Development of a rapid solvent extraction apparatus for aqueous chemistry of the heaviest elements

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(The SHE aqueous chemistry collaboration at GARIS)

Introduction: Aqueous chemistry of SHEs

Chemistry of SHEs

104 Rf	105 Db	106 Sg	107 Bh	108 Hs	112 Cn	113	114 Fl

Gas: Z = 104–108, 112–114
Aqueous: Z = 104–106

Nuclide	Half-life	Production rate*
^{261}Rf[a]	68 s	420 atoms/h
^{262}Db	34 s	70 atoms/h
^{265}Sg[a,b]	8.5 s/14.4 s	12 atoms/h
^{266}Bh	10.7 s	1.7 atoms/h

* ^{248}Cm target thickness: 300 μg/cm^2; Beam intensity: 2 pμA

Pioneering cation-exchange studies of Sg in HNO_3/HF and HNO_3
Schädel et al., Radiochim. Acta **77**, 149 (1997).; Radiochim. Acta **83**, 163 (1998).

Conventional aqueous chemistry apparatus used for Rf, Db, and Sg
ARCA and AIDA: batch-wise column chromatography apparatuses with Si detectors for α/SF spectrometry

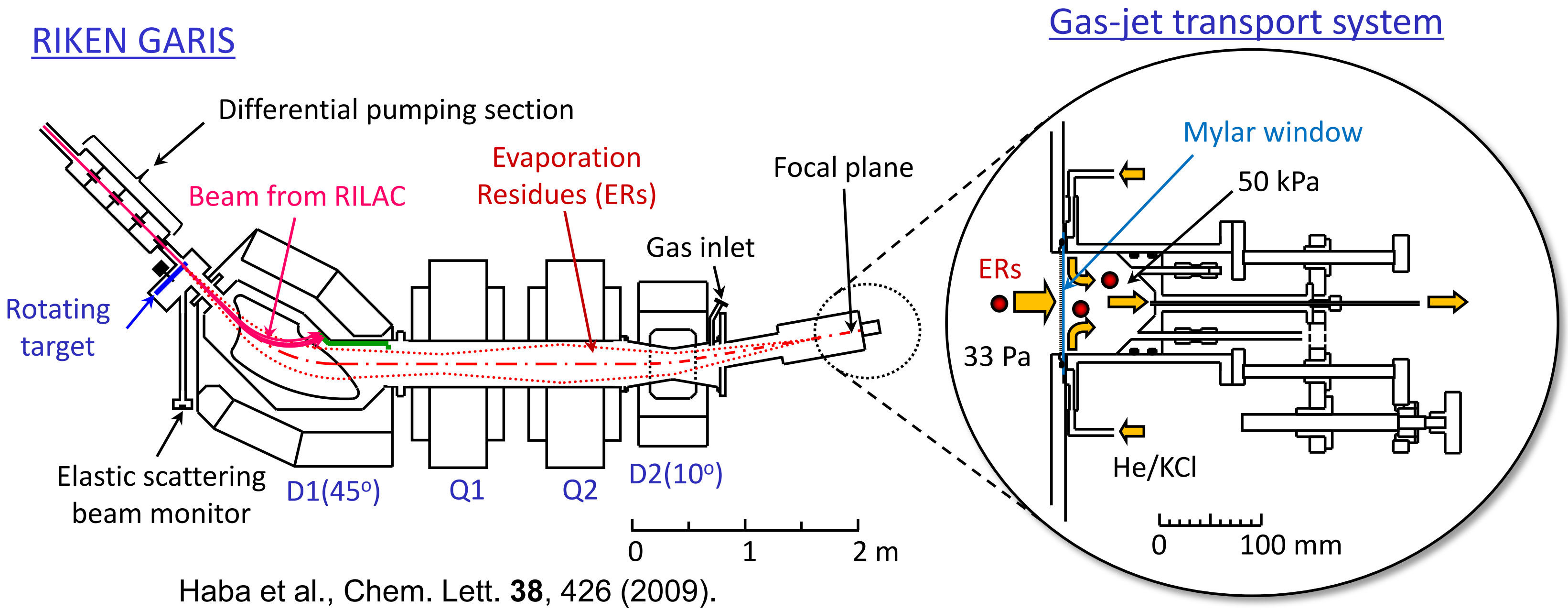
- Decay loss during aerosol collection (~30 s)
- Decay loss during α-source preparation (~30 s)
- Low detection efficiency: eff.(α) = ~30%
  → eff.(α-α) = ~9%; eff.(α-α-α) = ~3%
- A huge amount of background radioactivities of by-products

RIKEN GARIS gas-jet system

<u>Requirements for aqueous chemistry studies of Sg and the heavier SHEs:</u>

- **Continuous and rapid chemical separation**
- **Rapid and efficient α/SF detection under low-background condition**

