18th Workshop on Targetry and Target Chemistry

New metallic germanium target fabrication and dissolution techniques for the cyclotron production of positron-emitting ^{71}As and ^{72}As

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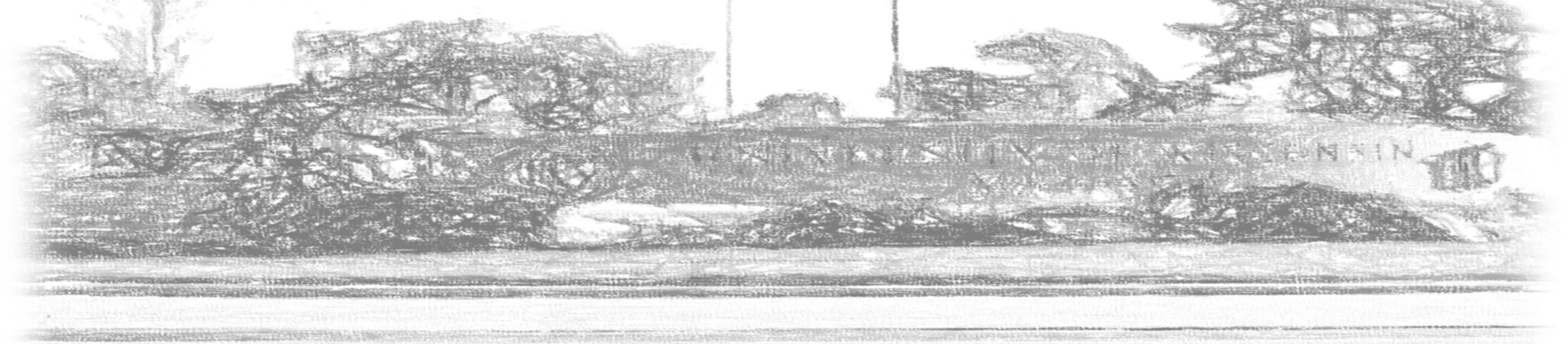


Department of Medical Physics
University of Wisconsin School of Medicine and Public Health

Research topic

^{77}As beta emitter and $^{71/72}$As positron emitter

^{72}Se 8.4 d Ec only	^{73}Se 7.2 h / 40 m	^{72}Se 0.89%	^{75}Se 119.8 d EC only	^{76}Se 9.4 %	^{77}Se 7.6 %	^{78}Se 23.8 %	^{79}Se 4 m / 3×10^{5}y
^{71}As 65.3 h β^{+}: 816 keV...	^{72}As 26 h β^{+}: 1117 keV.	^{73}As 80.3 h Ec only	^{74}As 17.8 d β^{+} / β^{-}	^{75}As 100 %	^{76}As 26.4 h β^{-}: 2962 keV	^{77}As 38.8 h β^{-}: 683 keV	^{78}As 90.7 m β^{-}: 4209 keV
^{70}Ge 20.57%	^{71}Ge 11.43d Ec only	^{72}Ge 27.45%	^{73}Ge 7.75%	^{74}Ge 36.5%	^{75}Ge 48 s / 83 m	^{76}Ge 7.73%	^{77}Ge 53 s / 11 h

^{119}Sb MAe^{-} emitter

- Homologous relationship with ^{119}Sb

N
P
As
Sb
Bi

[1] P.A. Ellison et al. Bioconjug. Chem. 27 (2016) 179–188.
[2] Y. Feng et al., Appl. Radiat. Isot. 143 (2019) 113–122.
[3] Matthew D.Gott et al., Journal of Chromatography A, 1441(2016) 68-74

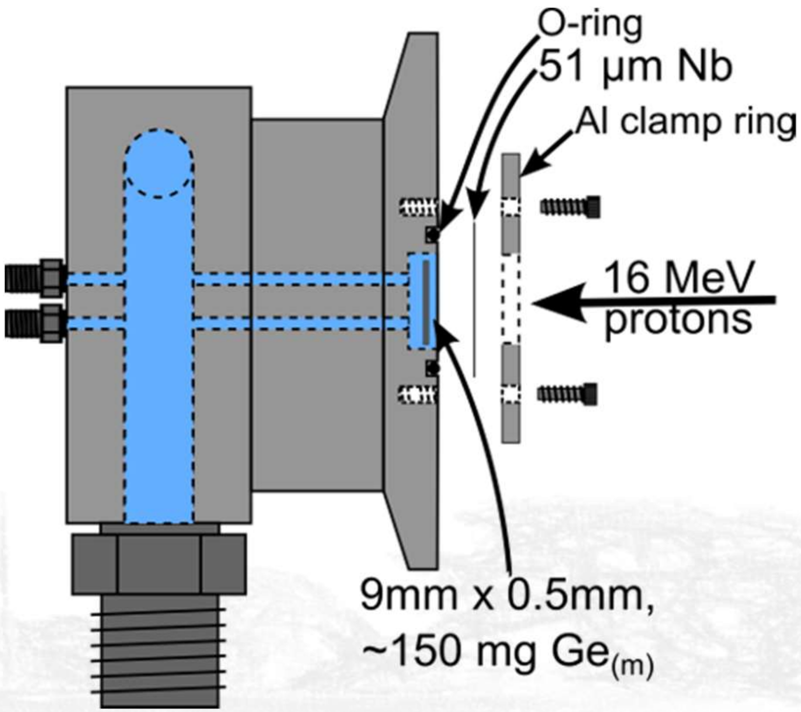
GeO_2 target

Pre irradiation: After 4 μA*

GeO_2

Difficult to dissolve it and As isolation yield deceased.

4π-water-cooled target



Problem…

Only tolerant to low beam.

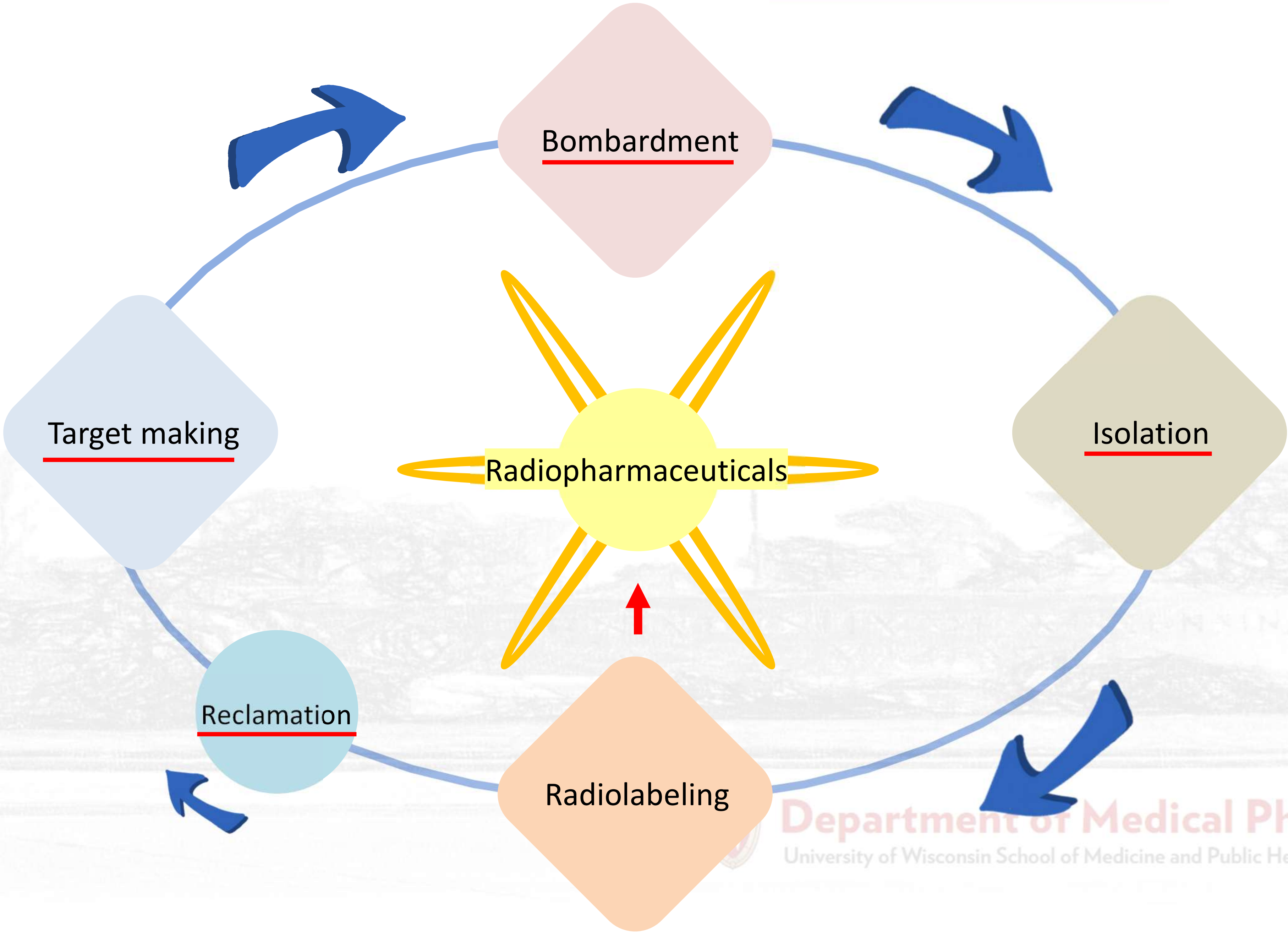
Problem…

it is incompatible with deuterons and commercial solid target irradiation systems.

