Electrochemical studies of the heaviest actinides

(Japan Atomic Energy Agency)
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Background

Oxidation-reduction (redox) study

Oxidation states, redox potentials *reflecting electronic structure and binding energy of valence electrons*

Early redox studies

Column chromatography with reducing and oxidizing agents

$Md^{3+} \rightarrow Md^{2+}$ and $No^{2+} \rightarrow No^{3+}$

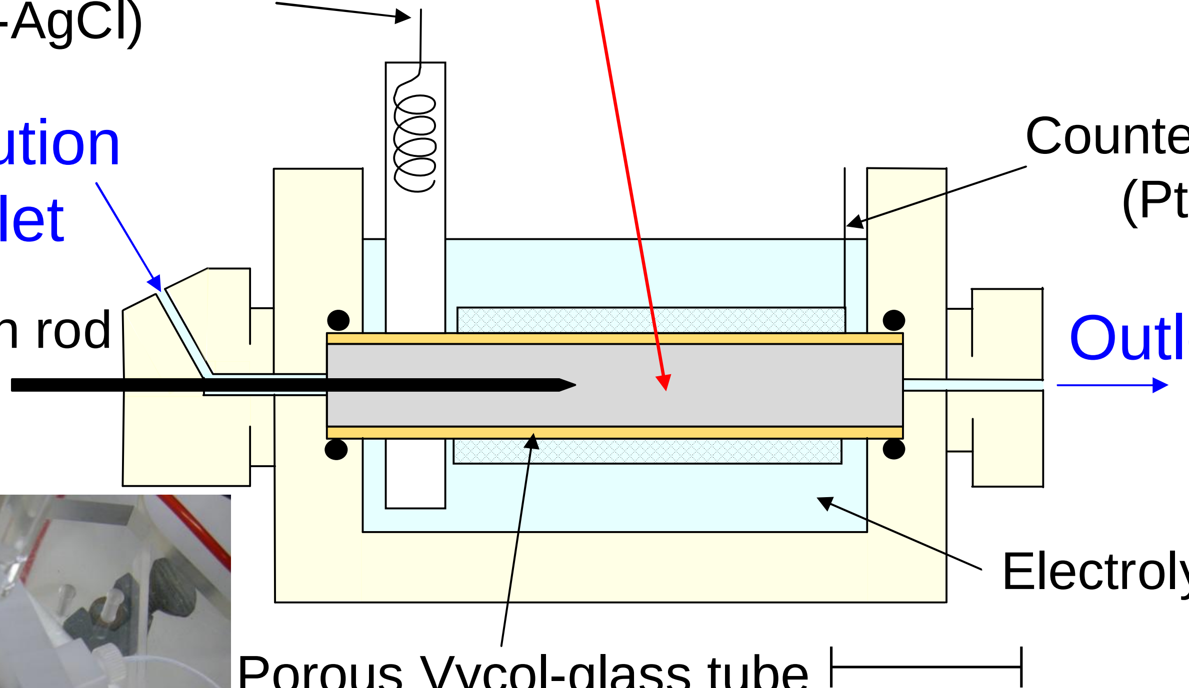
Complicated and time-consuming procedures

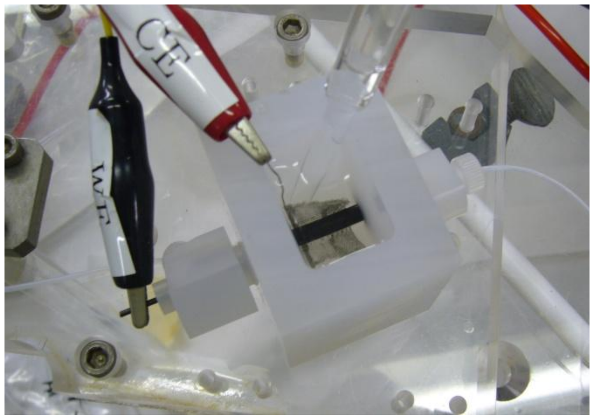
Requirement: more simple and rapid method

Present work

- Development of an electrochemistry apparatus available for single atom chemistry
- Oxidation of nobelium (No): $No^{2+} \rightarrow No^{3+} + e^-$
- Reduction of mendelevium (Md): $Md^{3+} + e^- \rightarrow Md^{2+}$

Flow electrolytic column





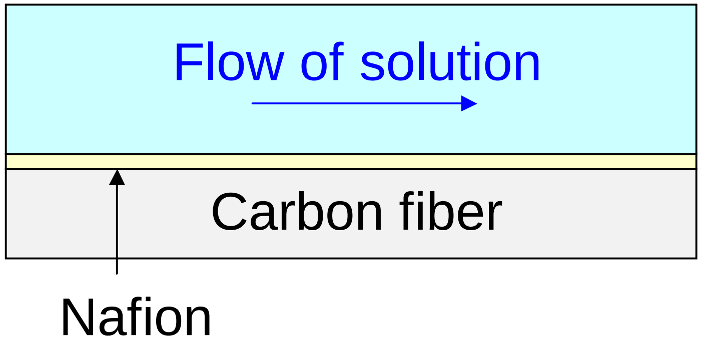
Toyoshima *et al*., Radiochim. Acta **96**, 323-326 (2008).

