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"Total Mass Accounting in Advanced Liquid-Fueled Reactors"

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ARSS Virtual Fall Program Review, November 2nd, 2023

Introduction

- How to measure and monitor the mass of molten salt in fuel salt or coolant salt reactor systems?

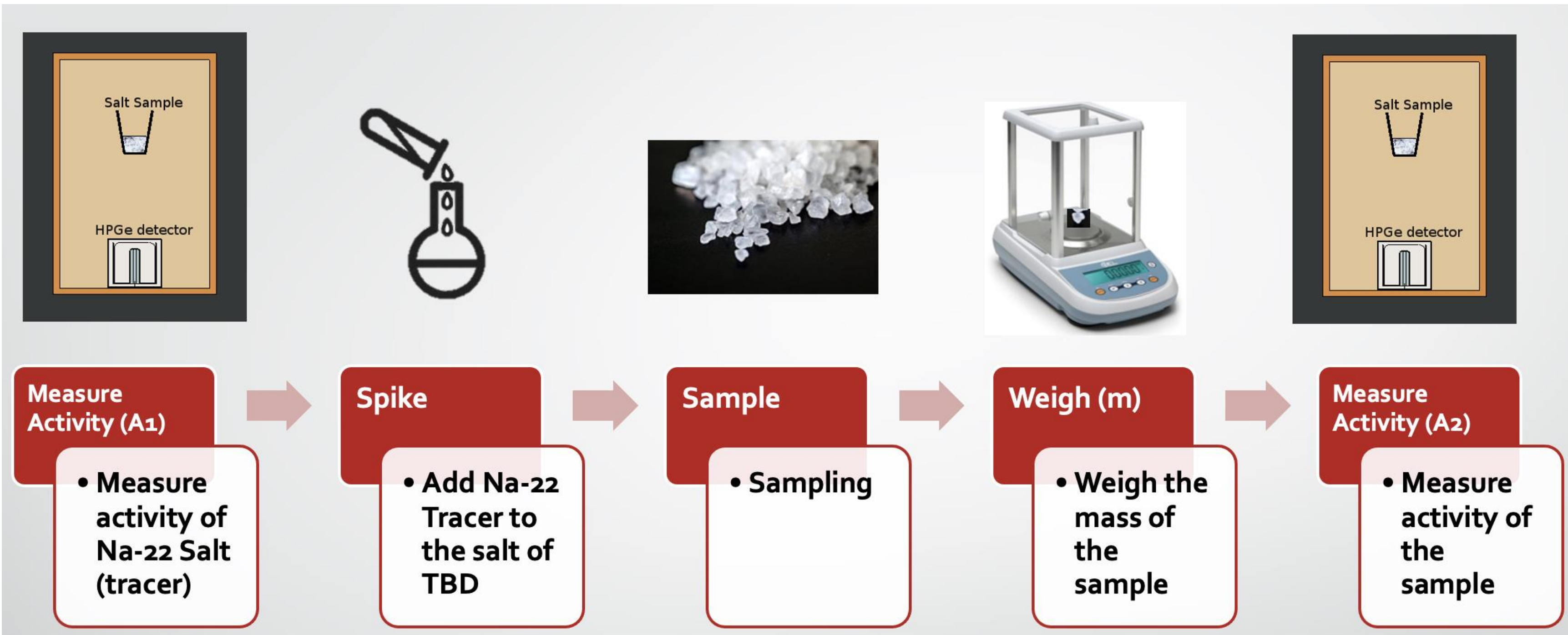
    - It’s hot
    - It’s corrosive
    - It’s radioactive
    - It’s non-accessible
    - Density could change all the time (burn-up, refueling etc)

- Important safeguard requirement for MC&A of advanced reactors

- We propose to add radioactive tracer in which the mass of total volume of salt may be determined - radioactive tracer dilution (RTD) method.

The principle of RTD

Tracer with activity A1 is added to salt of unknown mass, then sampled with known mass and activity of A2.