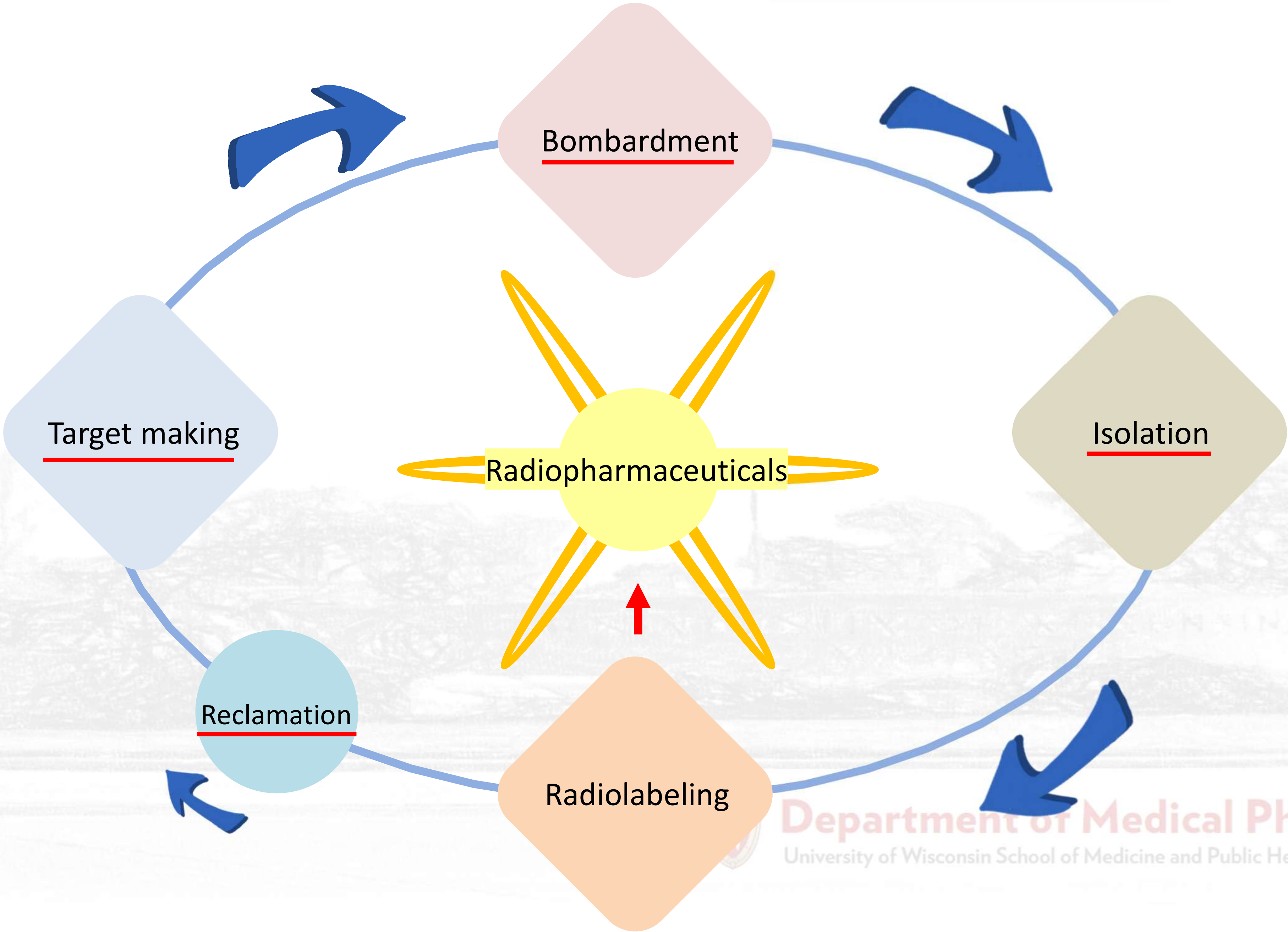
[4] P.A. Ellison et al., AIP Conf. Proc. 1509 (2012) 135-140.

[1] P.A. Ellison et al. Bioconjug. Chem. 27 (2016) 179–188.

Research topic



Research topic



Research topic

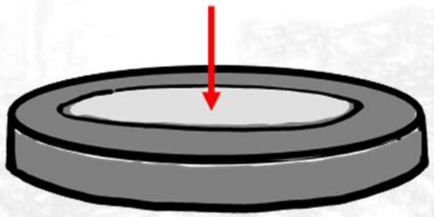
Target making

Reclamation

Bombardment

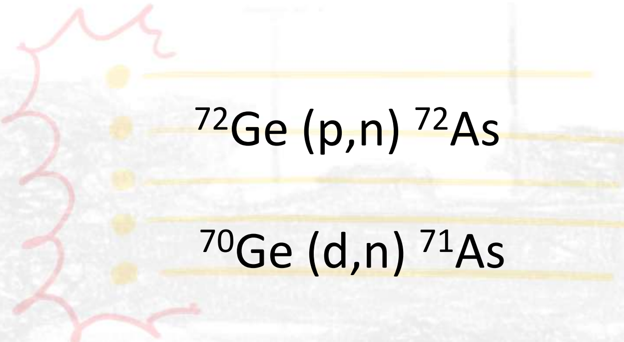
Isolation
(Cold experiment)

$^{70/72}Ge$



Target preparation

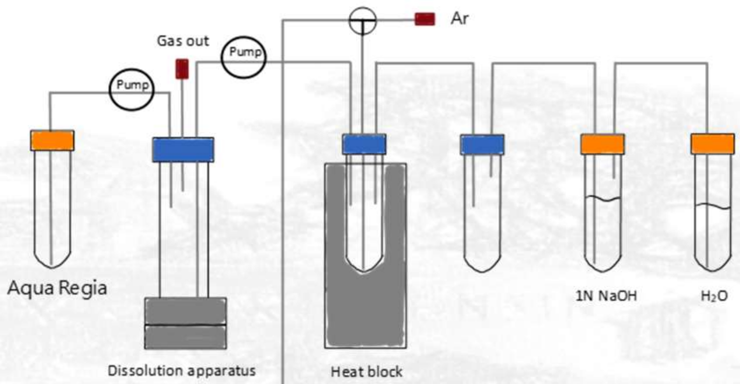
Ta coin
(⌀=10 mm, 1 mm deep)