Chemically modified electrode

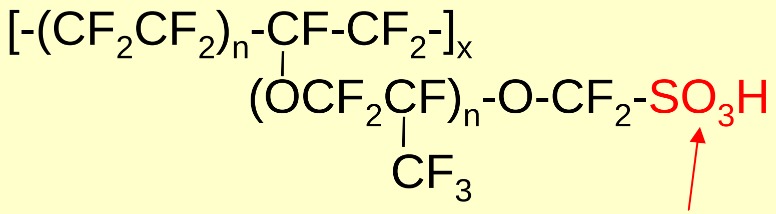
Chemical Separation on a Chemically Modified Electrode employed as a working electrode as well as a cation-exchanger

Chemically Modified Electrode

Carbon fibers modified with Nafion



Nafion perfluorinated ion-exchange resin



polyelectrolyte material

Cation-exchange group

On the Nafion electrode

- ➢ Electrolysis
- ➢ Cation-exchange separation

→ Simple and rapid electrochemical technique for single atoms

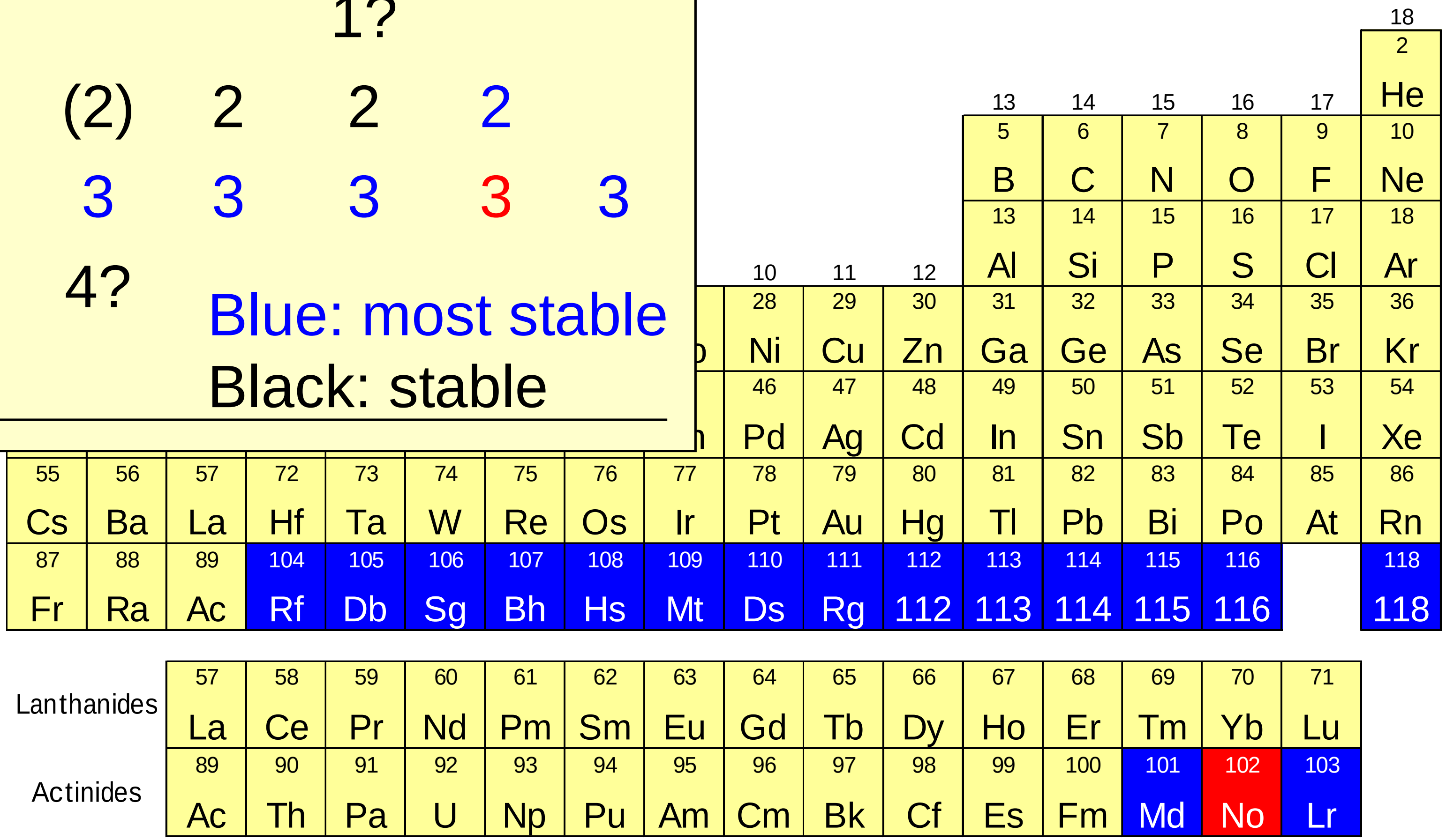
Oxidation of No^{2+}

Oxidation states in solution

Cf	Es	Fm	Md	No	Lr
			1?		
(2)	(2)	2	2	2	
3	3	3	3	3	3
4	4?				
5?					

Blue: most stable
Black: stable

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



Oxidation experiment of No^{2+}

JAEA tandem accelerator

$^{248}Cm(^{12}C, 5n)^{255}No$
($T_{1/2}$ = 3.1 min)
$Gd(^{12}C, xn)^{162}Yb^{3+}$
$Ge(^{12}C, xn)^{81}Sr^{2+}$

He/KCl
gas-jet

1) Collection
for 10 min

2) 0.1 M α-hydroxyisobutyric acid
(α-HIB) (pH 3.9)