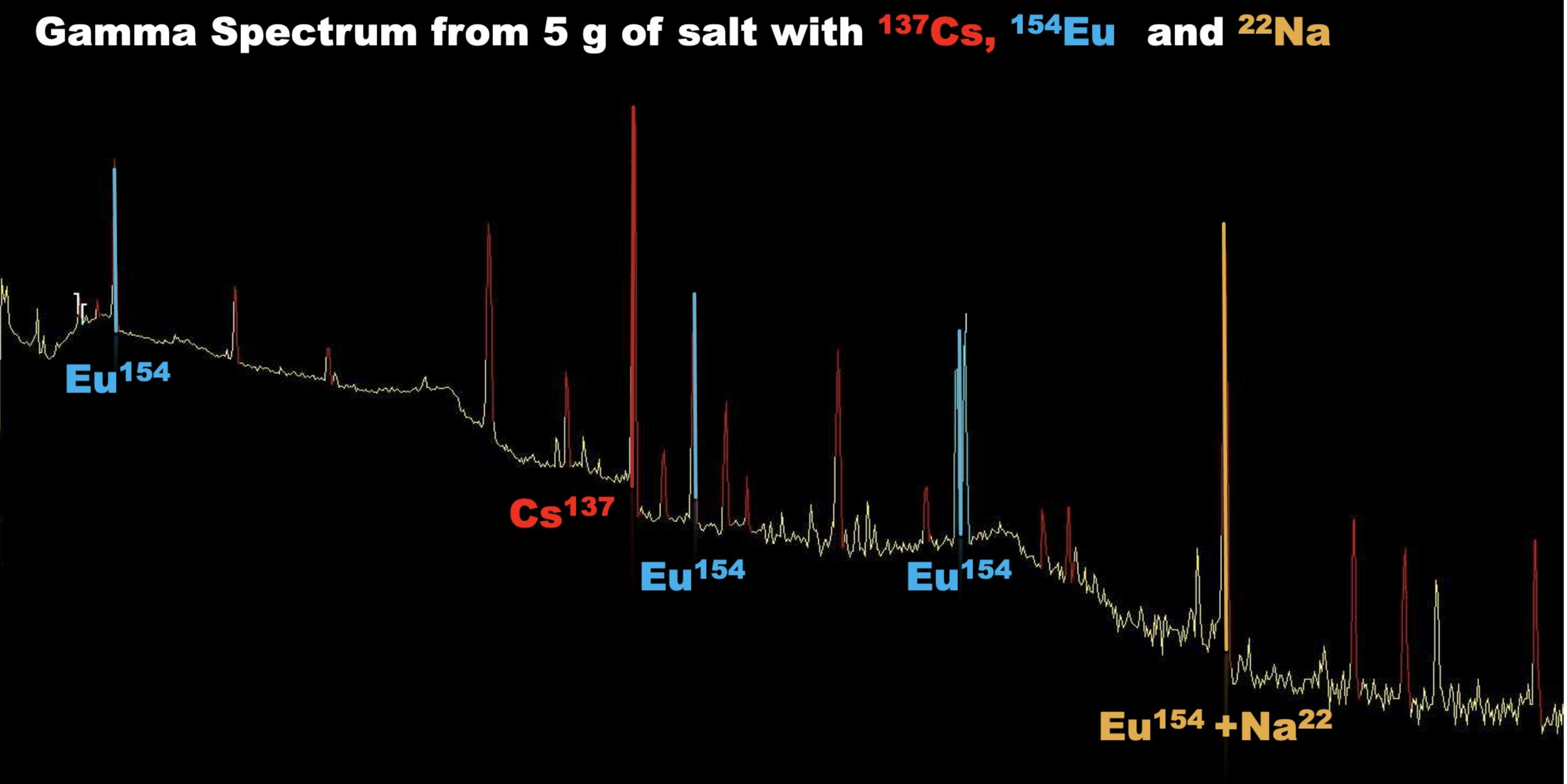
$$Mass_{tot} = \left(\frac{A_1 \pm \sigma}{A_2 \pm \sigma}\right) * m_{sample}$$

Radioactive tracer selection

^{22}Na has been selected as the proper radioactive tracer.

- It undergoes beta+ decay (non-fission product characteristic)
- known chemical compatibility with actinides and fission products in molten chloride and fluoride salts
- Availability and half life (2.6 y) for handling
- Emits 1274.54 keV gamma-ray (99.94%), high enough to be outside of the Compton plateau of many fission products' gamma-rays in a gamma energy spectrum
- Only known overlapped peak is 1274.43 keV from ^{154}Eu
- High thermal neutron capture cross-section helps to remove Na-22 after spiking

Gamma Spectroscopy of non-fuel salt from previous proof-of-concept study



OSU Nuclear Reactor Lab (2018)

Lei Cao et al. "Determination of molten salt mass using Na-22 tracer mixed with Eu-154 and Cs-137." Journal of Radioanalytical and Nuclear Chemistry 318 (2018): 457-463.

Objectives

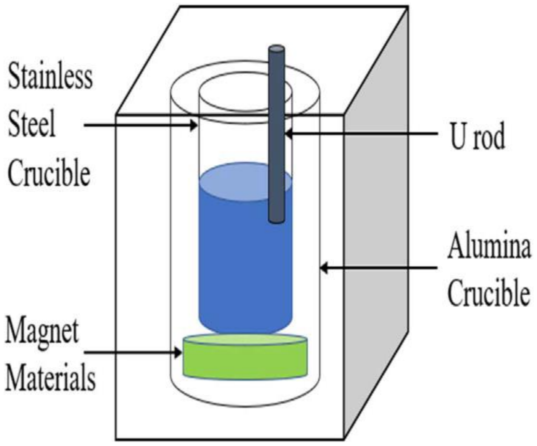
The objective of this research is to validate a radioactive tracer dilution (RTD) method for the irradiated fuel-bearing molten salt mass determination to evaluate the possibilities of its deployment in NMA scenarios, e.g., in molten salt loop in LFMSRs.

Questions to be answered:

Q1.) Are there any other unknown interferences at 1274 keV?
Q2.) How to do sampling?
Q3.) How long should IAEA inspector wait before counting?