^{72}Ge (p,n) ^{72}As

^{70}Ge (d,n) ^{71}As

Bombardment



Dissolution and Separation

Target making

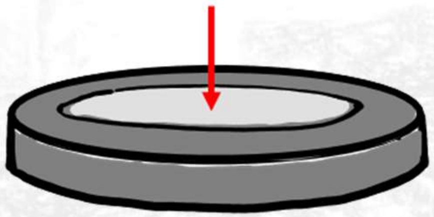
Target making

Reclamation

Bombardment

Isolation

$^{70/72}Ge$



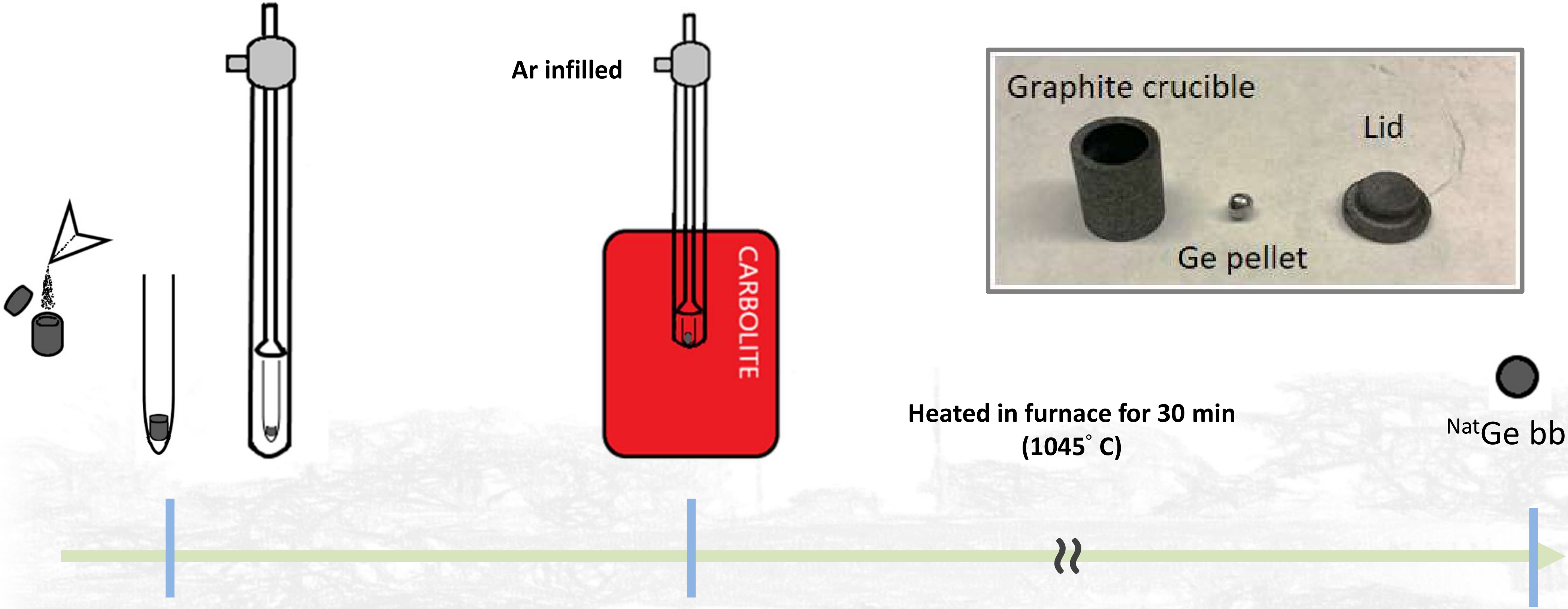
Target preparation

Ta coin
(⌀=10 mm, 1 mm deep)

Ge bb making → **Hot pressing** → **Ge Target**

Target making: Germanium bb making

Method

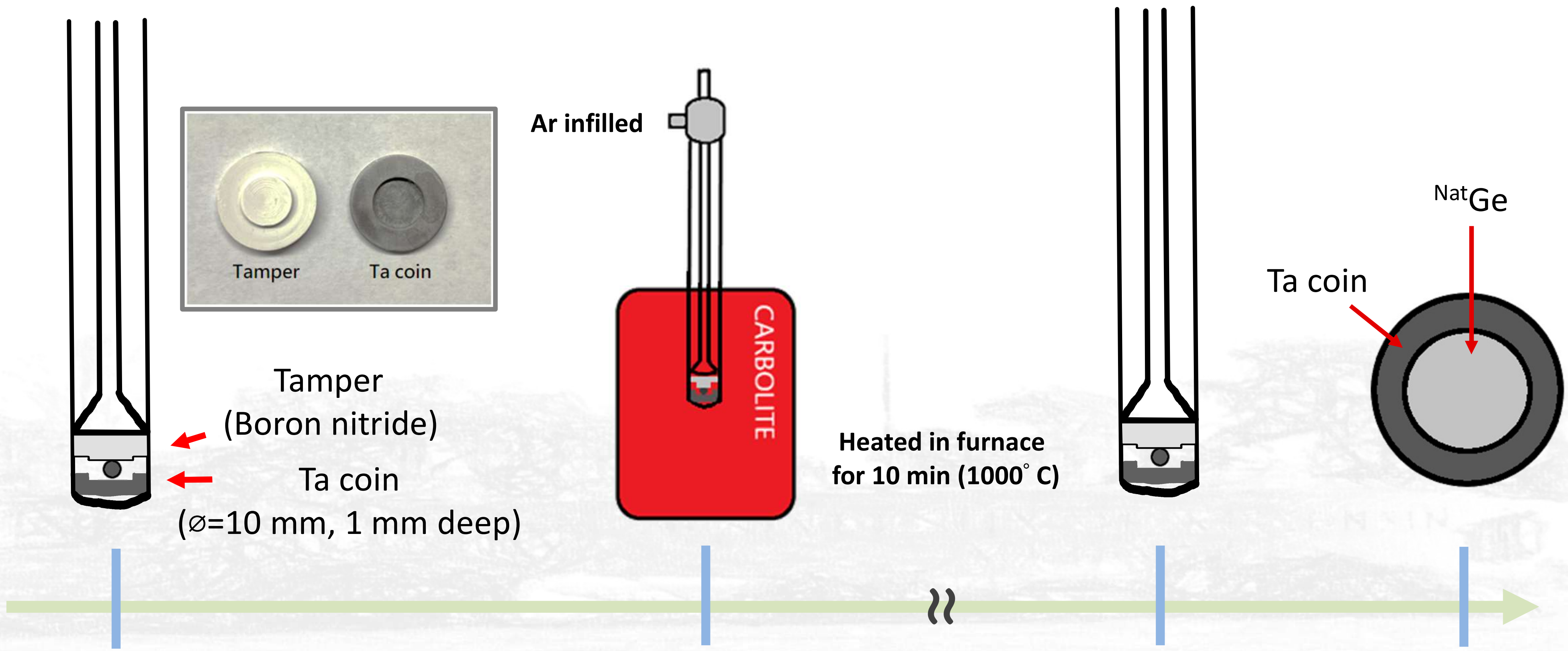


① Prepare ^{Nat}Ge (~70 mg) powder in carbon crucible.

② Use furnace to heat Ge to form Ge bb.

Target making: Ge target production

Method



① Prepare ^{Nat}Ge bb (~70mg) on Ta coin.

② Heated in furnace at 1000 ° C for 5 min

③ Hot pressing in furnace

Target making: Germanium bb making and Ge target production

Result

Ge bb making	Initial Ge powder mass (mg)	Ge Loss (mg)	Ge % Loss	
	~70	0.3 ± 0.27	0.5 ± 0.35	-
Ge-Ta target making	Initial Ge bb mass (mg)	Ge loss on target (mg)	Ge % Loss	Ge thickness (μm)
	~70	0.7 ± 0.73	0.9 ± 1.0	325 ± 44

Target making: Germanium bb making and Ge target production

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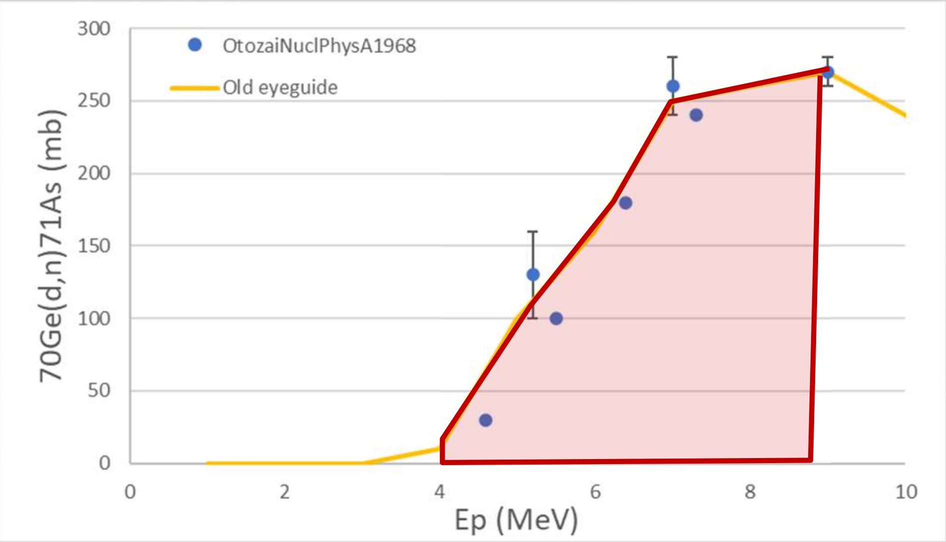


Theoretical thickness: 166 µm

$$\text{Thickness} = \frac{mass}{\rho \times area} = \frac{0.07\ g}{5.35\frac{g}{cm^3} \times 0.25\pi cm^2}$$

[5] K. Otozai, et al., Nucl. Phys. A. 107 (1968) 427–435.
[6] J.F. Ziegler et al., Nucl. Phys. B. 268 (2010) 1818–1823.