<u>GARIS gas-jet system is ready for SHE chemistry at RIKEN:</u>

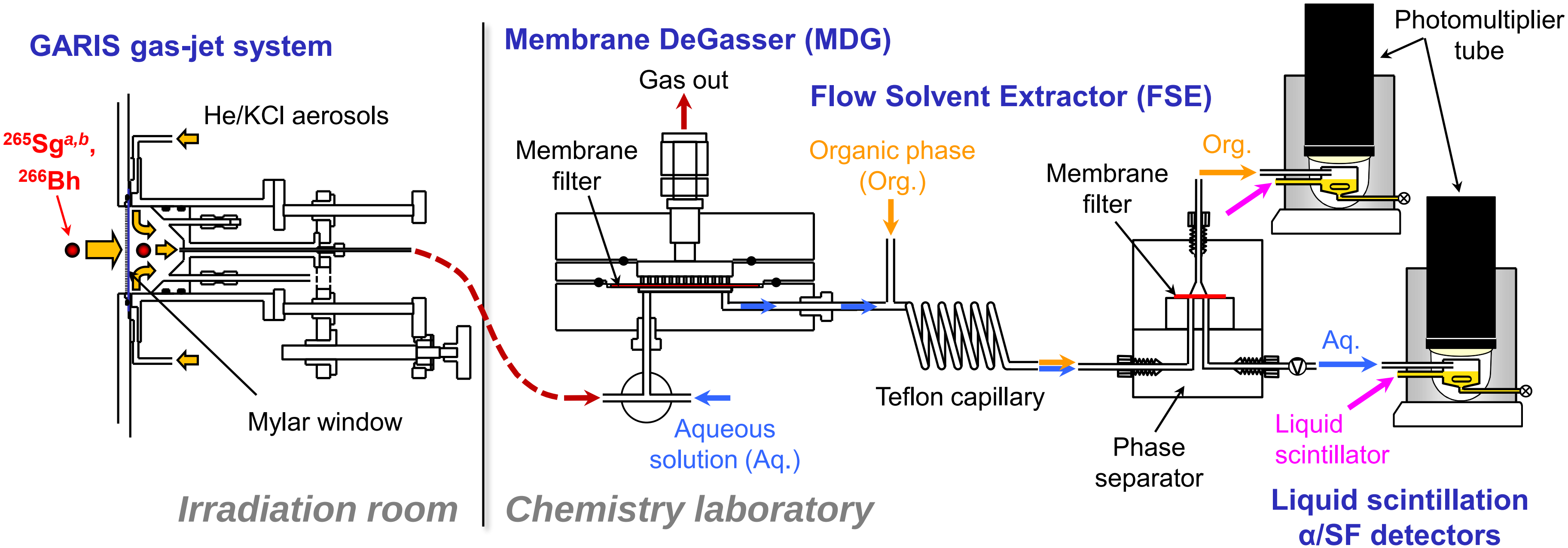


Haba et al., Chem. Lett. **38**, 426 (2009).

- By-products can be removed almost completely.
- Liquid scintillation (LS) detectors with a high detection efficiency (~100%) will become available for aqueous chemistry of SHEs.

Purpose of this study

Development of a continuous and rapid solvent extraction apparatus coupled to the GARIS gas-jet system for aqueous chemistry of the heaviest SHEs



Continuous dissolution (MDG), solvent extraction (FSE), and radiation detection with a flow LS detector

- **Rapid chemical separation and α-source preparation**
  → Minimum decay loss
- **High-detection efficiency (~100%) for α-α and α-SF correlations**

Feasibility of aqueous chemistry of Sg and Bh

Production and decay studies of $^{265}Sg^{a,b}$ ($T_{1/2}$ = 8.5 s,14.4 s) and ^{266}Bh (10.7 s):

$^{248}Cm(^{22}Ne,5n)^{265}Sg^{a,b}$ Haba et al., Phys. Rev. C **85**, 024611 (2012).

$^{248}Cm(^{23}Na,5n)^{266}Bh$ Haba et al., TASCA15 contribution.

Continuous solvent extraction and LS detection (Present apparatus)

Nuclide	$T_{1/2}$ [s]	σ [pb]	Target [μg/cm^2]	Beam [pμA]	Cool. T. [s]	Chem. Y. [%]	Detec. eff.* [%]	Event rate [/d]
$^{265}Sg^{a}$	8.5	180	300	4	10	50	100	**3.2**
$^{265}Sg^{b}$	14.4	200	300	4	10	50	100	**5.3**
^{266}Bh	10.7	55	300	4	10	50	100	**1.2**

Batch-wise chemical separation (e.g. ARCA and AIDA)

Nuclide	$T_{1/2}$ [s]	σ [pb]	Target [μg/cm^2]	Beam [pμA]	Coll. T. [s]	Cool. T. [s]	Chem. Y. [%]	Detec.* eff. [%]	Event rate [/d]
$^{265}Sg^{a}$	8.5	180	300	4	30	30	50	9	**0.02**
$^{265}Sg^{b}$	14.4	200	300	4	30	30	50	9	**0.1**
^{266}Bh	10.7	55	300	4	30	30	50	9	**0.01**

* Efficiencies for α-α correlations.