$MgCl_2$-KCl-UCl_3 salt for irradiation (UoU)

- 13.8 g of $MgCl_2$-KCl-UCl_3 (DU) fuel salt was prepared at the University of Utah
- High purity (99.99%) $MgCl_2$ and KCl was acquired through commercial vendors and mixed with a 0.3:0.7 molar ratio.
- UCl_3 was synthesized by using DU metal rod and $FeCl_2$ in $MgCl_2$-KCl at ~500°C.
- Salt samples were taken and measured by ICP-MS, the U concentration was determined to be 12.16 wt%. The $FeCl_2$ concentration is 0.045 wt%. UCl_3 is 17.6 wt%.
- U-235 concentration in the entire salt is (2.76 mg/13.8 g) = 200 ppm
- $MgCl_2$-KCl-UCl_3 salt will be packed in an argon glovebox and shipped to OSU by a commercial carrier



Schematic for preparing UCl_3 salt from DU metal rod and NaCl-KCl-$FeCl_2$

Huan Zhang et al 2021, J. Electrochem. Soc. 168 056521

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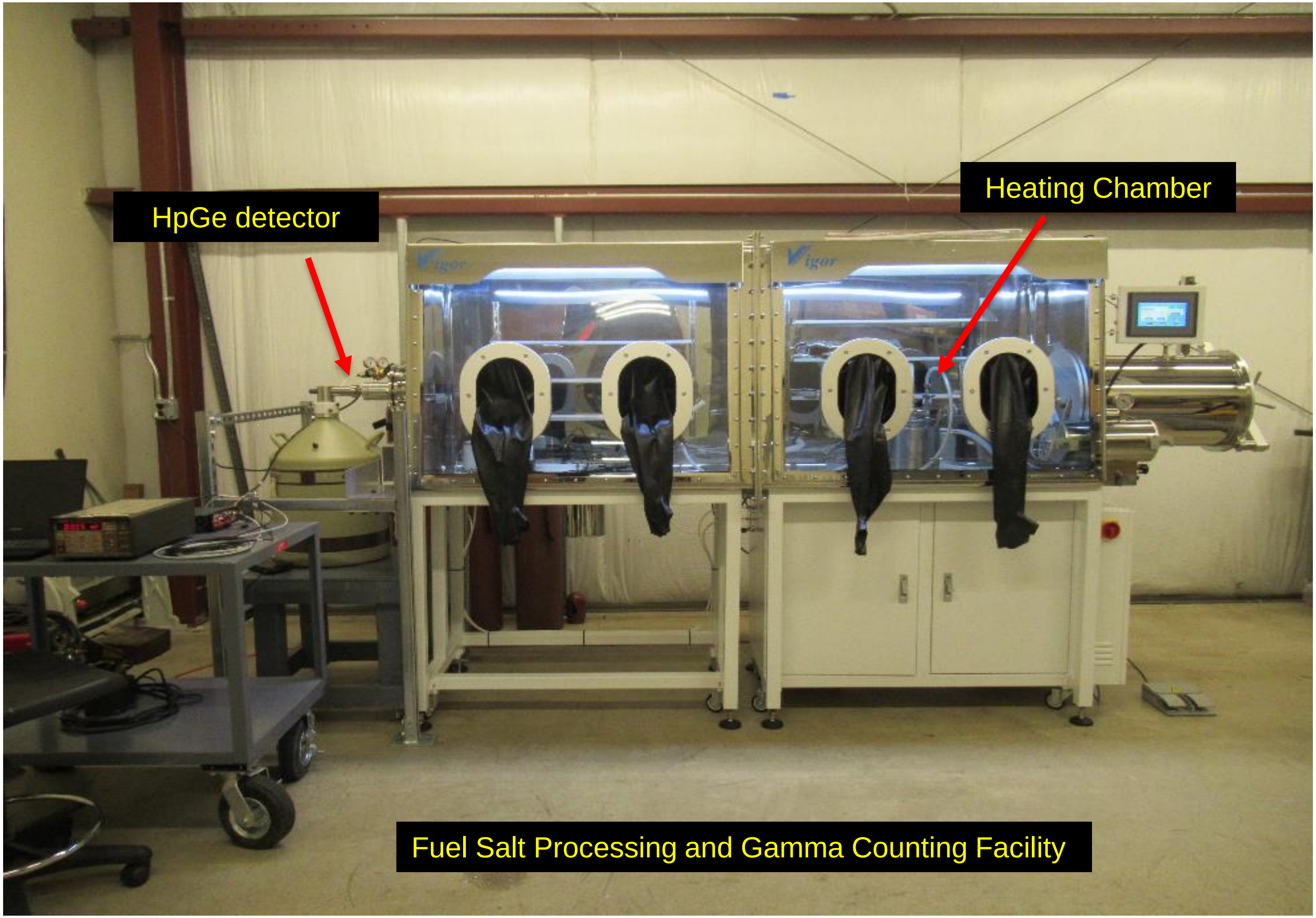
Newly build OSU fuel salt processing facility at Nuclear Reactor Laboratory



