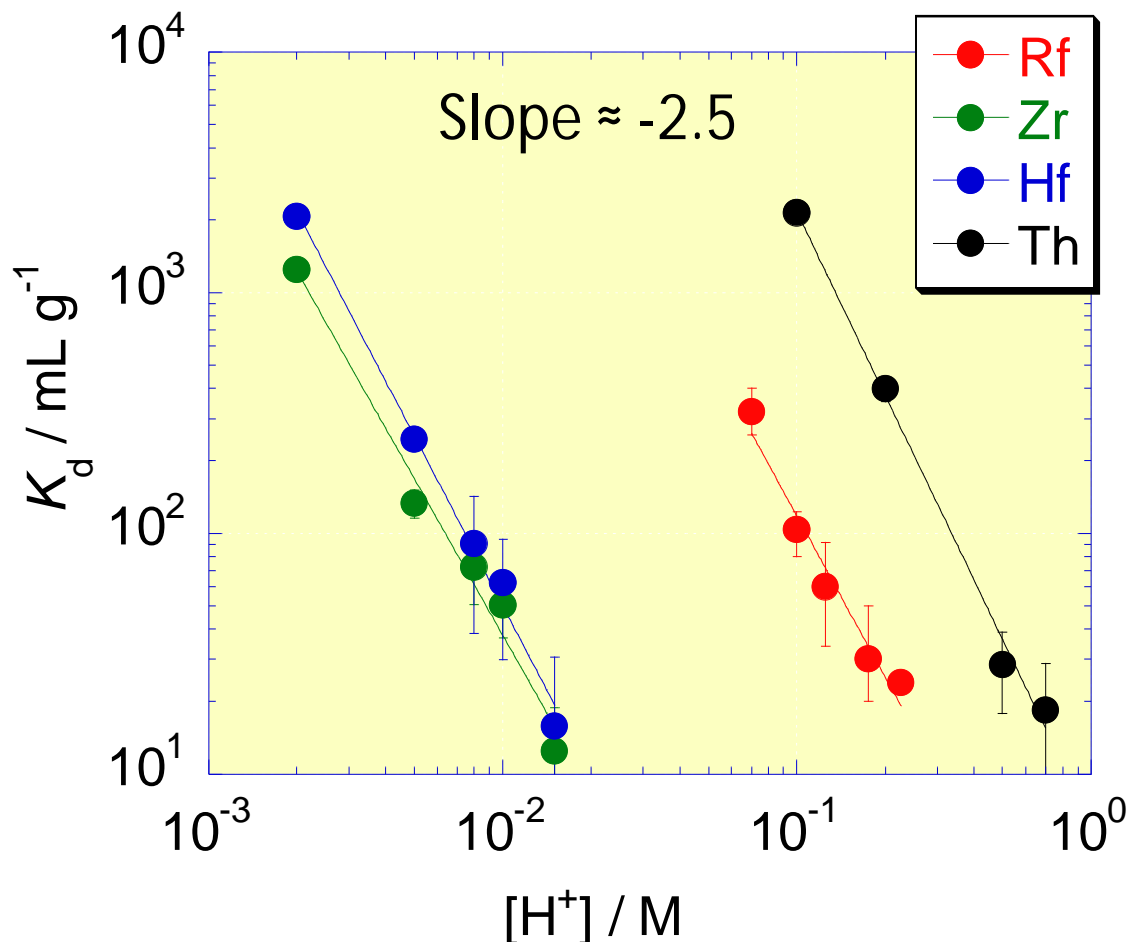
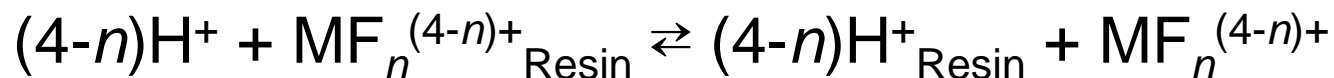
Univ. Mainz - J. V. Kratz



Thank you for your attention



Cation-exchange behavior of Rf in HF/HNO₃ at [F⁻] = 1.06 × 10⁻⁴ M



$$\log K_d = -(4-n)\log[H^+] + C$$

n : average number of the coordinated fluoride ions to M⁴⁺