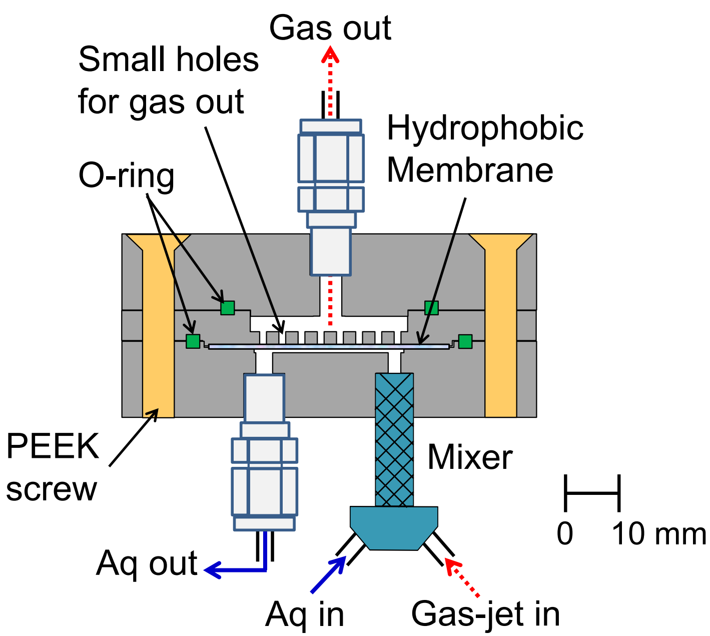
This study

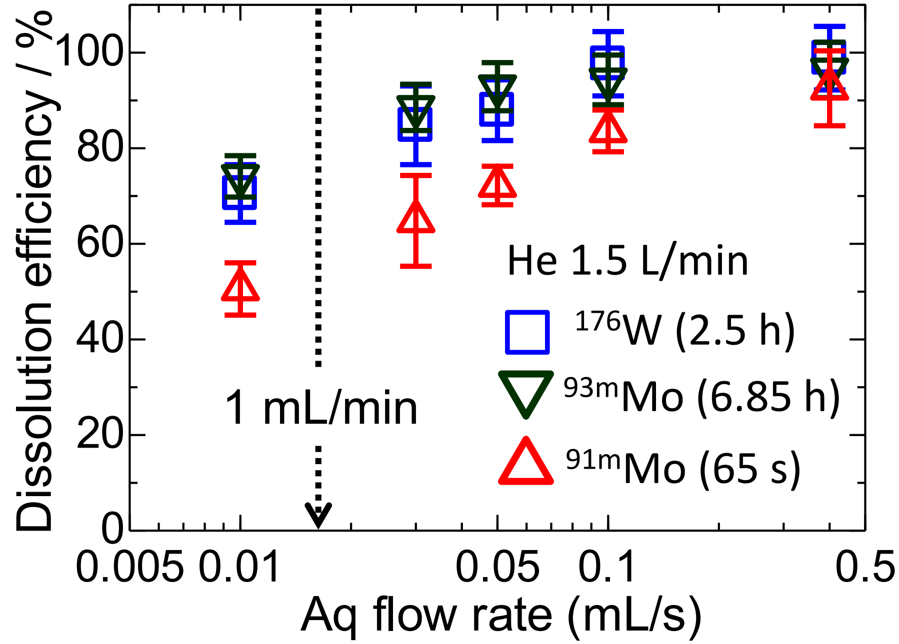
- Development of Membrane DeGasser (MDG) and Flow Solvent Extractor (FSE)
- Performance evaluation of MDG and FSE
- Online solvent extraction of Tc and Re with MDG-FSE

Development (1): MDG

Univ. Oslo/JAEA Membrane DeGasser (MDG)

Ooe et al., J. Radioanal. Nucl. Chem. **303**, 1317 (2015).





Dissolution efficiency of ^{91m}Mo ($T_{1/2}$ = 65 s):

- > 80% at high flow rates of 6–24 mL/min
- decreases with a decrease of the aq. flow rate.
  50–60% at a lower flow rate of 1 mL/min

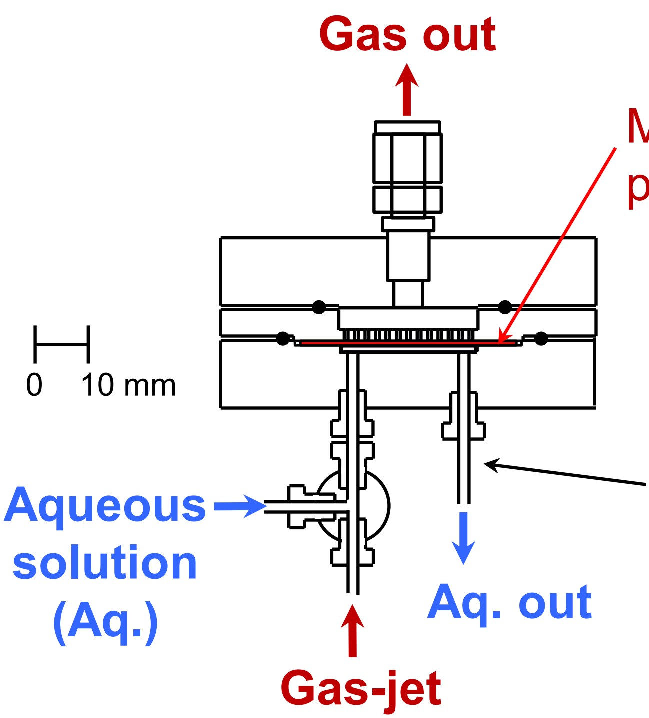
Development (1): MDG

RIKEN Membrane DeGasser (RIKEN-MDG)

A new MDG was fabricated by modifying Univ. Oslo/JAEA-MDG to dissolve shorter-lived nuclides with high efficiencies at a low flow rate of ~1 mL/min.

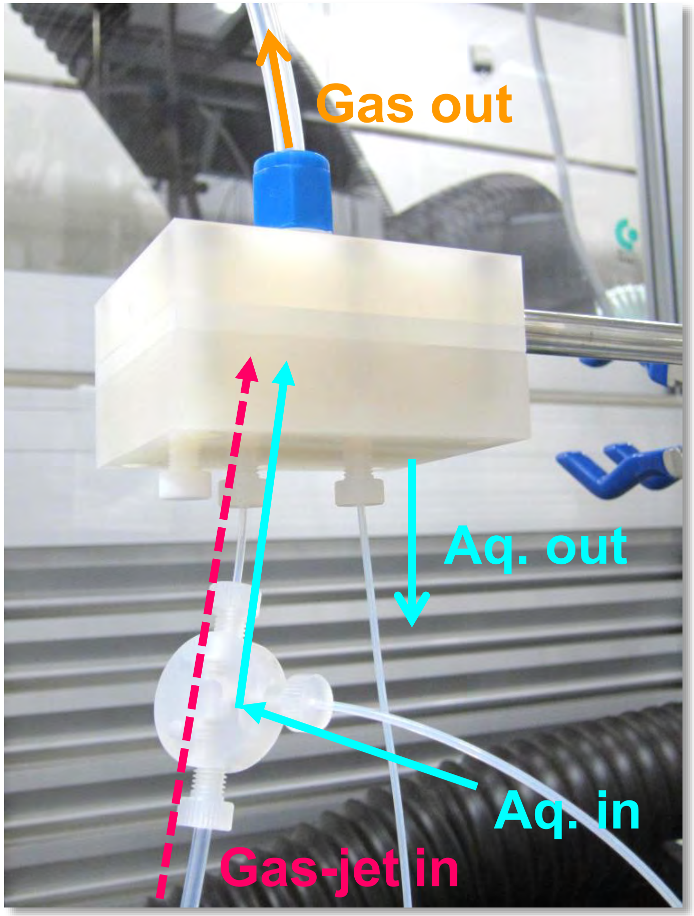
Major modifications:

- Dead volume: ~90 μL → ~23 μL
- Static mixer → Simple T-connecter



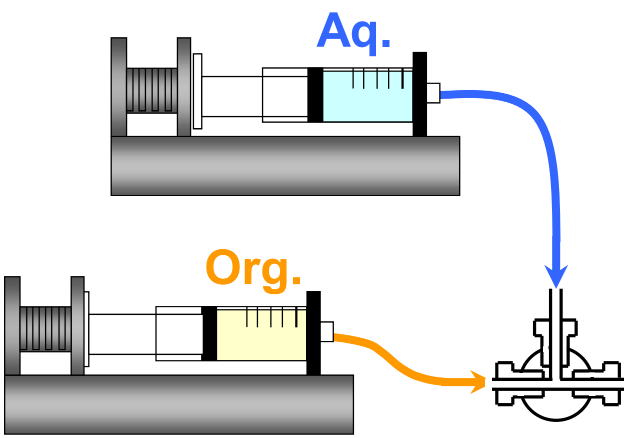
Millipore Fluoropore
No. FGLP04700
Pore size: 0.2 μm