Adding fuel salt for in-core irradiation

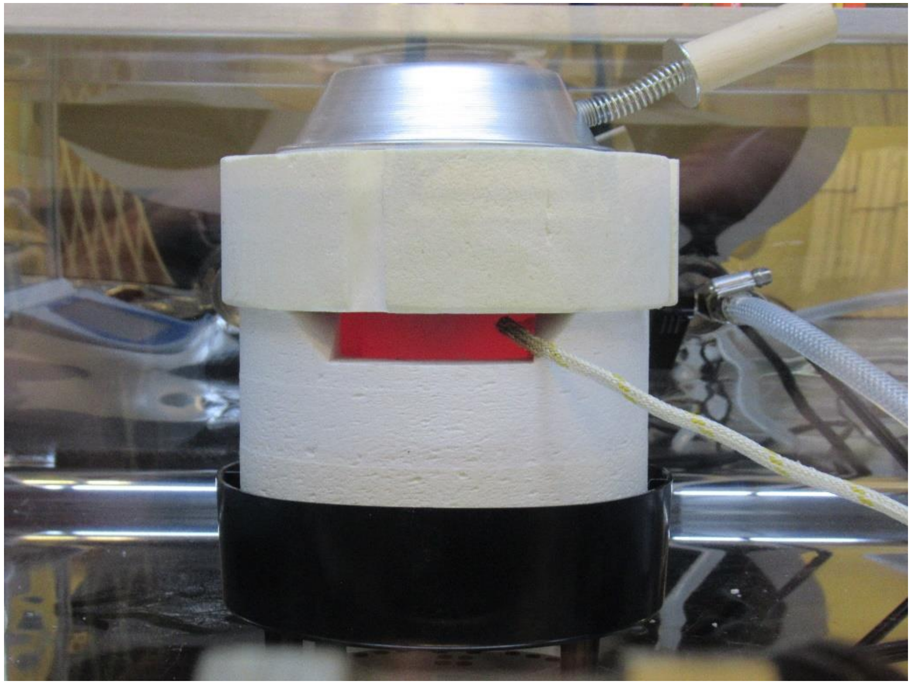
Quartz Bottle Mass	**10.99 g**
Added $^{22}NaCl$	**0.1 mL (1.7 μCi)**
Fuel salt mass	**6.065 g**
U-235 in sample	**1.21 mg**

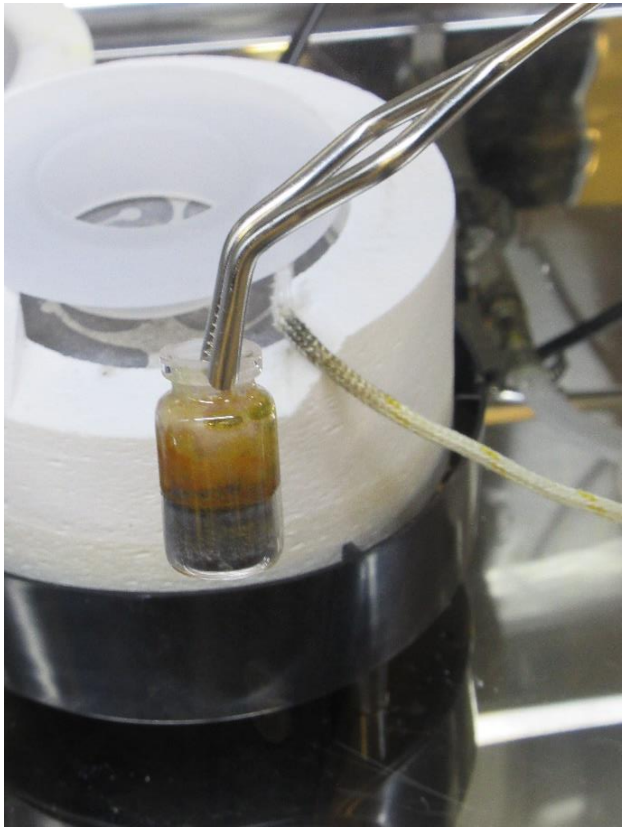
Fuel salt is being added into quartz bottle for irradiation

$MgCl_2$-KCl-UCl_3 (DU) composition:

- U-235 concn in salt sample at 0.02 wt%
- U-238 concn in salt sample at 12.14 wt%.
- **U-235 enrichment 0.2%**

Melting fuel salt to mix with $^{22}NaCl$





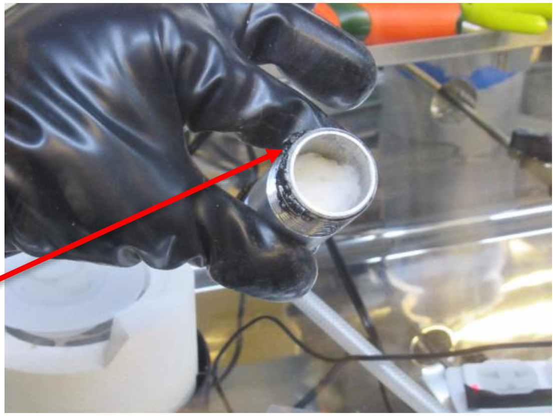
Heating Scheme in Ar glovebox:

- Temp raised to ~ 500°C for 30 min
- Verified in molten state
- Continued heating 500−550°C for 2 hours (to allow mixing of $^{22}NaCl$ with fuel salt)

- Once cooled, the bottle was weighed and crimp sealed with Grafoil/aluminum cap.