Bombardment: Irradiation study

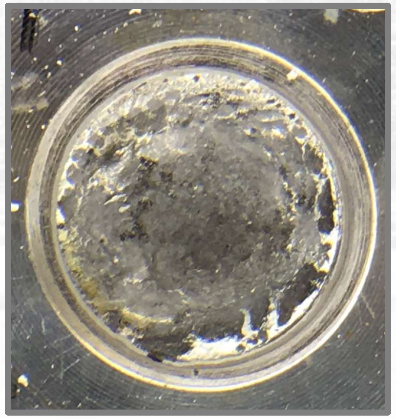
Method & Result

Irradiation condition		
Projectile	Proton	Deuteron
Energy	12 MeV	8 MeV
Current	30µA	18.5 µA
Target	^{nat}Ge	

Targetry	Reaction	Energy (MeV)	Experiment (mCi/µAh)	Theory (mCi/µAh) [5,7]
Prototype coin-type target	^{72}Ge(p,n)^{72}As	12	2.5	5.7
	^{70}Ge(d,n)^{71}As	8	0.17	0.17

*Enriched target yields extrapolated from experimental proton and deuteron irradiations of a ^{nat}Ge target

Before irradiation (proton)



After irradiation (proton)

Before irradiation (deuteron)

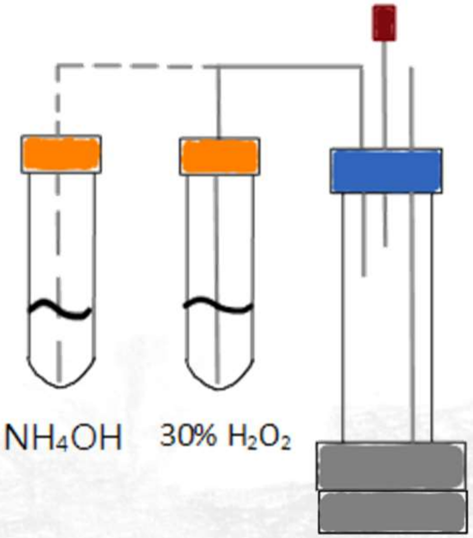
After irradiation (deuteron)

[5] K. Otozai, et al., Nucl. Phys. A. 107 (1968) 427–435. [7] I. Spahn, et al., Appl. Radiat. Isot. 65 (2007) 1057–1064

Isolation: Dissolution of Ge

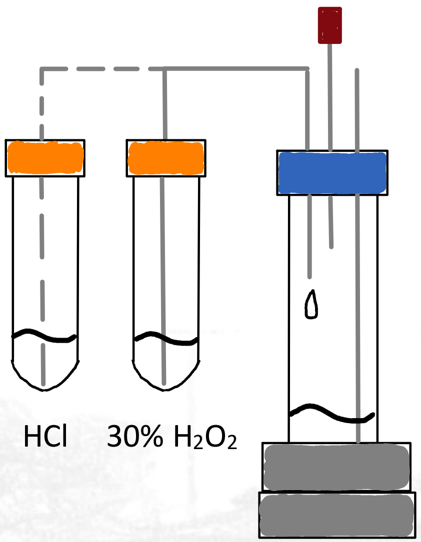
Method

NH_4OH method



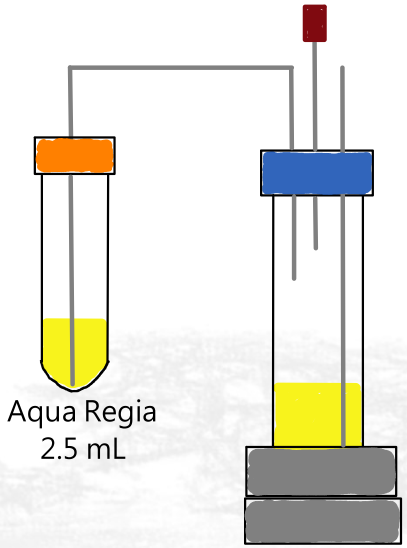
① Add 2 mL 0.48M NH_4OH in 30% H_2O_2
② Heated at 100 °C for 15 min.

HCl method



① Add 2 mL 37% HCl
② Heated at 100 °C for 15 min.
③ Dropwise addition of 2 ml of 30% H_2O_2

Aqua Regia method



① Add 2.5 mL aqua regia
② Heated at 100 °C for 30 min.

Isolation: Dissolution of Ge

Result

Condition	Ge-coated Ta coin		
Dissolution solution	0.48M NH_4OH [M] in 30% H_2O_2 [7]	37% HCl with 30% H_2O_2 [8]	Aqua regia [1]
Solution volume (mL)	2	2	2.5
Total reaction time (min)	15	15	30
Reaction Temp. (˚C)	100	100	100
Ge mass dissolved (mg)	6.9 ± 0.7 (14±2%) n=20	20.7 ± 7.4 (25±10%) n=5	153± 12 (100%) n-=6
Ta coin mass dissolved (mg)	1.1 ± 0.2 n=4	0.1± 0.1 n=3	0.0±0.1 n=3

Conclusion

- Aqua regia condition dissolved more mass of Ge than others under the same reaction time.
- No significant mass lost for Ta coin under aqua regia condition.

[8] Y. Feng et al., Appl. Radiat. Isot. 143 (2019) 113–122. [9] J. W. Irvine, Jr., J. Phys. Chem. 46, 910 (1942) 910-914

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Reclamation: Dissolution and Distillation

Method

Dissolution:

$$Ge + 4HNO_3 \longrightarrow GeO_2 + 4NO_2 + 2H_2O$$

$$GeO_2 + 4HCl \rightleftharpoons GeCl_4 + 2H_2O$$

Distillation and Hydrolysis:

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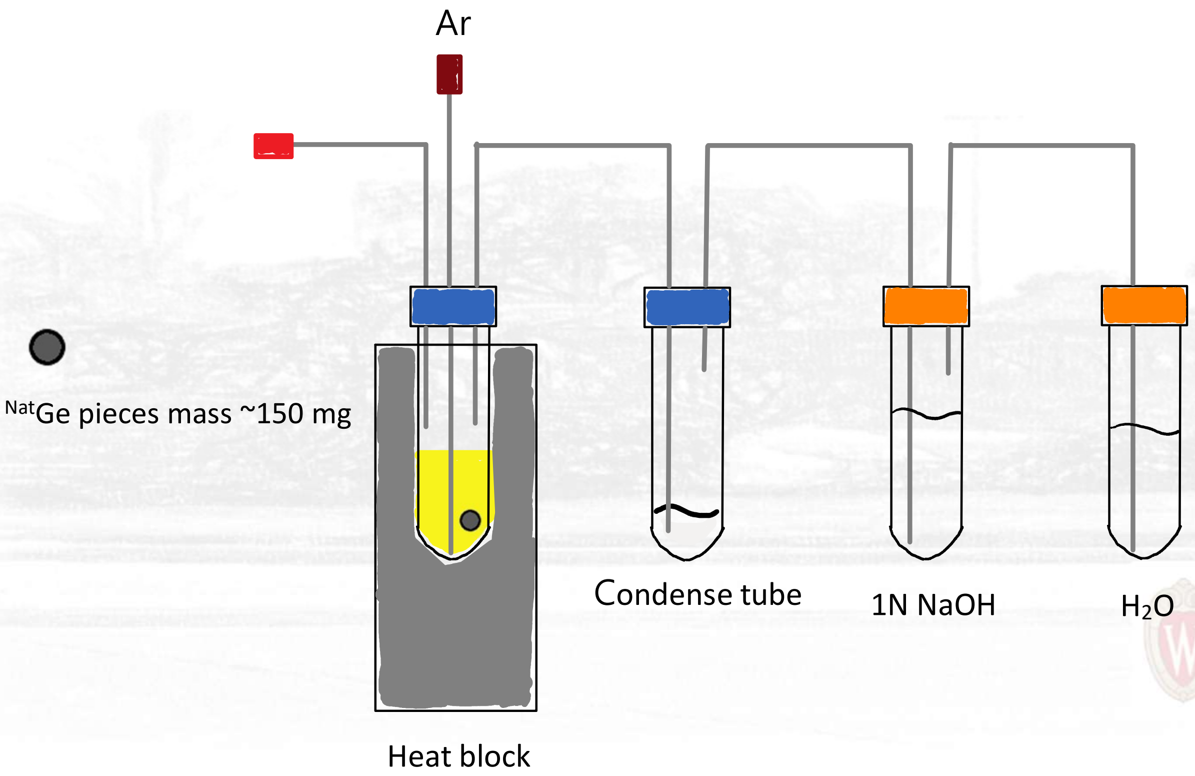
$$GeCl_4 + 2H_2O \rightleftharpoons GeO_2 + 4HCl$$