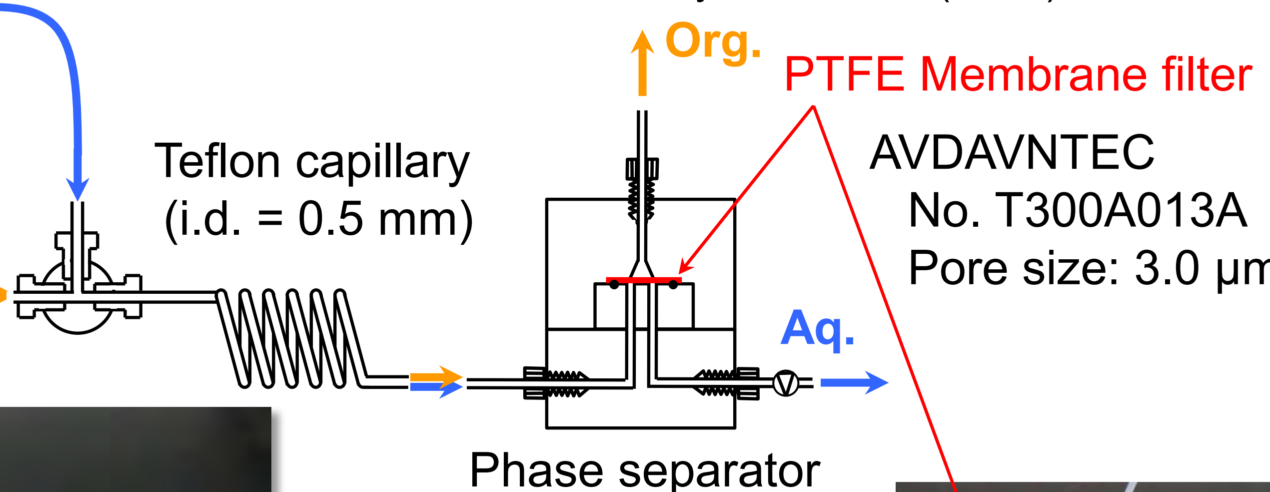
Aq. outlet capillary
(i.d. = 0.5 mm)

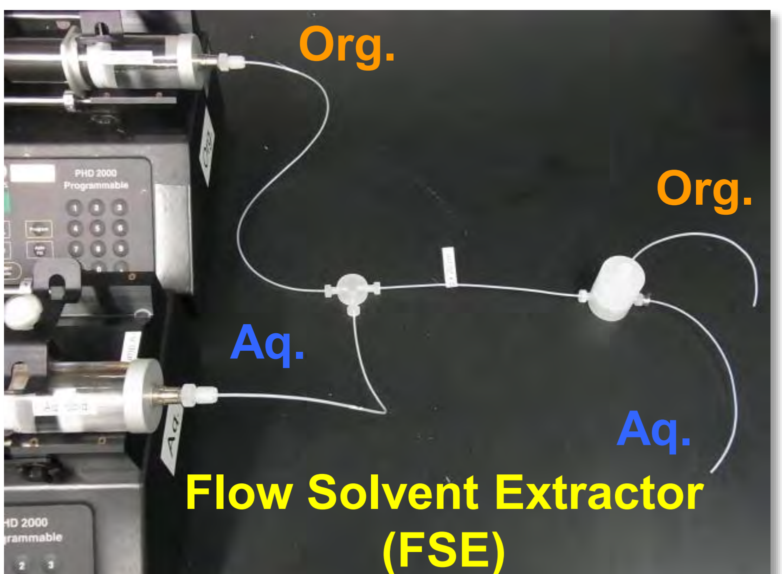


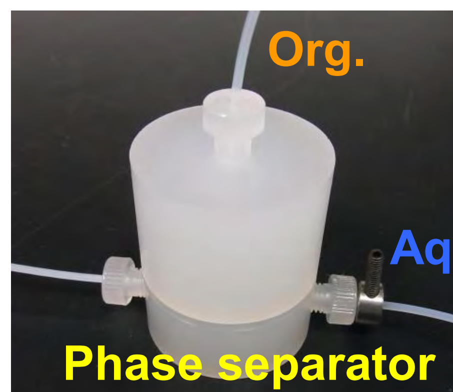
Flow Solvent Extractor (FSE)

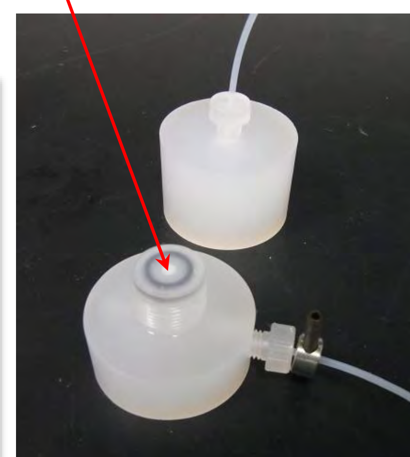
Karlberg and Thelander, Anal. Chim. Acta **98**, 1 (1978).
Bergamin et al., Anal. Chim. Acta **101**, 9 (1978).
Motomizu and Oshima, Analyst **112**, 295 (1987).