Preparing encapsulation of fuel salt and ^{22}Na for in-core irradiation

Grafoil paste for sealing Aluminum cap

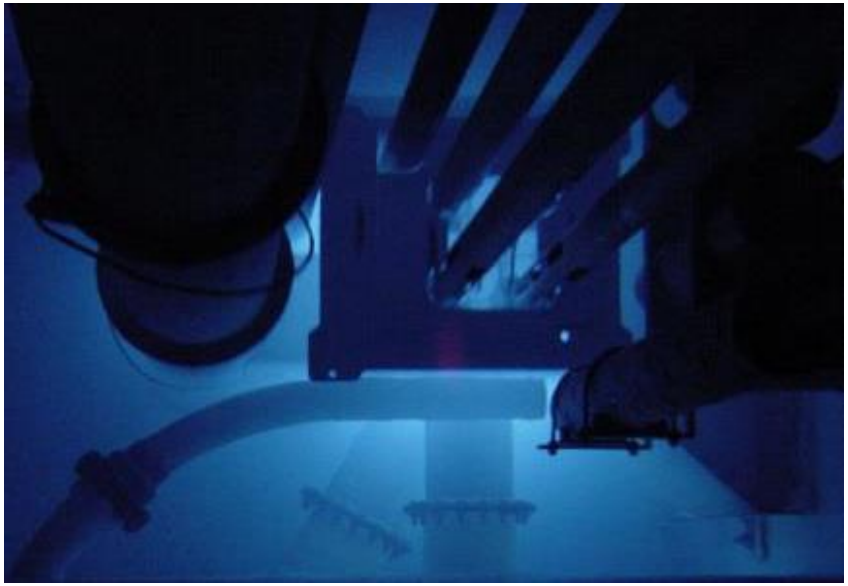


- Silica insulation inserted as cushion above quartz bottle.
- Initial spectroscopy conducted at heights of 38 cm and 67 cm above the HPGe detector end cap.
- Measurements were repeated with a 0.1 inch thick lead sheet underneath, which will be used for reducing dead time at post-irradiation.

In-core irradiation

Fission product gasses produced from 15 grams of salt mixture (ORIGEN)

Nuclide	Activity (Ci)	Activity (Bq)	Half-Life (days)	l (1/s)	# atoms	Moles (mol)
I-131	3.91E-05	1.45E+06	8.025	1.00E-06	1.45E+12	2.40E-12
I-132	1.44E-04	5.34E+06	0.096	8.39E-05	6.36E+10	1.06E-13
I-133	1.88E-03	6.97E+07	0.868	9.24E-06	7.54E+12	1.25E-11
I-134	3.71E-02	1.37E+09	0.036	2.20E-04	6.25E+12	1.04E-11
I-135	1.17E-02	4.32E+08	0.149	5.38E-05	8.03E+12	1.33E-11
Kr-85m	3.16E-03	1.17E+08	0.187	4.30E-05	2.72E+12	4.53E-12
Kr-87	1.93E-02	7.16E+08	0.053	1.51E-04	4.73E+12	7.85E-12
Kr-88	1.40E-02	5.18E+08	0.118	6.82E-05	7.60E+12	1.26E-11
Xe-131m	3.24E-10	1.20E+01	11.840	6.78E-07	1.77E+07	2.94E-17
Xe-133	3.97E-06	1.47E+05	5.248	1.53E-06	9.60E+10	1.59E-13
Xe-133m	7.38E-07	2.73E+04	2.198	3.65E-06	7.49E+09	1.24E-14
Xe-135	6.23E-04	2.31E+07	0.381	2.11E-05	1.09E+12	1.82E-12
Xe-135m	3.72E-03	1.38E+08	0.011	7.56E-04	1.82E+11	3.03E-13
					Total =	6.61E-11