$^{71/72}AsCl_5$ would remain in heating tube during distillation

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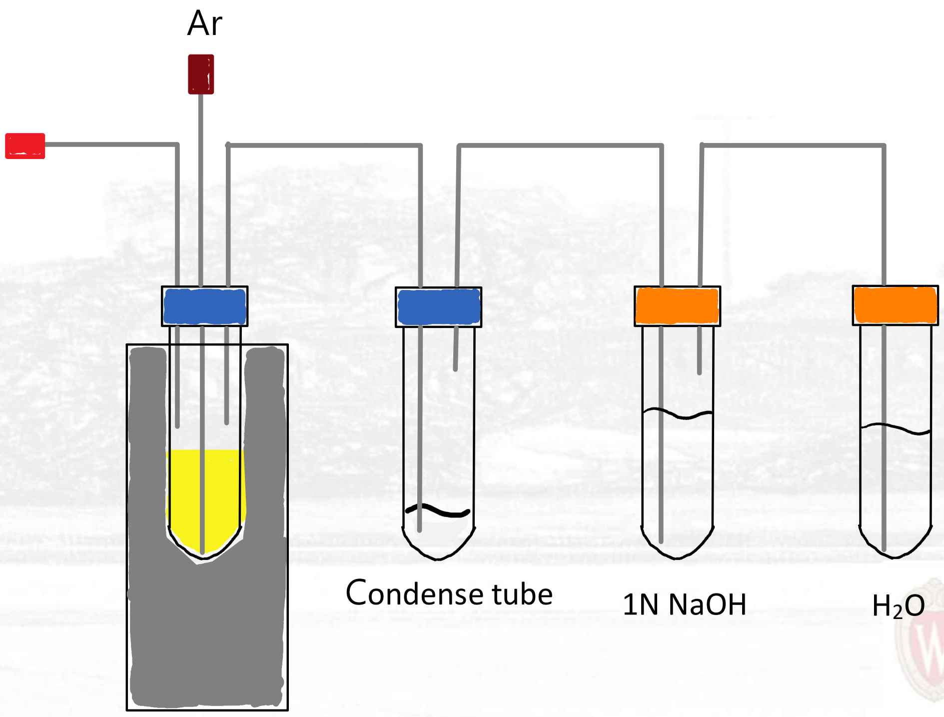

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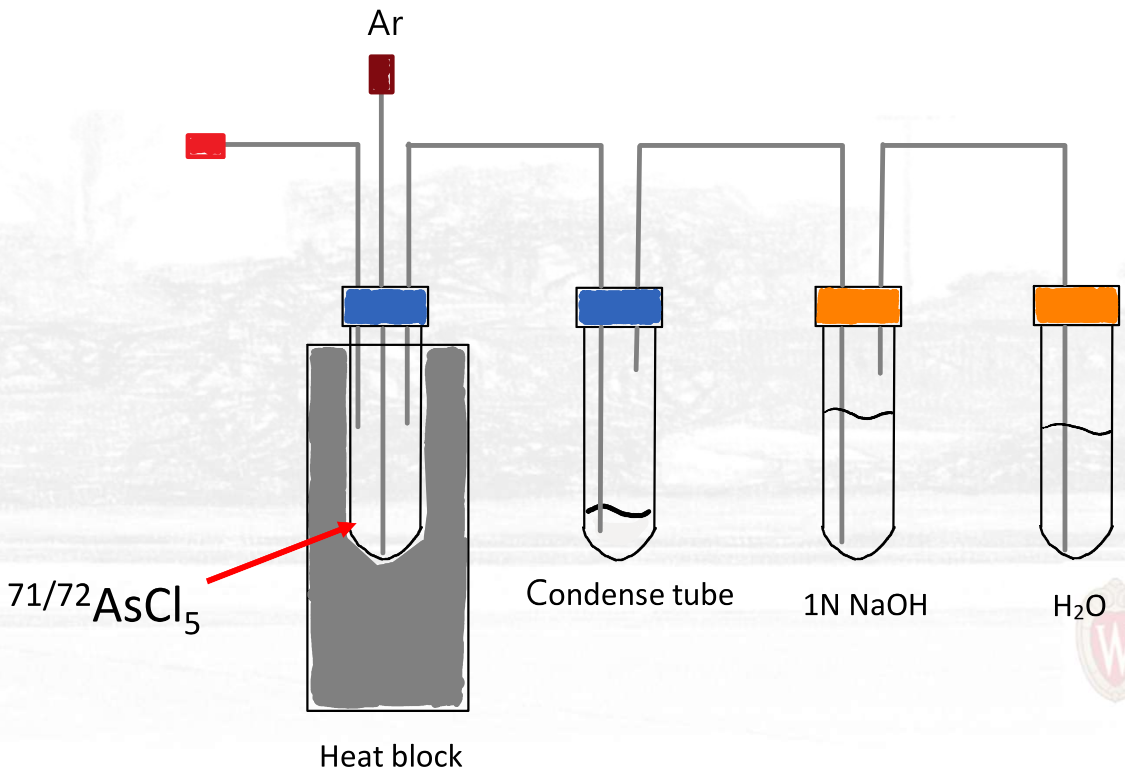

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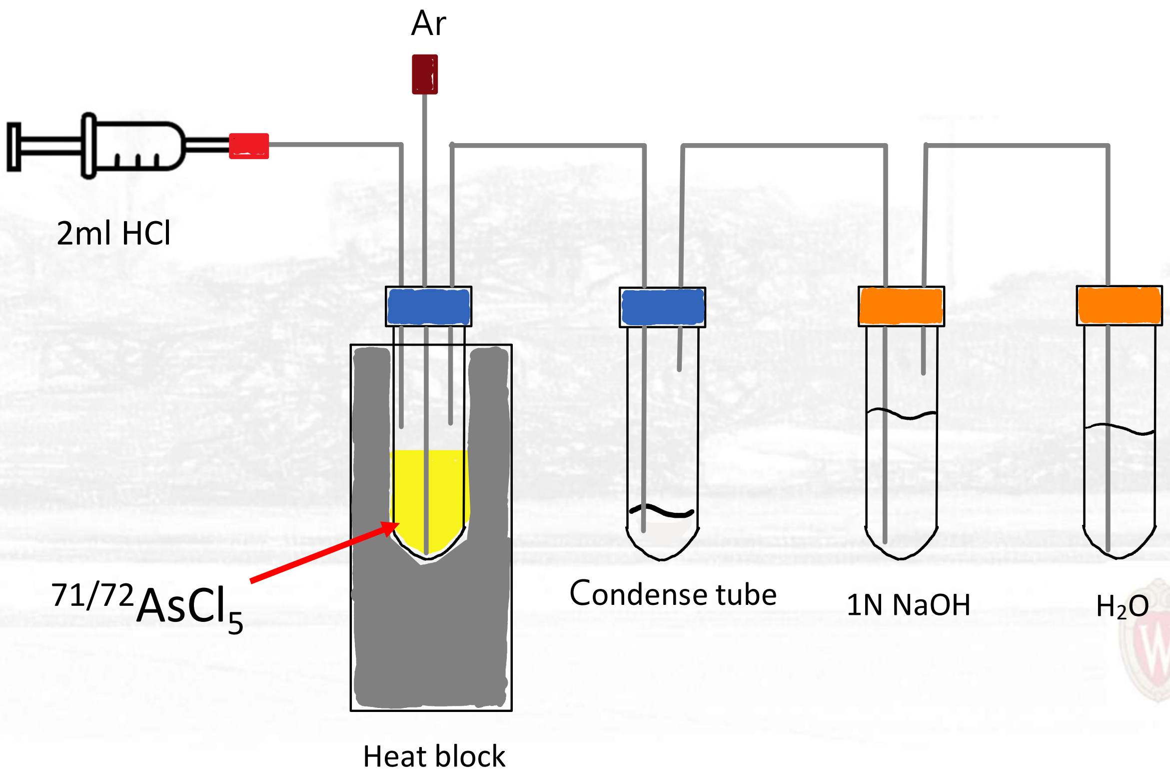