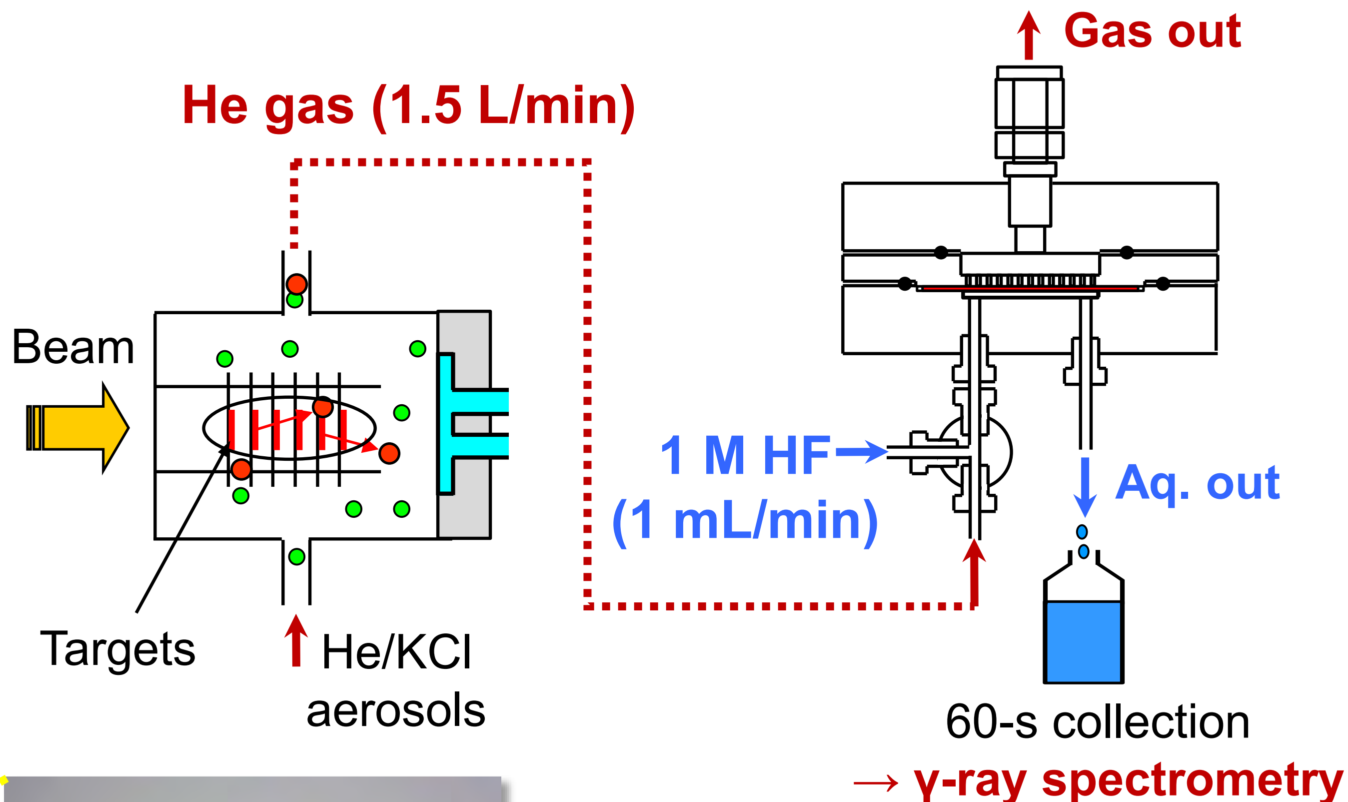


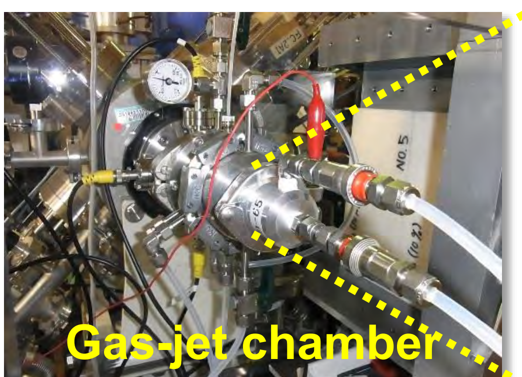


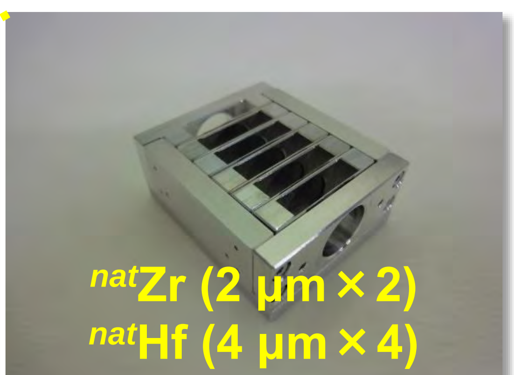




Experimental (1): Performance evaluation of MDG







Nuclear reactions:

^{nat}Zr(d,xn)^{90m}Nb ($T_{1/2}$ = 18.8 s),

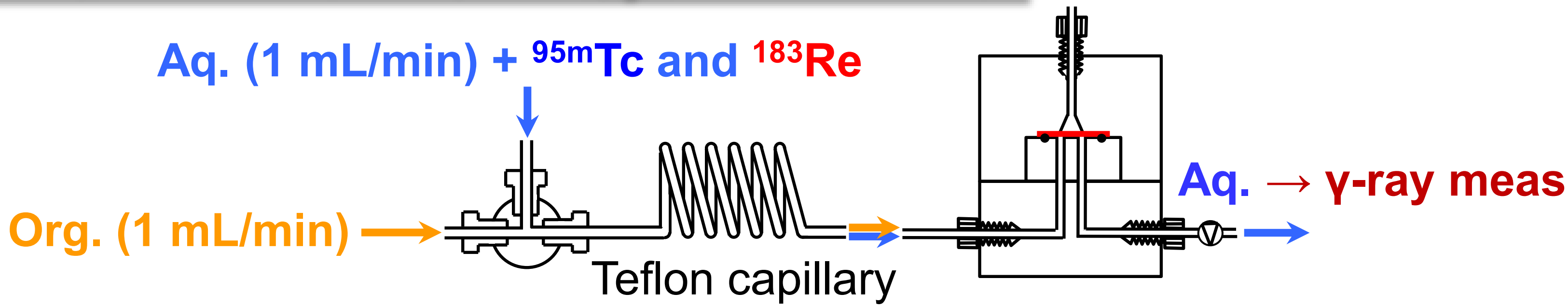
^{90g}Nb ($T_{1/2}$ = 14.6 h)

^{nat}Hf(d,xn)^{178a}Ta ($T_{1/2}$ = 2.36 h)