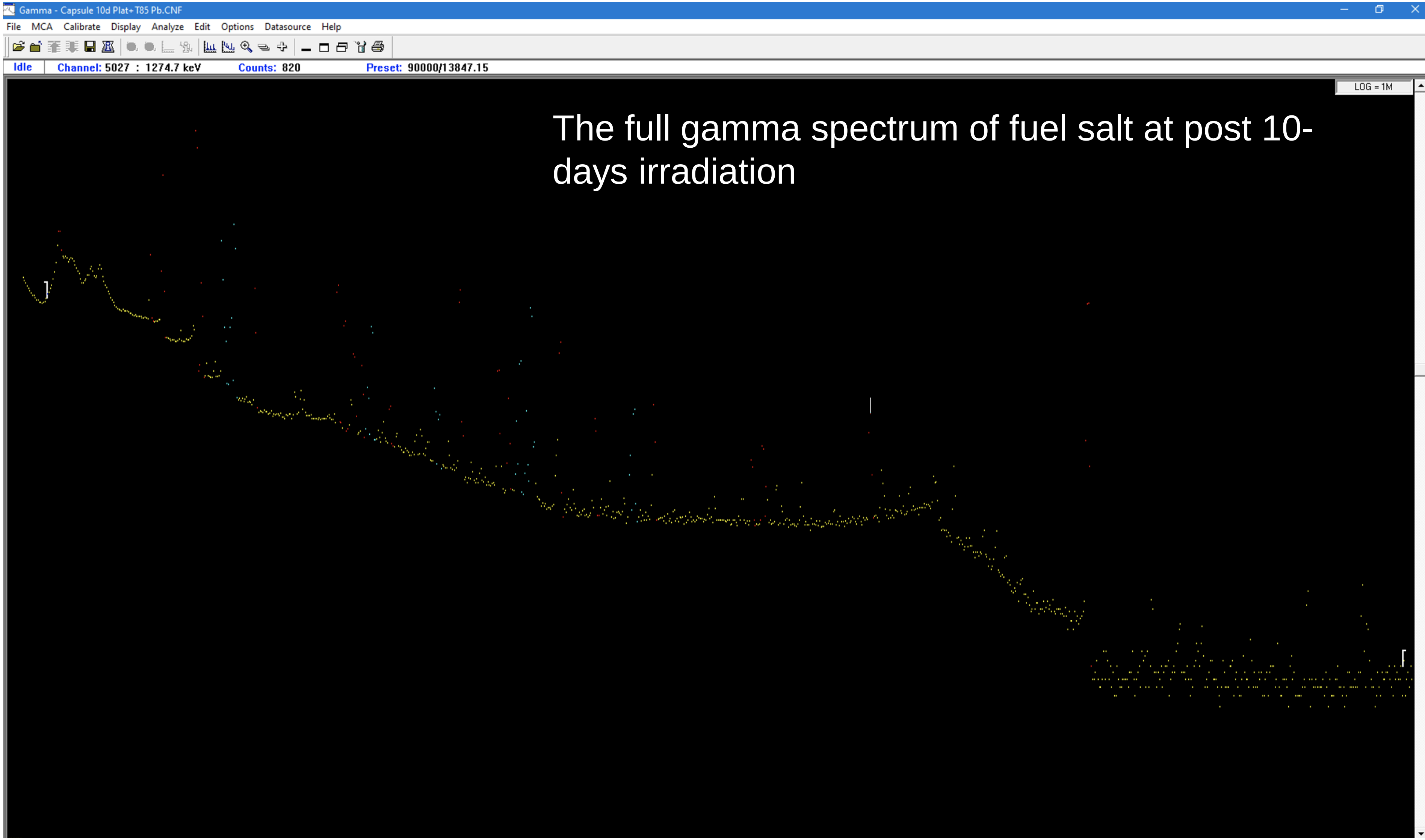
Picture of in-core irradiation at OSURR

Thermal Neutron Flux: 6.0×10^{12} n/cm^2/s

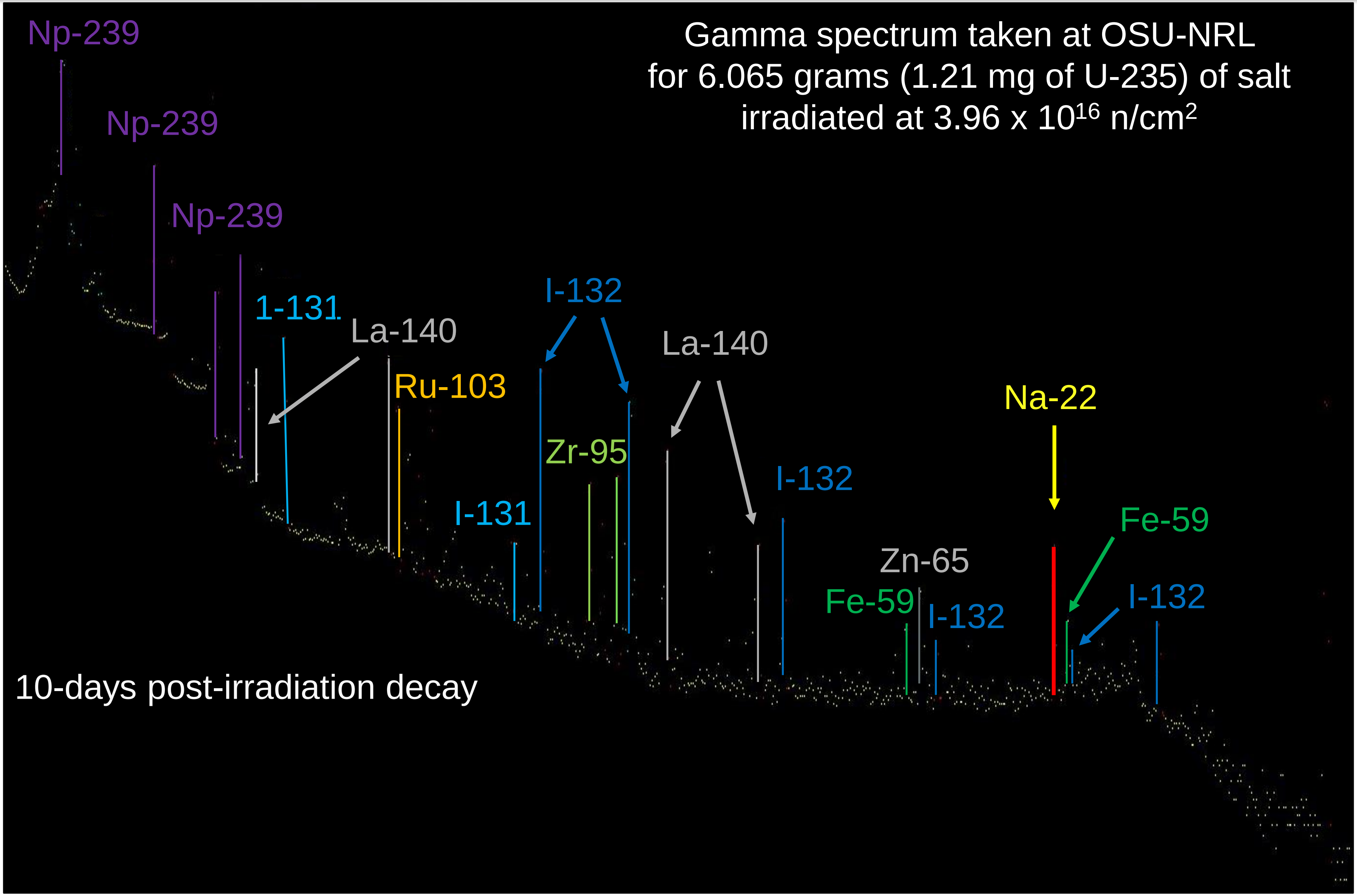
Total Neutron Flux: 1.1×10^{13} n/cm^2/s