3) 3.0 M HCl

Flow electrolytic column
4.8 mm i.d. × 30 mm
Applied potential : 0.2 to 1.2 V

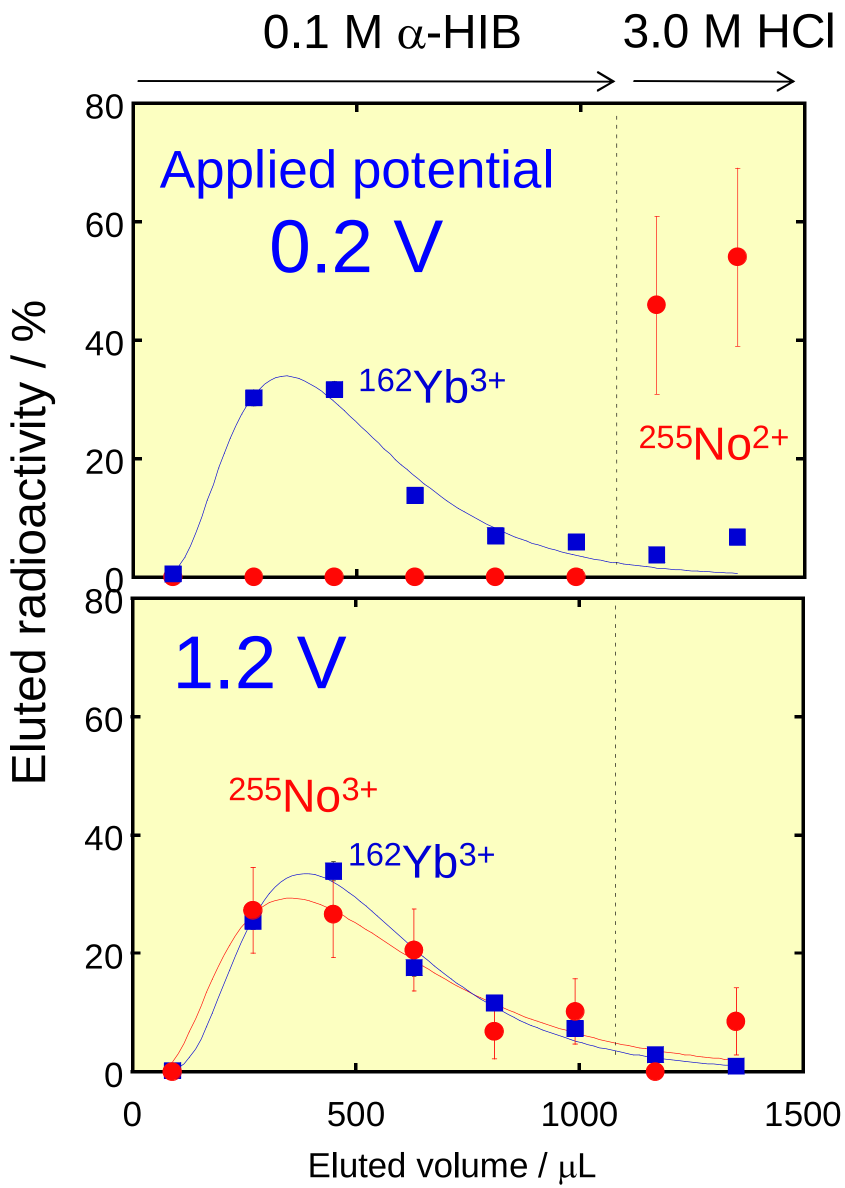
on Ta discs

No^{3+}, Yb^{3+}
6 fractions

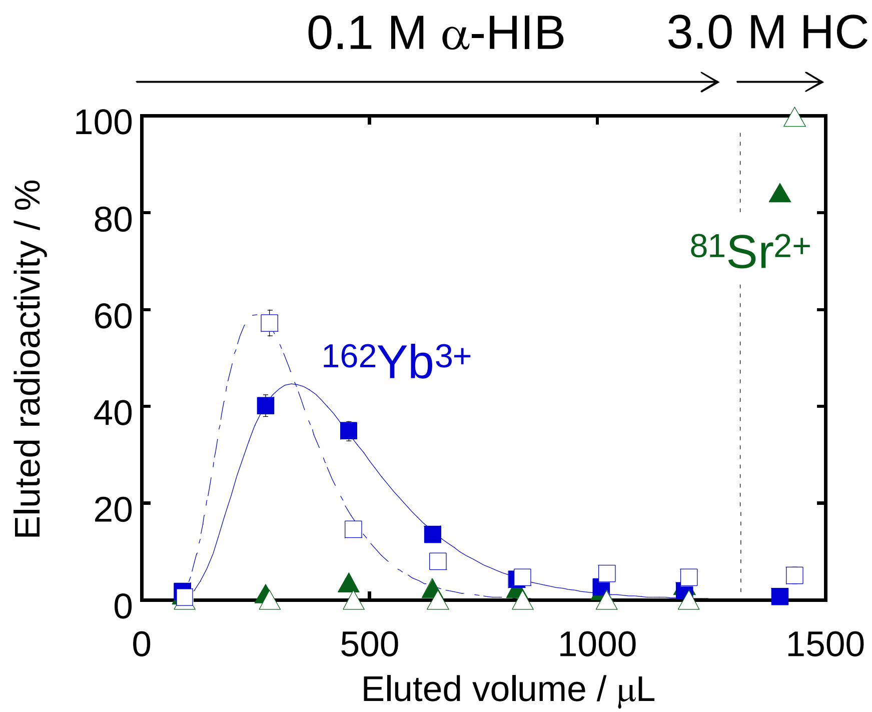
No^{2+}, Sr^{2+}
2 fractions

These procedures were accomplished within 3 min.