Experimental (2): Performance evaluation of FSE

- Production of long-lived and no-carrier-added radiotracers at RIKEN AVF: ^{nat}Mo(*d*,*xn*)^{95m}Tc ($T_{1/2}$ = 61 d) and ^{nat}W(*d*,*xn*)^{183}Re ($T_{1/2}$ = 70 d)
- Extraction with FSE: HNO_3-Tri-*n*-octylamine (TOA) / toluene

$H^+ + [MO_4]^- + TOA \rightleftharpoons [HMO_4 \cdot TOA]_{org.}$ (M = **Tc** and **Re**)

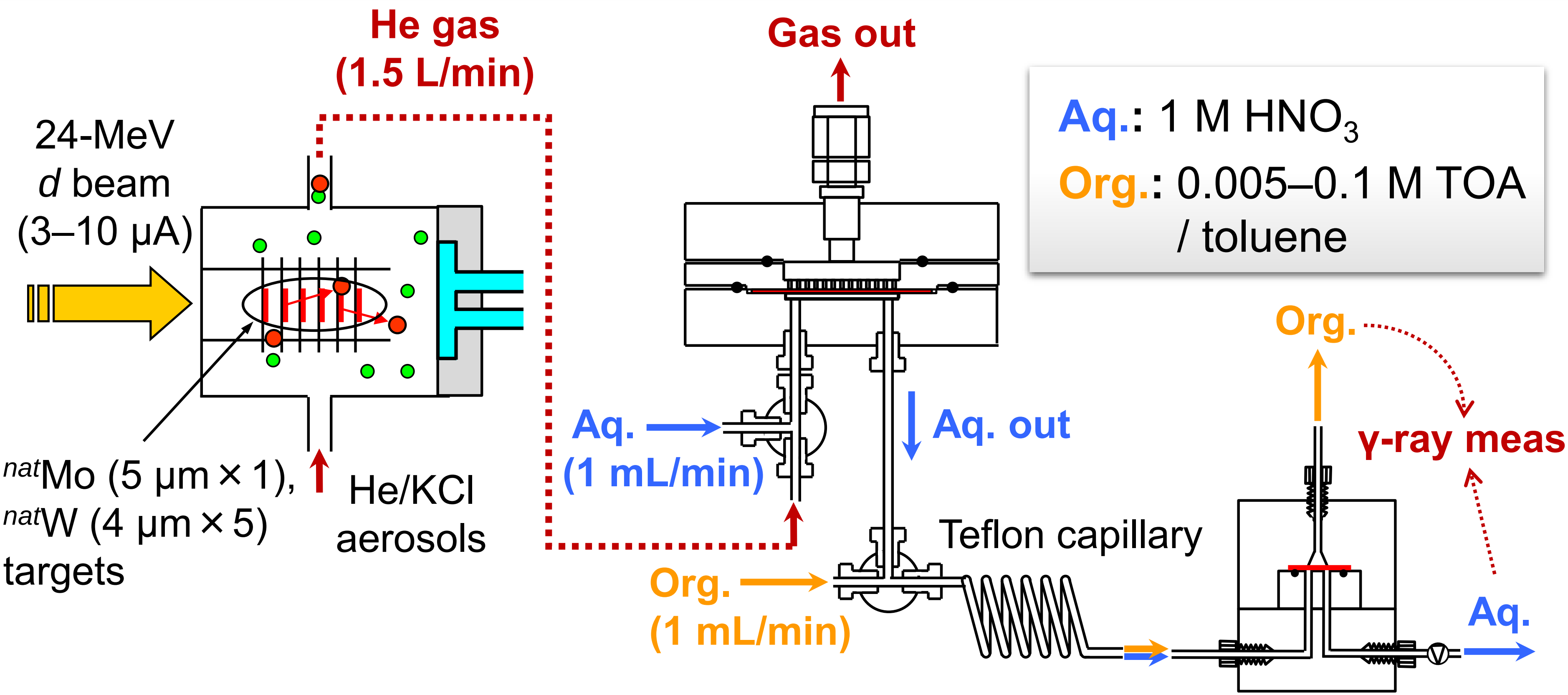


→ Determination of distribution ratio, $D = [A]_{org.}/[A]_{aq.}$; *A*: radioactivities

	***D* vs. Capillary length**	***D* vs. [TOA]**
Aq. phase	0.1, 1 M HNO_3 + ^{95m}Tc, ^{183}Re	1 M HNO_3 + ^{95m}Tc, ^{183}Re
Org. phase	0.01 M TOA / toluene	0.01, 0.05, 0.1 M TOA / toluene
Capillary length	5, 10, 20, 30, 40, 50, (60), 100 cm	100 cm

→ Comparison with *D* in equilibrium in the batch extraction (30-min shaking)

Experimental (3): Online solvent extraction of Tc and Re with MDG-FSE



Aq.: 1 M HNO_3
Org.: 0.005–0.1 M TOA / toluene

Nuclear reactions:

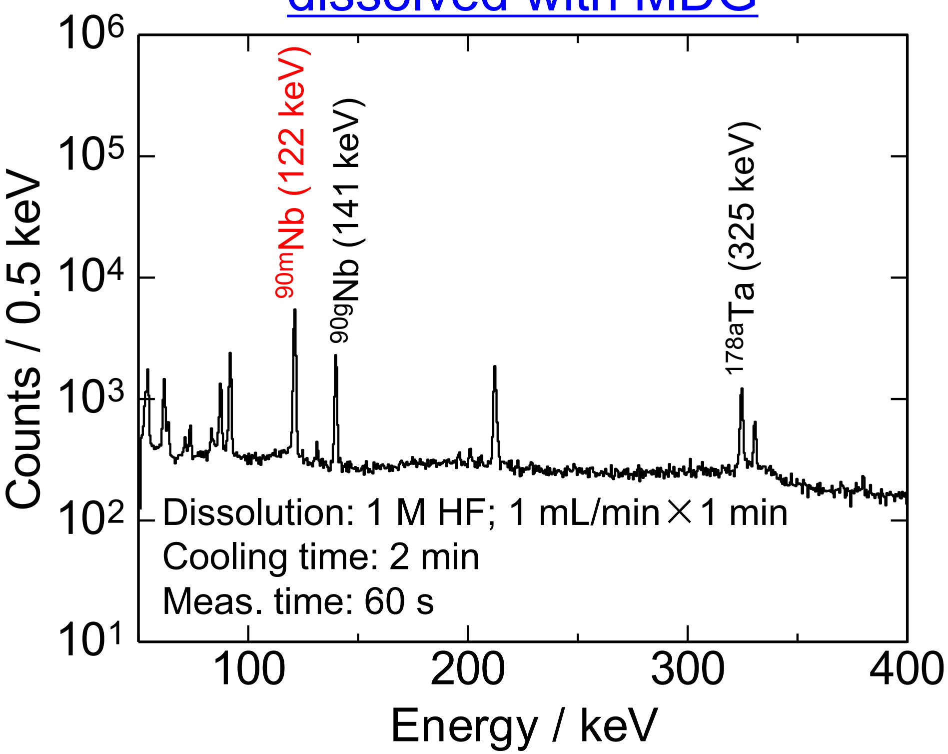
$^{nat}Mo(d,xn)^{92}Tc$ ($T_{1/2}$ = 4.25 min),
^{94g}Tc ($T_{1/2}$ = 293 min)