Irradiation time: 1 hour

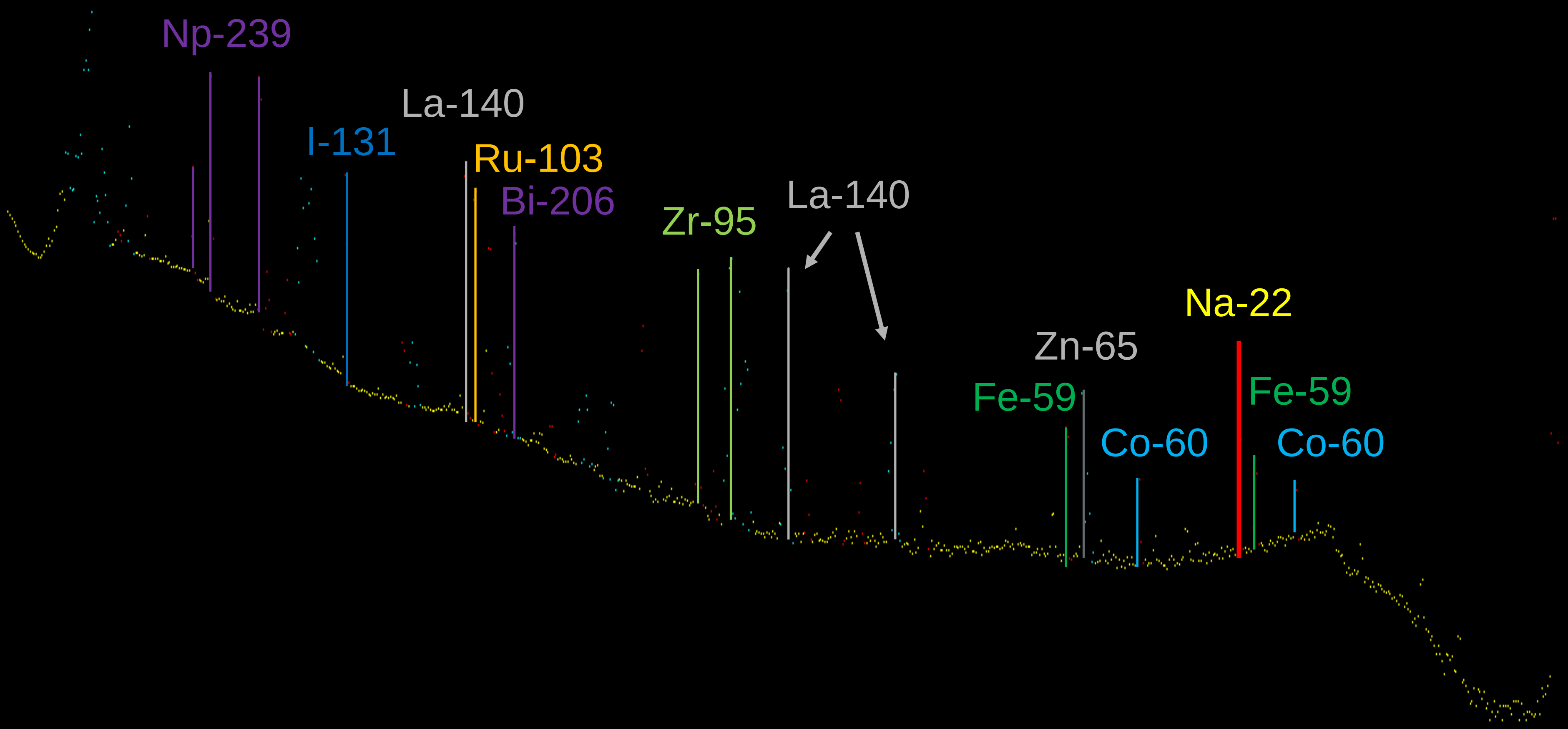
Fluence: 3.96×10^{16} n/cm^2



The full gamma spectrum of fuel salt at post 10-days irradiation

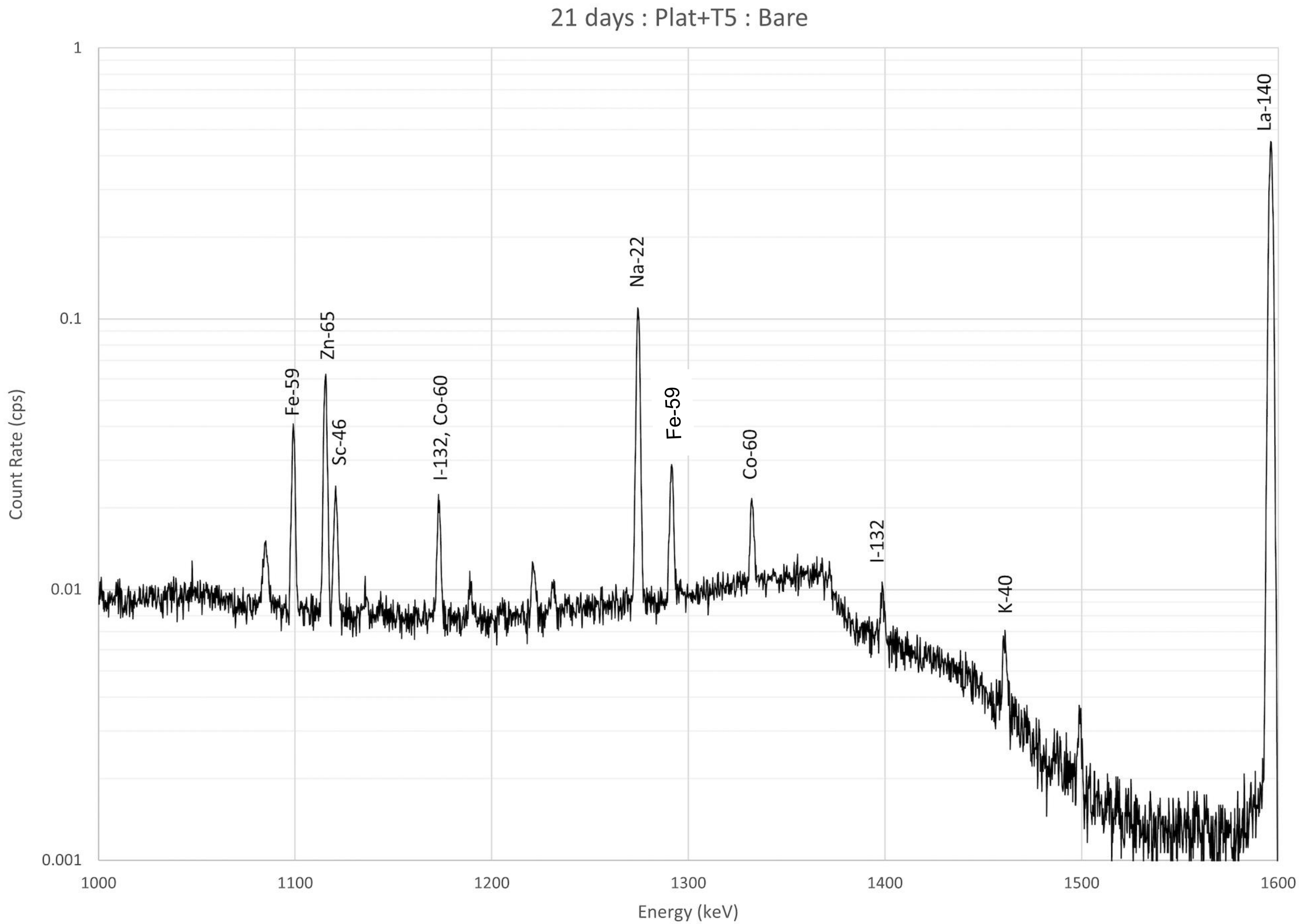

Gamma spectrum taken at OSU-NRL
for 6.065 grams (1.21 mg of U-235) of salt
irradiated at 3.96 x 10^{16} n/cm^2
Np-239
Np-239
Np-239
1-131