Elution behavior of ^{255}No



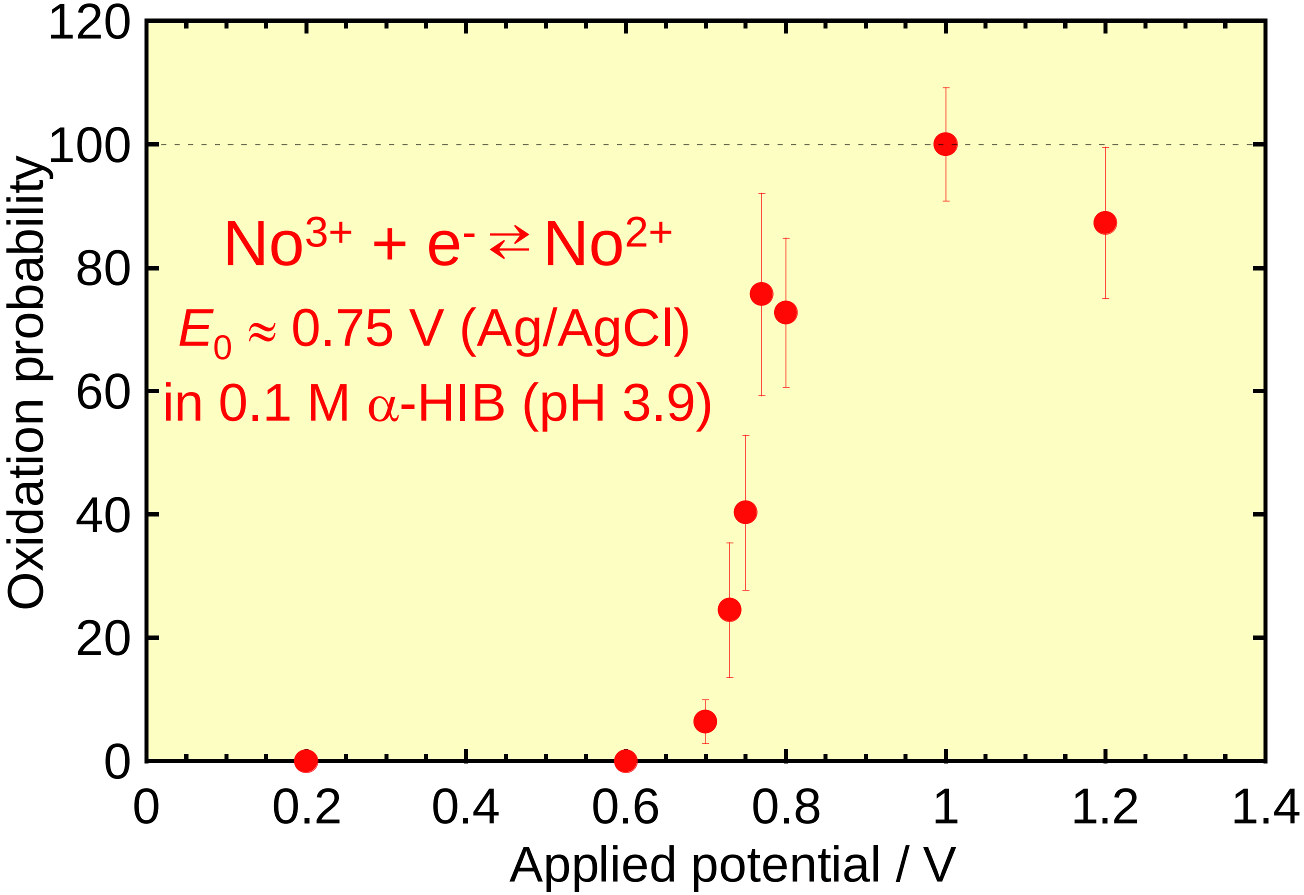
Elution behavior of $^{81}Sr^{2+}$ and $^{162}Yb^{3+}$



Successful oxidation of No^{2+} to No^{3+}

Toyoshima *et al*., J. Am. Chem. Soc. **131**, 9180-9181 (2009).

Oxidation probability of No



$$\text{Oxidation probability} = \frac{100 \times [No^{3+}]}{[No^{3+}] + [No^{2+}]}$$

Toyoshima *et al.*, J. Am. Chem. Soc. **131**, 9180-9181 (2009).