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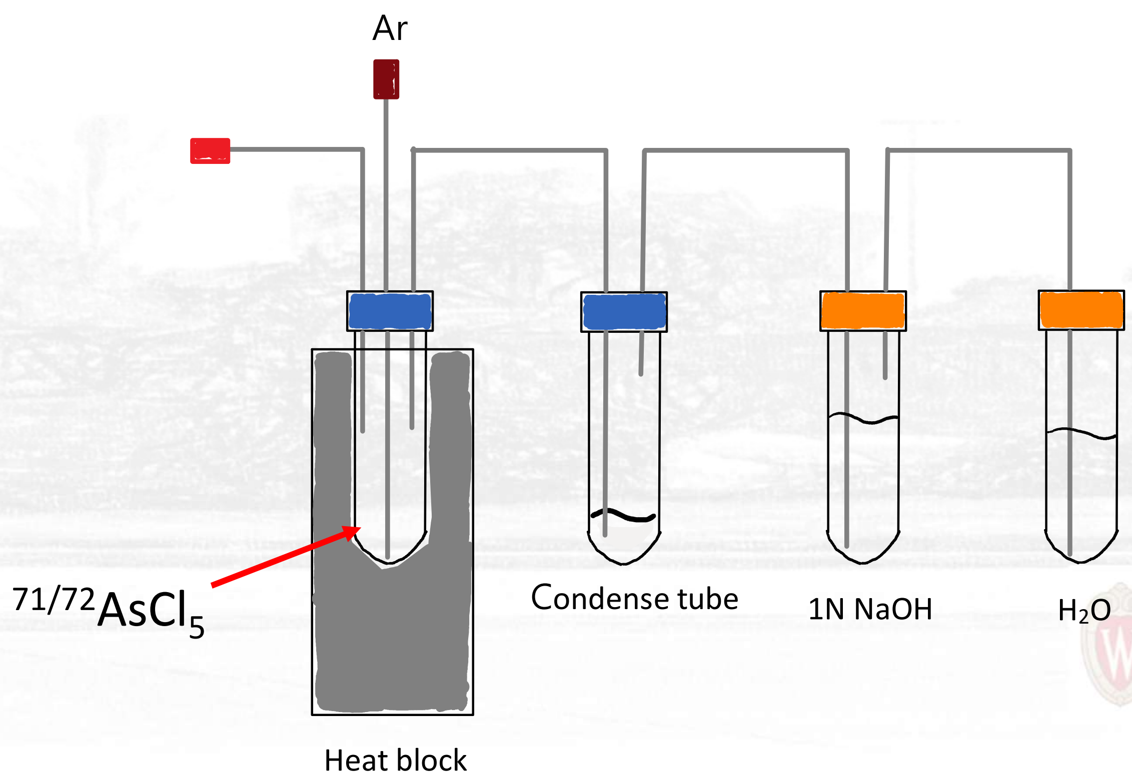

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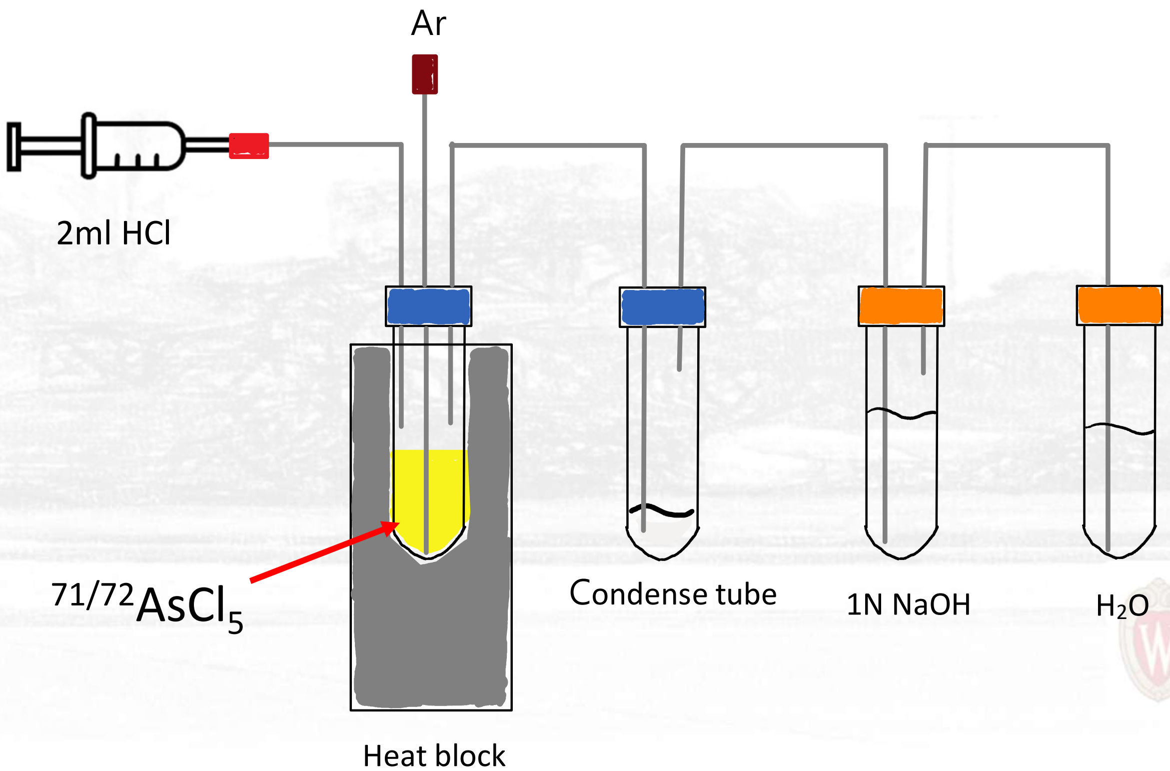

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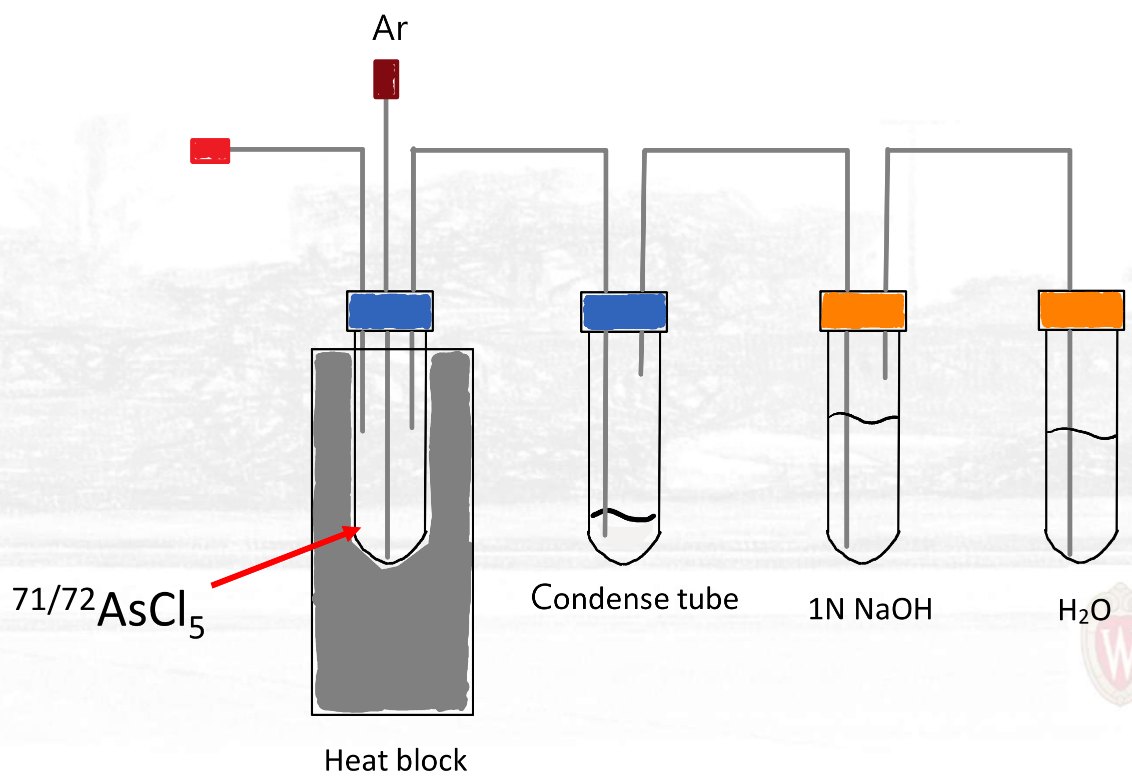

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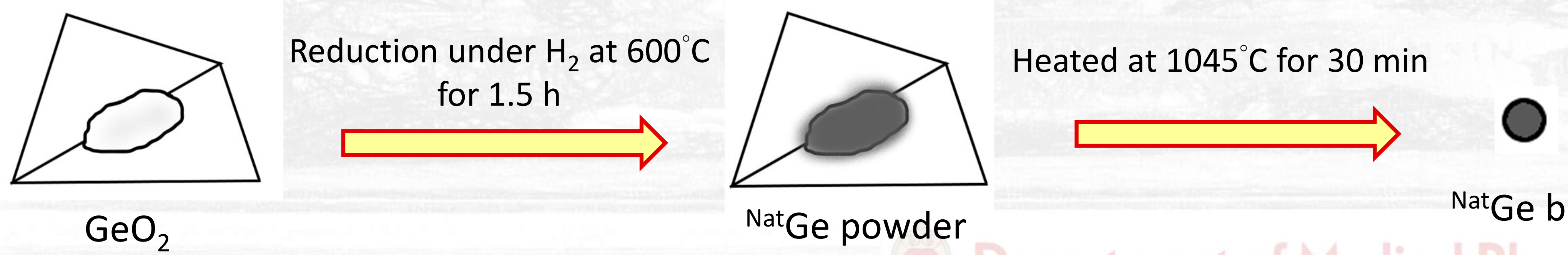
Reclamation:



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Reclamation:

HCl capture method

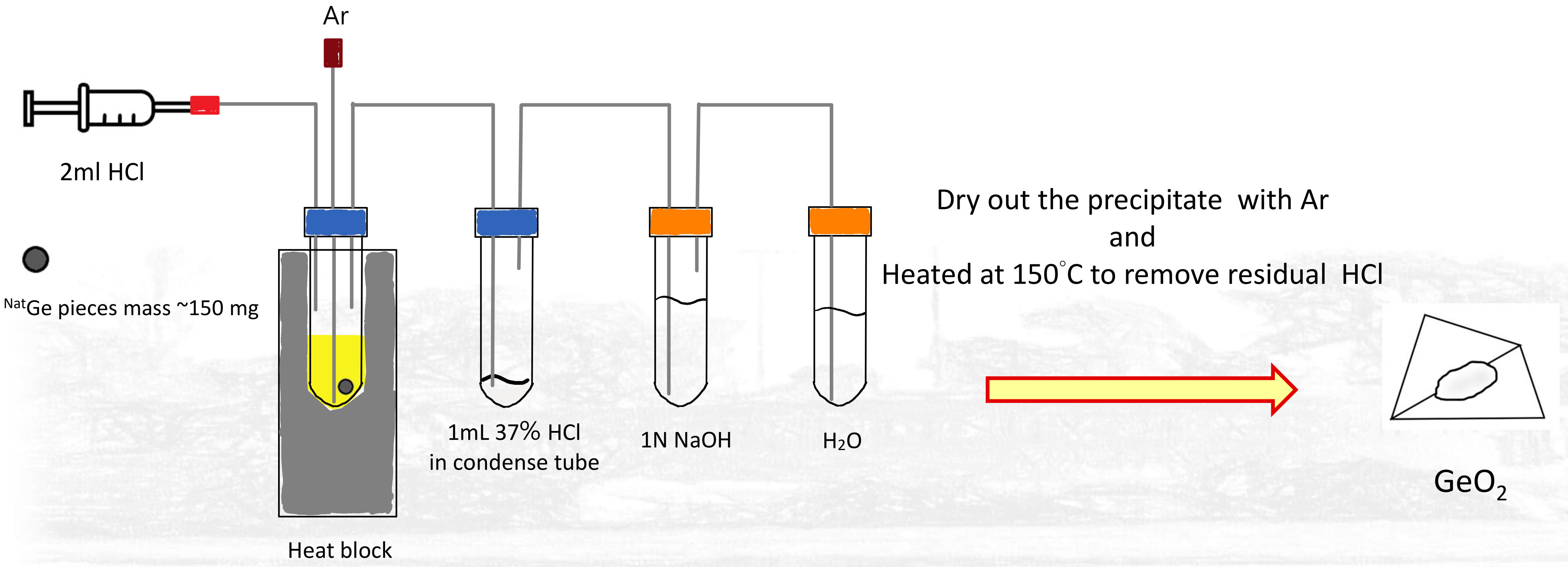
NH_4OH neutralization method

NaOH neutralization method

Reclamation: Distillation and Reclamation

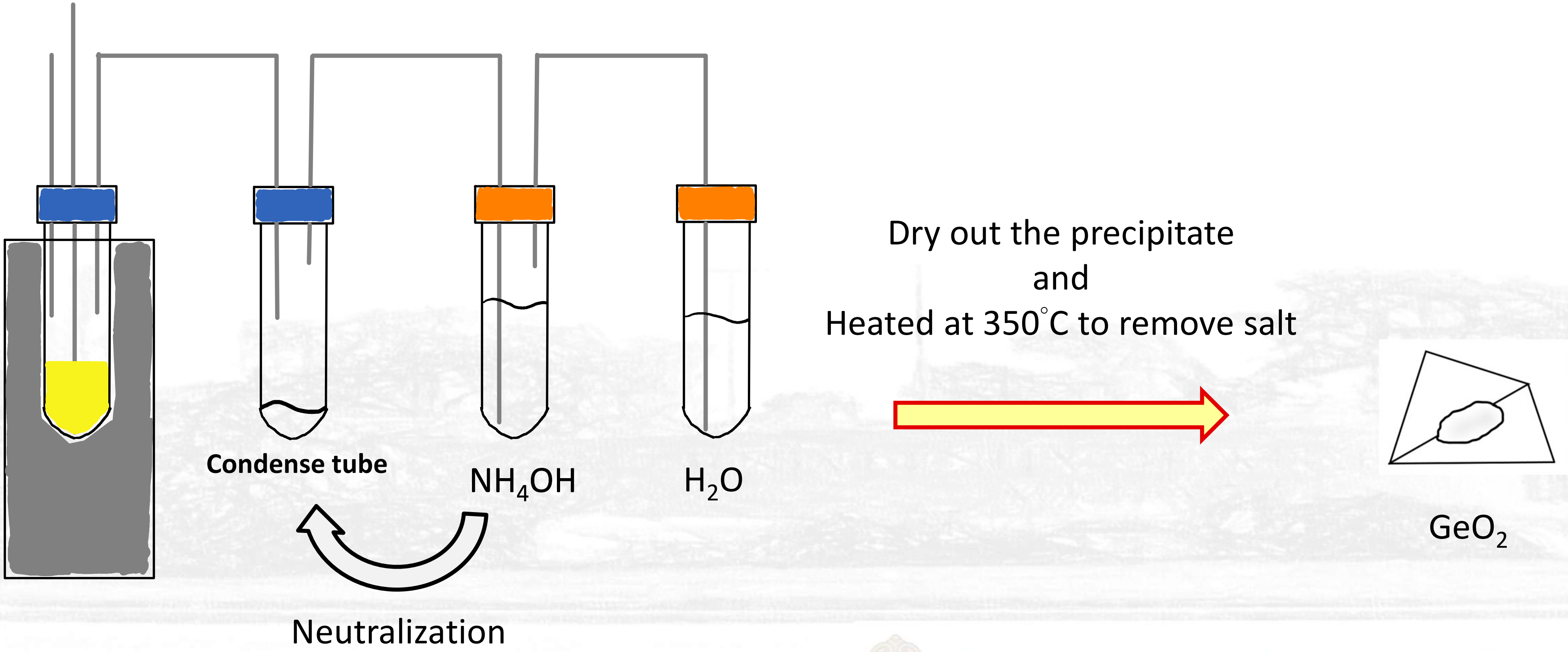
Method

HCl capture method



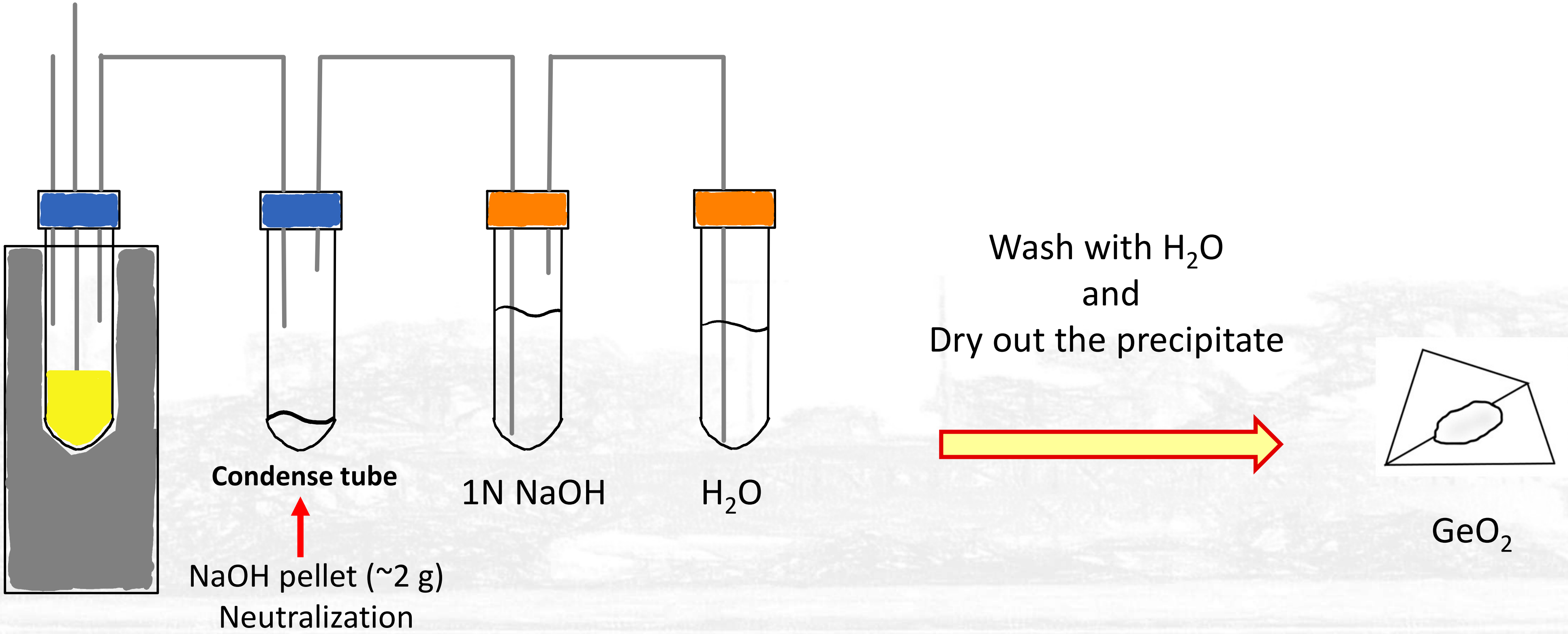
Reclamation: Distillation and Reclamation

Method *NH_4OH neutralization method*



Reclamation: Distillation and Reclamation

Method *NaOH neutralization method*



Reclamation

Result

Condition	HCl capture	NH_4OH neutralization	NaOH neutralization
Ge piece mass (mg)	142.2	153.6	151.7
	After removing residual HCl or salt		
$^{Nat}GeO_2$ mass (mg)	103.5	86.4	53.8
	After reduction by H_2		
Ge mass	67.5	55.3	19.6
	After bb making		
Ge bb mass	68.7	58.6	14.8
Reclamation efficiency %	48.3%	38.2%	9.8%

Conclusion

Target making

Reclamation

Bombardment

Isolation

- Target production: Improve the target production procedure to get fully covered Ge target.
- Reclamation: HCl capture method. Optimization for the procedure to increase the efficiency is needed.

- Target cooling problem: The Ge is melted during irradiation. We will use thinner Ta coin and try to make the thickness of Ge thinner.

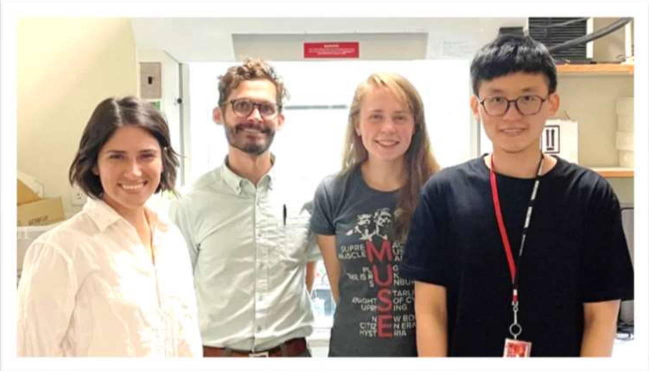
- Separation of As from Ge: Aqua regia method displayed higher Ge mass dissolved and shorter dissolving time.

Acknowledgement

Thanks to

Department of Energy Isotope Program, managed by the Office of Science for Isotope R&D and Production grant DE-SC0022032.

Paul Ellison's Group



University of Missouri

Professor Heather M. Hennkens

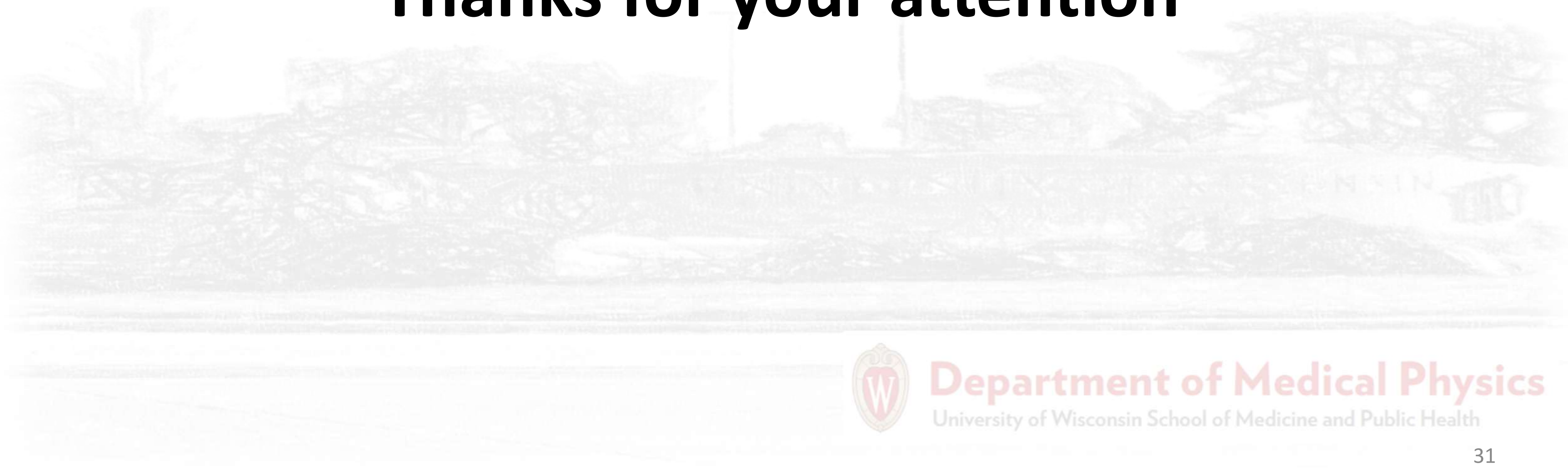
Professor Silvia S. Jurisson

Cyclotron Group

Professor Jonathan W. Engle

Todd E. Barnhart, PhD

Thanks for your attention



Department of Medical Physics