$^{nat}W(d,xn)^{181}Re$ ($T_{1/2}$ = 19.9 h)

- **FSE ext. (1): *D* vs. Capillary length, *L***
  L = 5, 10, 20, 30, 40, 50, 70, and 100 cm
- **FSE ext. (2): *D* vs. [TOA]**
  [TOA] = 0.005, 0.01, 0.05, and 0.1 M
- **Batch ext. (3-min shaking)**

Results and discussion (1): Performance of MDG

γ-ray spectrum of aq. solution dissolved with MDG



Dissolution efficiency with MDG

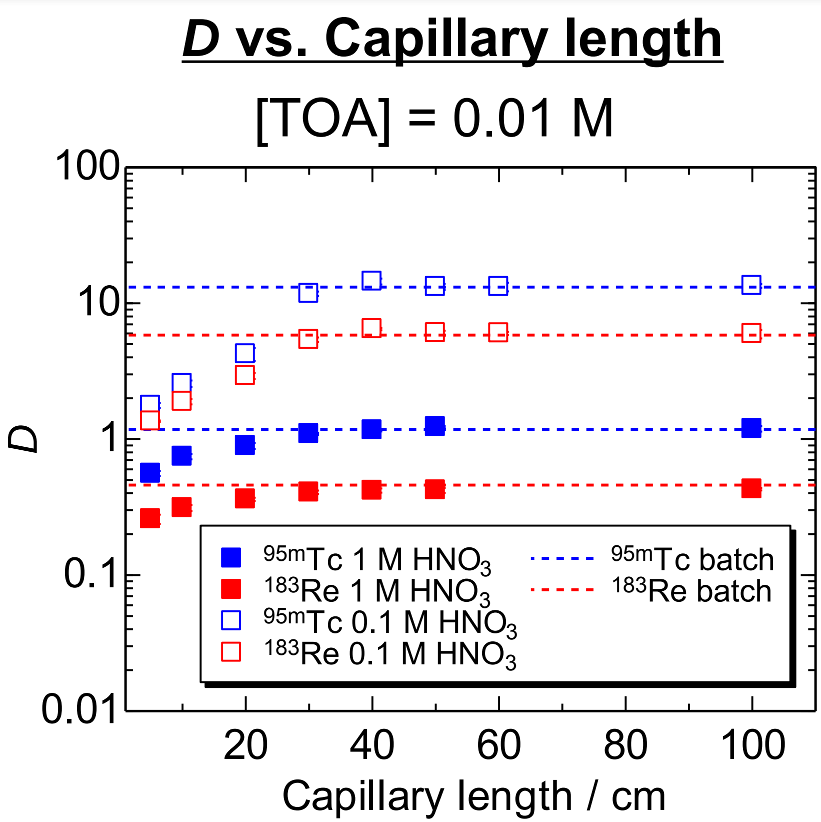
Nuclide	$T_{1/2}$	Dissolution eff.*
^{90m}Nb	18.8 s	56 ± 2%
^{90g}Nb	14.6 h	88 ± 6%
^{178a}Ta	2.36 h	82 ± 7%

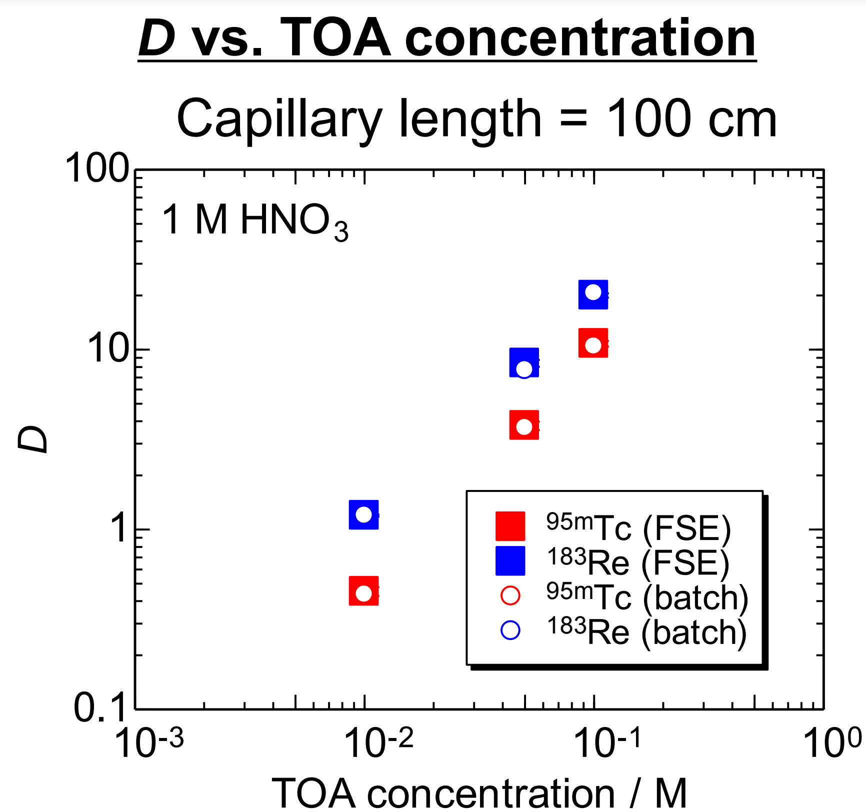
* He gas: 1.5 L/min; 1 M HF: 1 mL/min

- **The dissolution efficiency of ~60% was obtained with RIKEN-MDG for the short-lived ^{90m}Nb even at a low aq. flow rate of 1 mL/min.**

→ **Reduction of chemicals and radioactive wastes**
Reduction of quenching effects and increase of energy resolution in α/SF-spectrometry with a LS detector.