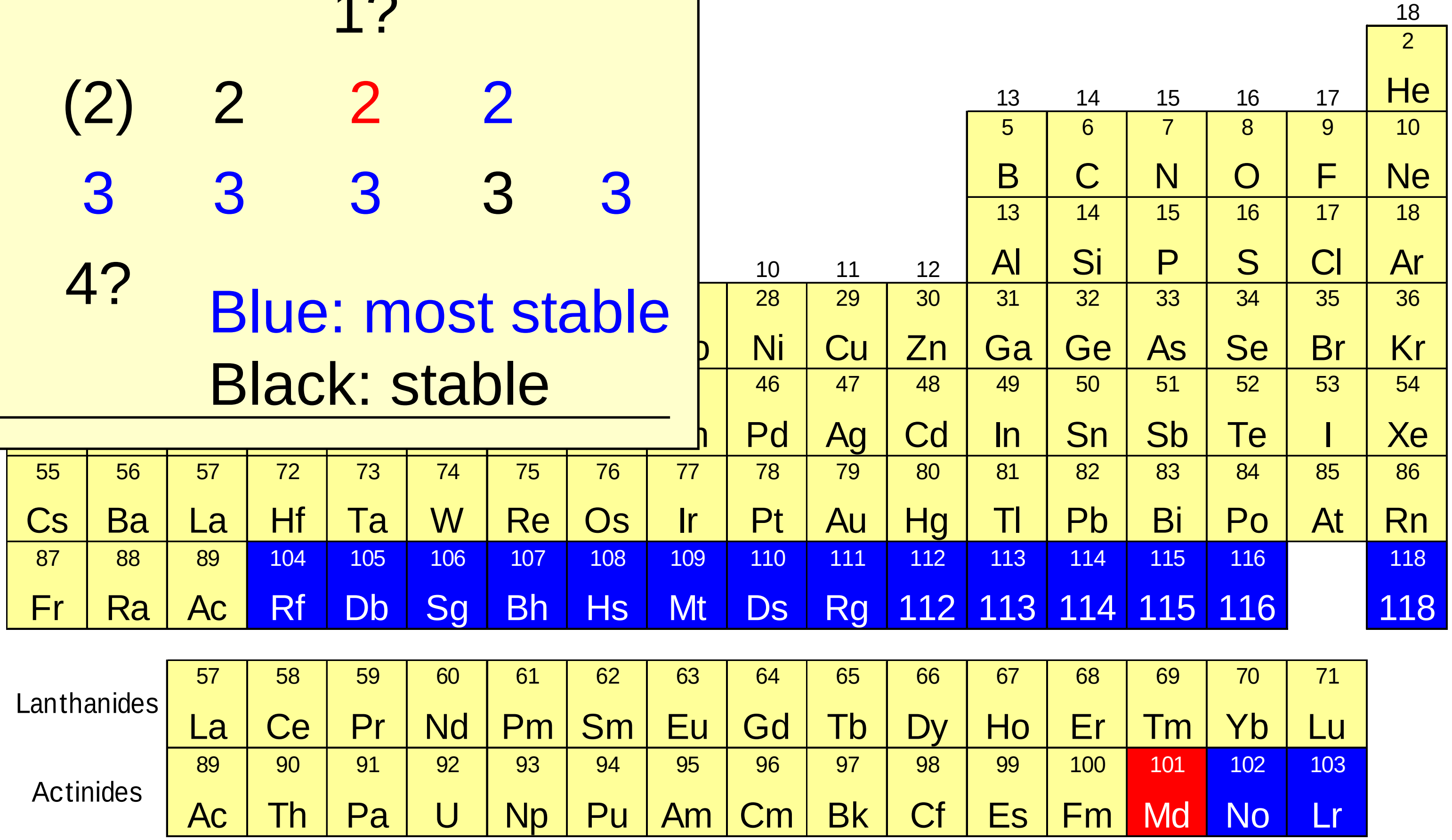
Reduction of Md^{3+}

Oxidation states in solution

Cf	Es	Fm	Md	No	Lr
			1?		
(2)	(2)	2	2	2	
3	3	3	3	3	3
4	4?				
5?					

Blue: most stable
Black: stable

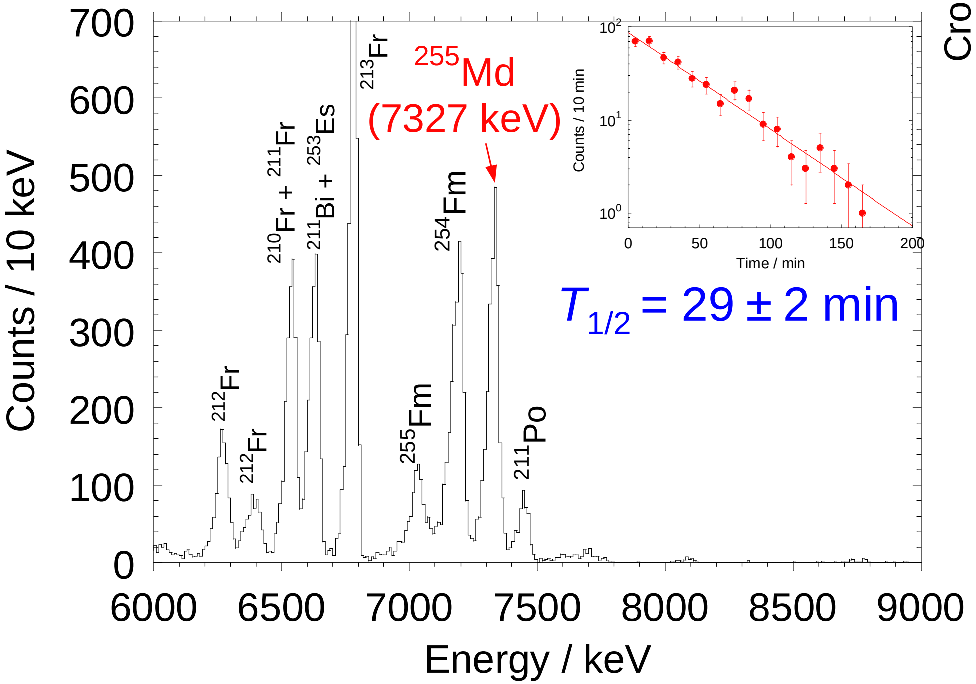
$$Md^{3+} + e^{-} \rightarrow Md^{2+}$$



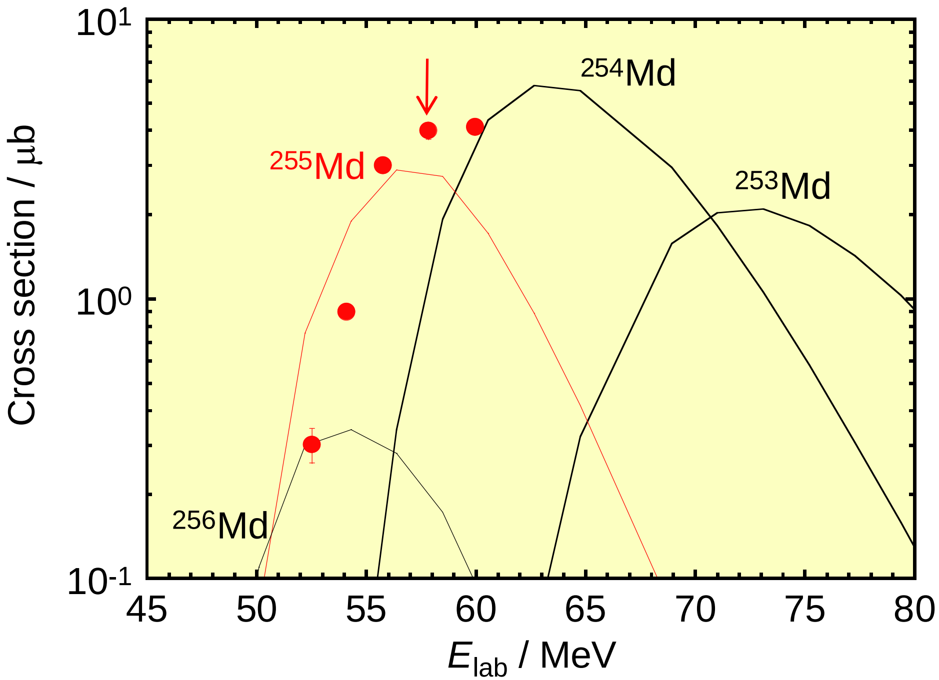
Production of ^{255}Md

The JAEA tandem accelerator
$^{248}Cm(^{11}B, 4n)^{255}Md$
using a rotating wheel system

