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**

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Half-life</th>
<th>Production rate*</th>
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<tbody>
<tr>
<td>$^{261}$Rf&lt;sup&gt;a&lt;/sup&gt;</td>
<td>68 s</td>
<td>420 atoms/h</td>
</tr>
<tr>
<td>$^{262}$Db</td>
<td>34 s</td>
<td>70 atoms/h</td>
</tr>
<tr>
<td>$^{265}$Sg&lt;sup&gt;a,b&lt;/sup&gt;</td>
<td>8.5 s/14.4 s</td>
<td>12 atoms/h</td>
</tr>
<tr>
<td>$^{266}$Bh</td>
<td>10.7 s</td>
<td>1.7 atoms/h</td>
</tr>
</tbody>
</table>

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

**Gas: $Z = 104$–$108$, $112$–$114$**

**Aqueous: $Z = 104$–$106$**

Pioneering cation-exchange studies of Sg in HNO<sub>3</sub>/HF and HNO<sub>3</sub>


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

Requirements for aqueous chemistry studies of Sg and the heavier SHEs:

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

GARIS gas-jet system is ready for SHE chemistry at RIKEN:

- 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.

Haba et al., Chem. Lett. 38, 426 (2009).
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 $\alpha$-source preparation
  - Minimum decay loss
- High-detection efficiency ($\sim$100%) for $\alpha$-$\alpha$ and $\alpha$-SF correlations
Feasibility of aqueous chemistry of Sg and Bh

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

$^{248}$Cm($^{22}$Ne,5$n$)$^{265}$Sg $^{a,b}$  

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

Continuous solvent extraction and LS detection (Present apparatus)

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</thead>
<tbody>
<tr>
<td>$^{265}$Sg$^a$</td>
<td>8.5</td>
<td>180</td>
<td>300</td>
<td>4</td>
<td>10</td>
<td>50</td>
<td>100</td>
<td>3.2</td>
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<tr>
<td>$^{265}$Sg$^b$</td>
<td>14.4</td>
<td>200</td>
<td>300</td>
<td>4</td>
<td>10</td>
<td>50</td>
<td>100</td>
<td>5.3</td>
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<tr>
<td>$^{266}$Bh</td>
<td>10.7</td>
<td>55</td>
<td>300</td>
<td>4</td>
<td>10</td>
<td>50</td>
<td>100</td>
<td>1.2</td>
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Batch-wise chemical separation (e.g. ARCA and AIDA)

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<td>8.5</td>
<td>180</td>
<td>300</td>
<td>4</td>
<td>30</td>
<td>30</td>
<td>50</td>
<td>9</td>
<td>0.02</td>
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<tr>
<td>$^{265}$Sg$^b$</td>
<td>14.4</td>
<td>200</td>
<td>300</td>
<td>4</td>
<td>30</td>
<td>30</td>
<td>50</td>
<td>9</td>
<td>0.1</td>
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<tr>
<td>$^{266}$Bh</td>
<td>10.7</td>
<td>55</td>
<td>300</td>
<td>4</td>
<td>30</td>
<td>30</td>
<td>50</td>
<td>9</td>
<td>0.01</td>
</tr>
</tbody>
</table>

* Efficiencies for $\alpha-\alpha$ 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
Univ. Oslo/JAEA Membrane DeGasser (MDG)


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
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.

**RIKEN Membrane DeGasser (RIKEN-MDG)**

Major modifications:
- Dead volume: ~90 μL → ~23 μL
- Static mixer → Simple T-connector

**Diagram:**
- Membrane filter with polyethylene support
- Millipore Fluoropore No. FGLP04700
- Pore size: 0.2 μm
- Aq. outlet capillary (i.d. = 0.5 mm)
Flow Solvent Extractor (FSE)

Development (2): FSE

Experimental (1): Performance evaluation of MDG

24-MeV $d$ beam (5 µA)
RIKEN AVF cyclotron

Gas-jet chamber

He gas (1.5 L/min)

Beam
Targets

He/KCl aerosols

Nuclear reactions:

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

$^{90}\text{Nb} \quad (T_{1/2} = 14.6 \text{ h})$

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

Gas out
Aq. out

60-s collection → γ-ray spectrometry
Experimental (2): Performance evaluation of FSE

- Production of long-lived and no-carrier-added radiotracers at RIKEN AVF: natMo(d,xn)⁹⁵mTc (T₁/₂ = 61 d) and natW(d,xn)¹⁸³Re (T₁/₂ = 70 d)
- Extraction with FSE: HNO₃-Tri-n-octylamine (TOA) / toluene

\[ \text{H}^+ + [\text{MO}_4^-] + \text{TOA} \rightleftharpoons [\text{HMO}_4 \cdot \text{TOA}]_{\text{org.}} \quad (M = \text{Tc and Re}) \]

→ Determination of distribution ratio, \( D = \frac{[A]_{\text{org.}}}{[A]_{\text{aq.}}} \); \( A \): radioactivities

<table>
<thead>
<tr>
<th></th>
<th>D vs. Capillary length</th>
<th>D vs. [TOA]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aq. phase</td>
<td>0.1, 1 M HNO₃ + ⁹⁵mTc, ¹⁸³Re</td>
<td>1 M HNO₃ + ⁹⁵mTc, ¹⁸³Re</td>
</tr>
<tr>
<td>Org. phase</td>
<td>0.01 M TOA / toluene</td>
<td>0.01, 0.05, 0.1 M TOA / toluene</td>
</tr>
<tr>
<td>Capillary length</td>
<td>5, 10, 20, 30, 40, 50, (60), 100 cm</td>
<td>100 cm</td>
</tr>
</tbody>
</table>

→ Comparison with \( D \) in equilibrium in the batch extraction (30-min shaking)
Experimental (3): Online solvent extraction of Tc and Re with MDG-FSE

- 24-MeV $d$ beam (3–10 $\mu$A)
- $n_{at}^{}\text{Mo (5 $\mu$m x 1), n}_{at}^{}\text{W (4 $\mu$m x 5) targets}$
- He/KCl aerosols
- He gas (1.5 L/min)
- Aq.: 1 M HNO$_3$
- Org.: 0.005–0.1 M TOA / toluene

Nuclear reactions:
- $n_{at}^{}\text{Mo}(d,xn)^{92}\text{Tc} (T_{1/2} = 4.25 \text{ min})$
- $^{94}\text{Tc} (T_{1/2} = 293 \text{ min})$
- $n_{at}^{}\text{W}(d,xn)^{181}\text{Re} (T_{1/2} = 19.9 \text{ h})$

- FSE ext. (1): $D$ vs. Capillary length, $L$
  $L = 5, 10, 20, 30, 40, 50, 70,$ and $100 \text{ cm}$
- 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

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 $\alpha$/SF-spectrometry with a LS detector.

### Dissolution efficiency with MDG

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

* He gas: 1.5 L/min; 1 M HF: 1 mL/min
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: $D = \sim 0.1 \text{ – } \sim 20$. 
Results and discussion (3): Online solvent extraction of Tc and Re with MDG-FSE

- Discrepancies in $D$ values between FSE and the batch extractions were found for $^{92,94}$Tc at [TOA] > 0.05 M.
- Online solvent extraction of Tc and Re was successfully performed with stable and high chemical yields: $92 \pm 3\% \left(^{181}\text{Re}\right)$ 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: $\sim$2.4 s (40-cm capillary)
  - Wide applicable $D$ range: $D = \sim$0.1 – $\sim$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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A. Sakaguchi and J. Inagaki

*Univ. Oslo*
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