Results and discussion (2): Performance of FSE



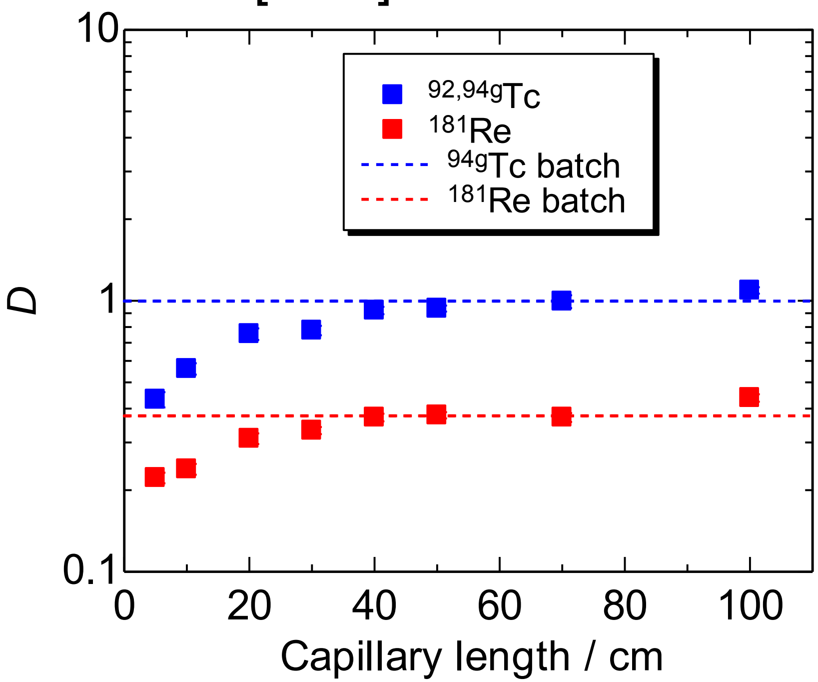


- **Extraction equilibrium is attained with the 40-cm capillary.**
  Time required for solutions to pass through the 40-cm capillary: ~2.4 s
- ***D* values with FSE consistent with those by the batch method.**
- **FSE is applicable to determine *D* values in the wide *D* range:**
  ***D* = ~0.1 – ~20.**

Results and discussion (3): Online solvent extraction of Tc and Re with MDG-FSE

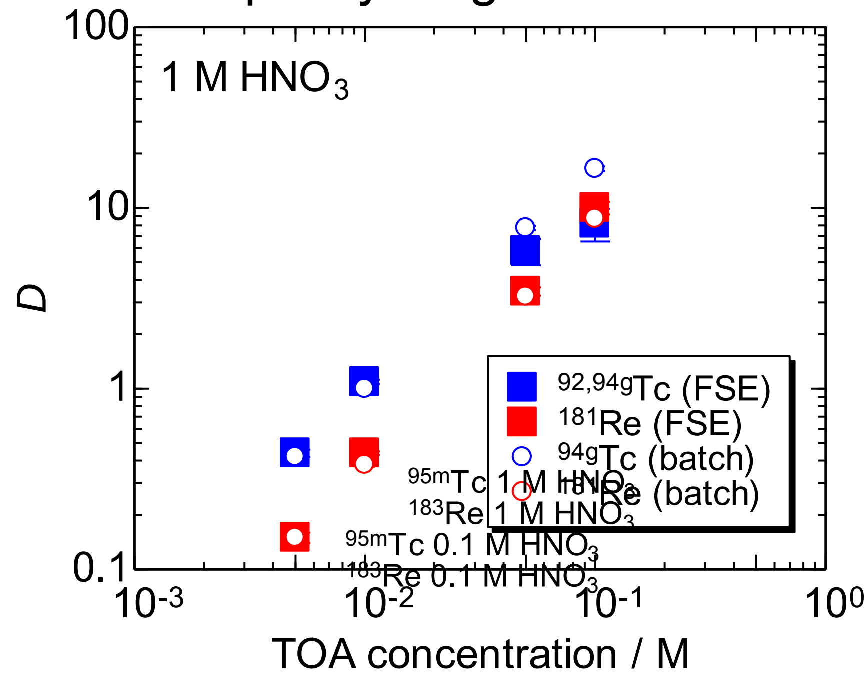
D vs. Capillary length

[TOA] = 0.01 M



D vs. TOA concentration

Capillary length = 100 cm



- **Discrepancies in *D* values between FSE and the batch extractions were found for ^{92,94g}Tc at [TOA] > 0.05 M.**

Time / s

0 1 2 3 4 5 6

- **Online solvent extraction of Tc and Re was successfully performed with stable and high chemical yields: 92±3% (^{181}Re) during the 6-h beam time**

Summary

- We have developed a new rapid chemistry apparatus which consists of MDG and FSE for the aqueous chemistry studies of Sg and Bh at GARIS.
- Online solvent extraction of Tc and Re was successfully performed with MDG-FSE in HNO_3-TOA/toluene.
  - Rapid extraction equilibrium: ~2.4 s (40-cm capillary)
  - Wide applicable *D* range: *D* = ~0.1 – ~20
  - High chemical yield: > 90% (^{181}Re)
  - Stable running: > 6 h
  - Low flow rate: 1 mL/min
- A flow liquid scintillation detector will be developed by referring to the knowhow from SISAK.
- Interesting chemistry systems for Sg and Bh are under study using radiotracers of their homologues.

Collaborators for the aqueous chemistry at GARIS

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