^{255}Md: $T_{1/2}$ = 27 ± 2 min
α-branch: 8%

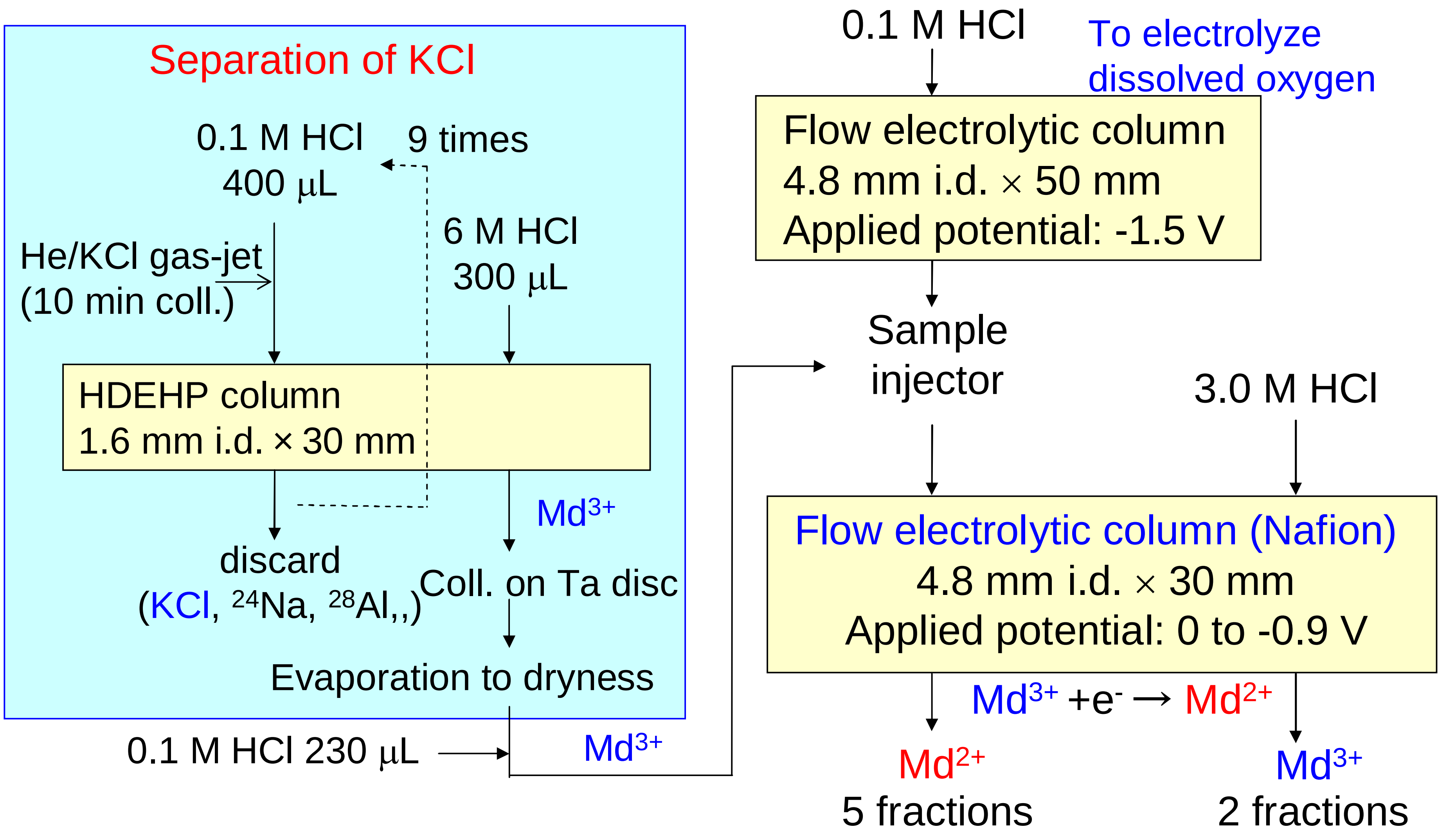


α-spectrum



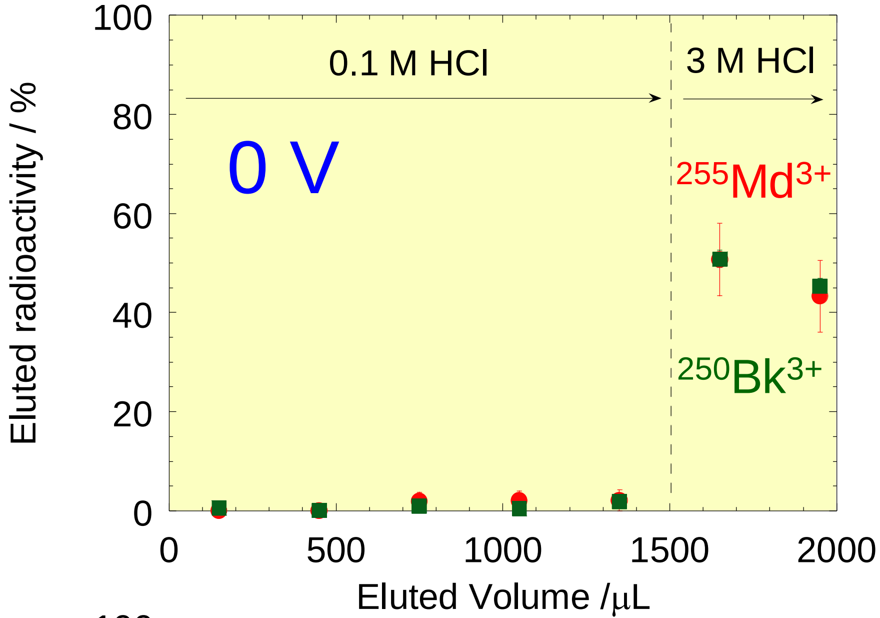
Excitation function of
$^{248}Cm(^{11}B, 4n)^{255}Md$
Lines: calculation with HIVAP code