University of Wisconsin School of Medicine and Public Health

Reference

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Prototype coin-type target	$^{72}Ge(p,n)^{72}As$	12	2.5	5.7
	$^{70}Ge(d,n)^{71}As$	8	0.17	0.17

*Enriched target yields extrapolated from experimental proton and deuteron irradiations of a ^{nat}Ge target

Energy (MeV)	Thickness (μm)	Cross section (bar)	Activity
8	0.036	0.26	1.6×10^5
.	.	.	.
.	.	.	.
.	.	.	.
4	0.024	0.01	4.2×10^3

Sum up!

$$A(Bq) = \rho\left(\frac{g}{cm^3}\right) \times x(cm) \times \sigma(cm^2) \times \frac{1}{A_W\left(\frac{g}{mol}\right)} \times A_N \times I\left(\frac{particles}{s}\right) \times (1 - e^{-\lambda t})$$

ρ = density
x = thickness
σ = cross section
A_W = atomic weight

A_N = Avogadro's
I = current intensity
t = irradiation time

Conclusion

Target making

Bombardment

Isolation

Reclamation

- Target production
  Improve the target production procedure to get fully covered Ge target.

- Reclamation
  HCl capture method.
  Optimization for the procedure to increase the efficiency is needed.

Metal, Metallic Element or Alloy	Temperature - *t* - (^oC) (K) (°F)	Thermal Conductivity - *k* - (W/m K) (Btu/(ft h °F))
Tantalum	-73	57.5
"	0	57.4
"	127	57.8
"	327	58.9
"	527	59.4
"	727	60.2
"	927	61
Titanium	-73	24.5
"	0	22.4
"	127	20.4
"	327	19.4
"	527	19.7
"	727	20.7
"	927	22

Research topic

^{77}As beta emitter

$^{77}Ge(n,\gamma)^{77}As$

- End point energy ≈683 keV
- $T_{1/2}$=38.8 h
- Problem…

  The lack of imaging property which can provide in patient selection, target verification and dosimetry.

$^{71/72}$As positron emitter

$^{72}Ge(p,n)^{72}As$--UWisc PETtrace cyclotron

- $T_{1/2}$: ^{71}As=65.3 h and ^{72}As=26 h
- End point energy: ^{71}As=816 keV and ^{72}As=2500 keV

^{119}Sb MAe$^-$ emitter

- Homologous relationship with ^{119}Sb

N
P
As
Sb
Bi