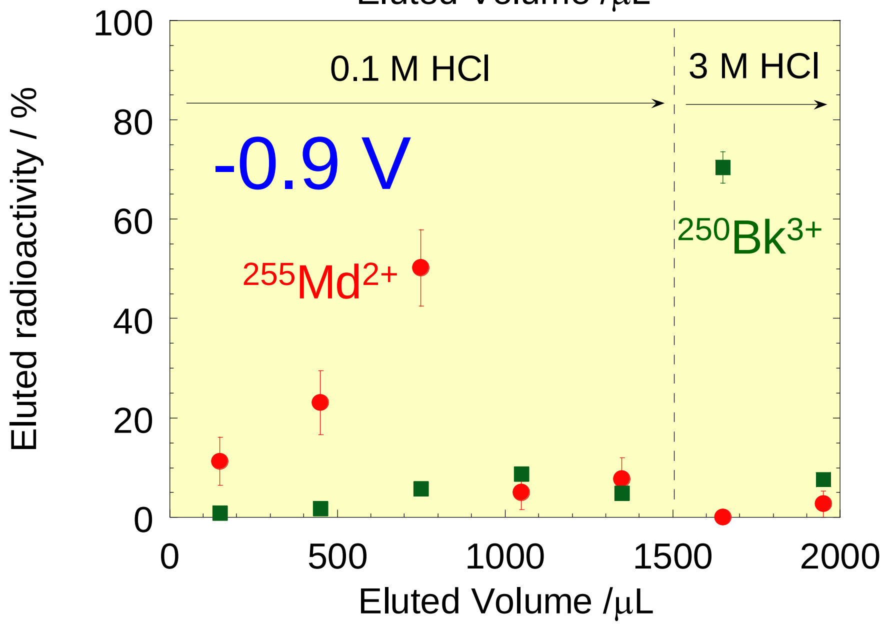
Reduction experiment of Md



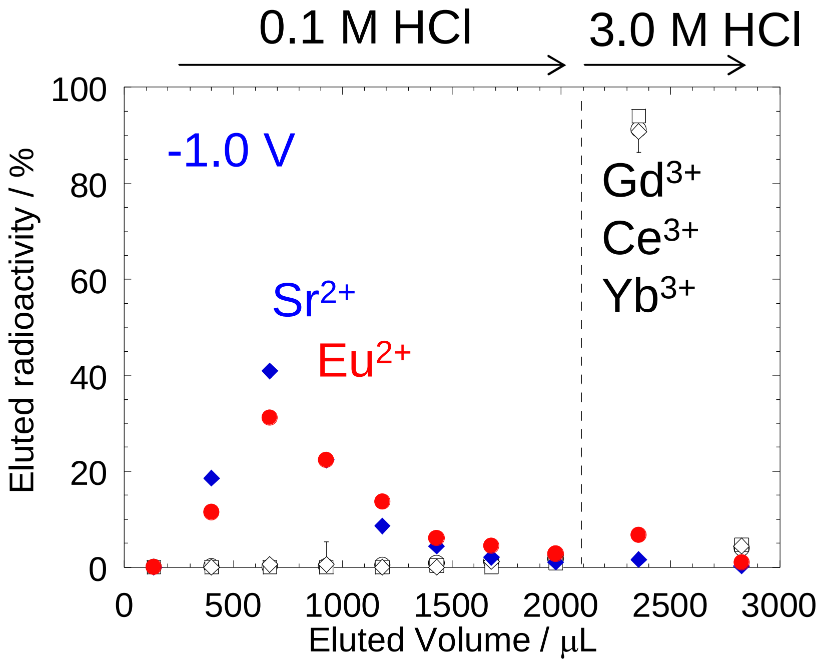
These procedures are accomplished within 15 min.

Elution behavior of Md



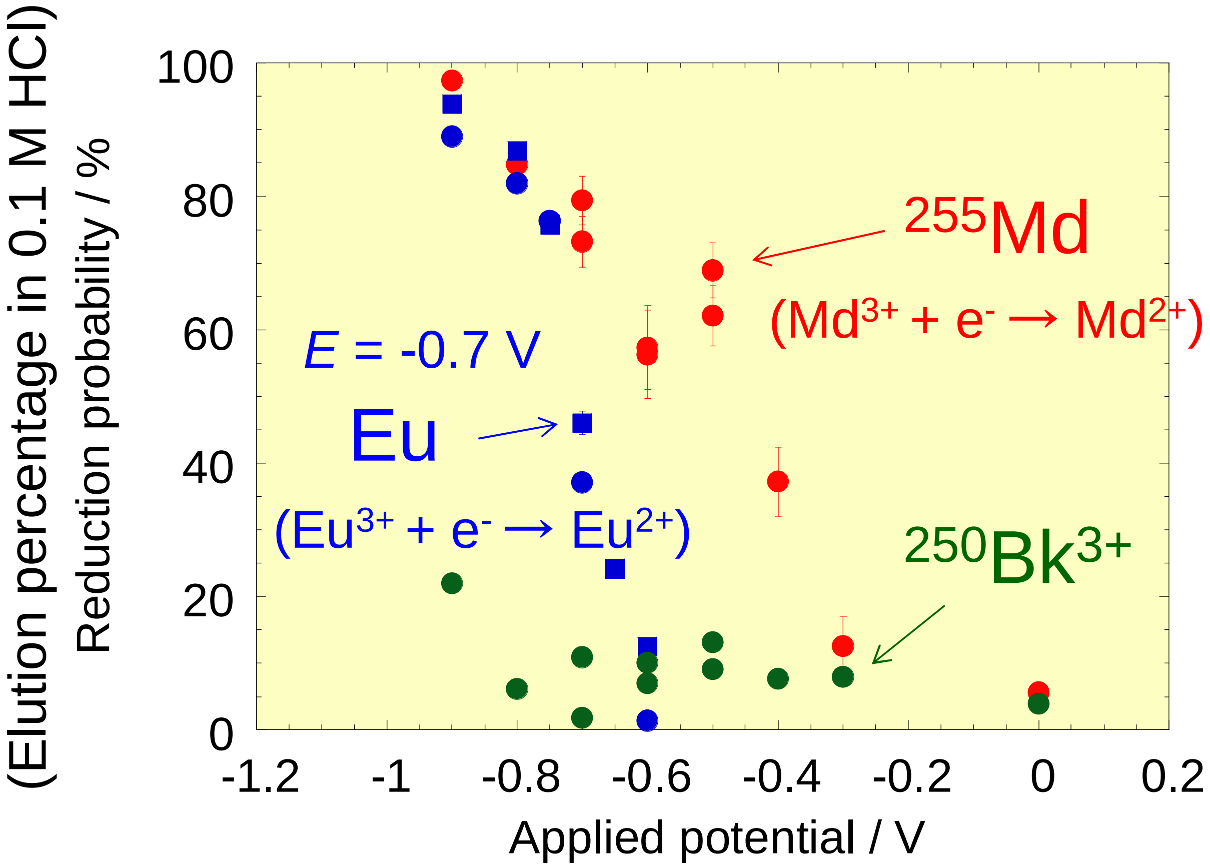


Elution behavior of Sr^{2+}, Eu^{2+}, Gd^{3+}, Ce^{3+}, and Yb^{3+} measured in a separate off-line experiment



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

Reduction probability



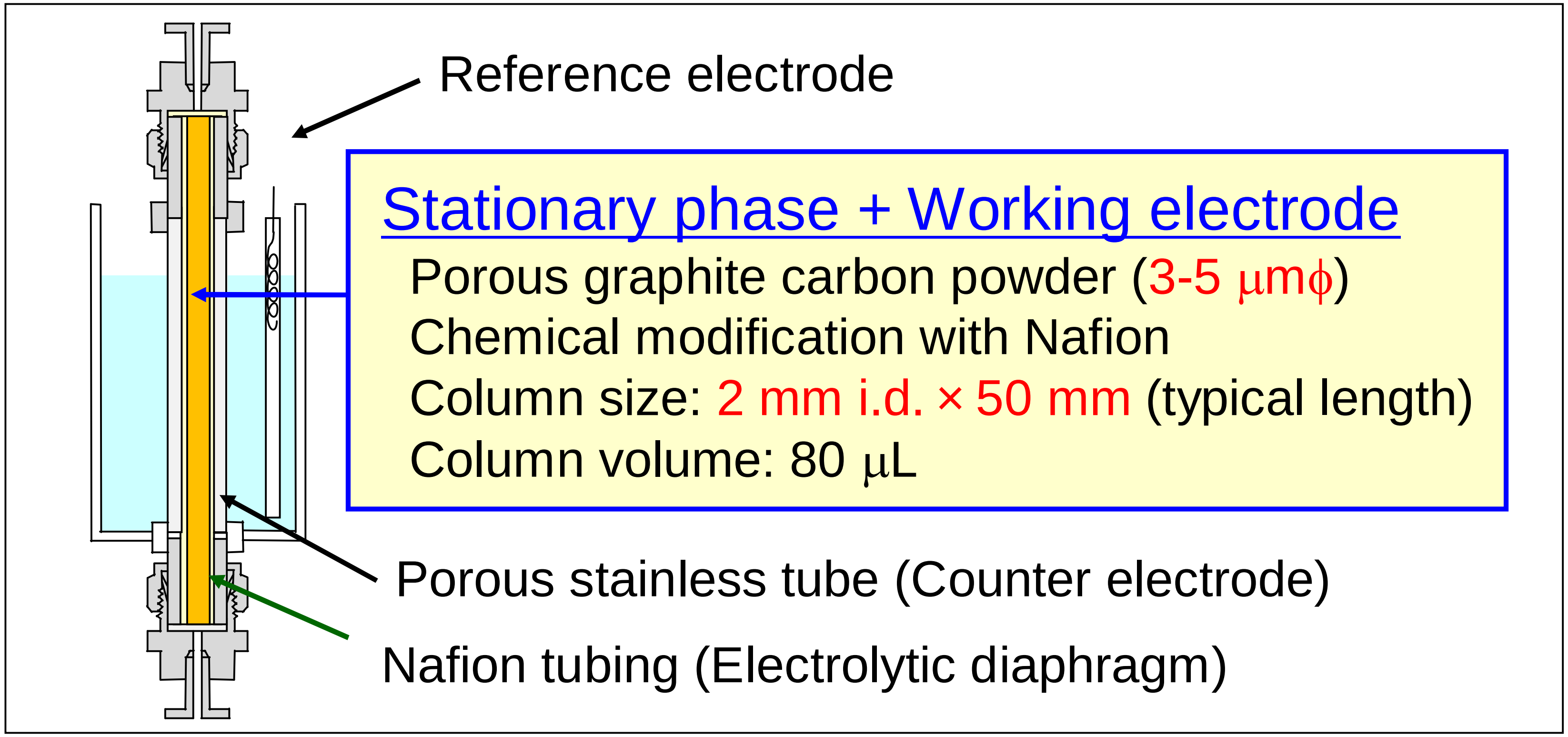
- The redox potential of Eu of -0.7 V agrees well with a result of cyclic voltammetry measurement with 0.01 M Eu.
- Gentle reducuction of Md
  →Incomplete removing of dissolved oxygen?
  Md experiment under conditions with less dissolved oxygen

Summary

- The electrochemistry apparatus available for single atoms was developed.
- Electrochemical oxidation of No^{2+} to No^{3+} was successfully performed.
- Md^{3+} was reduced to Md^{2+}.
- We will carry out reduction experiments of Md under conditions with less dissolved oxygen to determine its redox potential.

Future plans

- Development of an electrochemical chromatographic apparatus *with higher separation ability and smaller column volume*



➢ Ionic radius of No^{3+}

➢ Reduction studies of Db^{5+} and Sg^{6+}

Thank you for your attention.