La-140
Ru-103
I-132
Zr-95
I-131
La-140
I-132
Na-22
Fe-59
Zn-65
Fe-59
I-132
I-132
10-days post-irradiation decay

Gamma spectrum taken at OSU-NRL
for 6.065 grams (1.21 mg of U-235) of salt
irradiated at 10^{16} n/cm^2



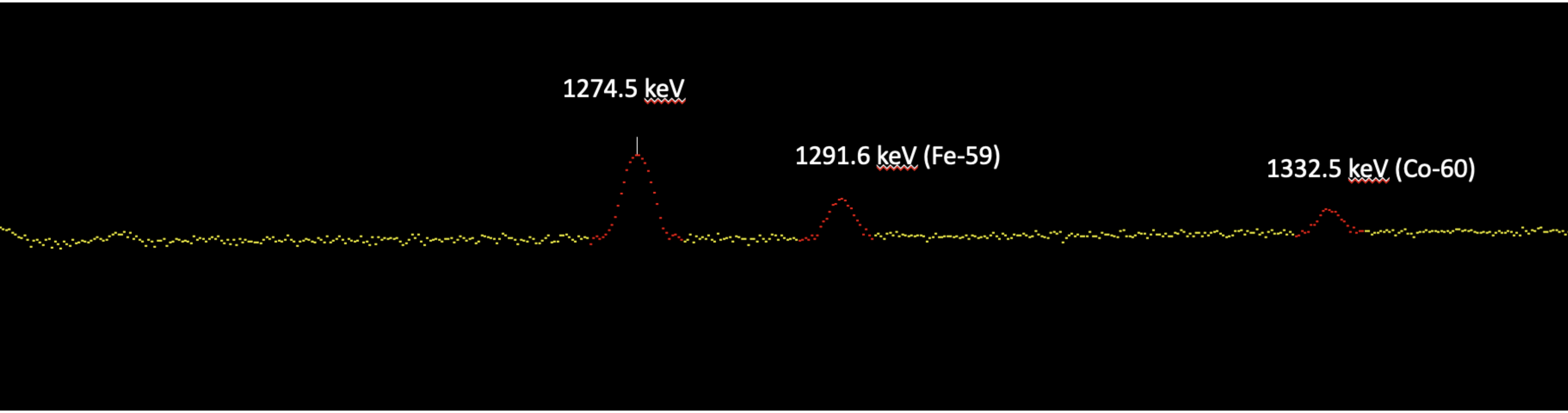
21-days post-irradiation decay

Zoom-in region of fuel salt at post 21-days irradiation

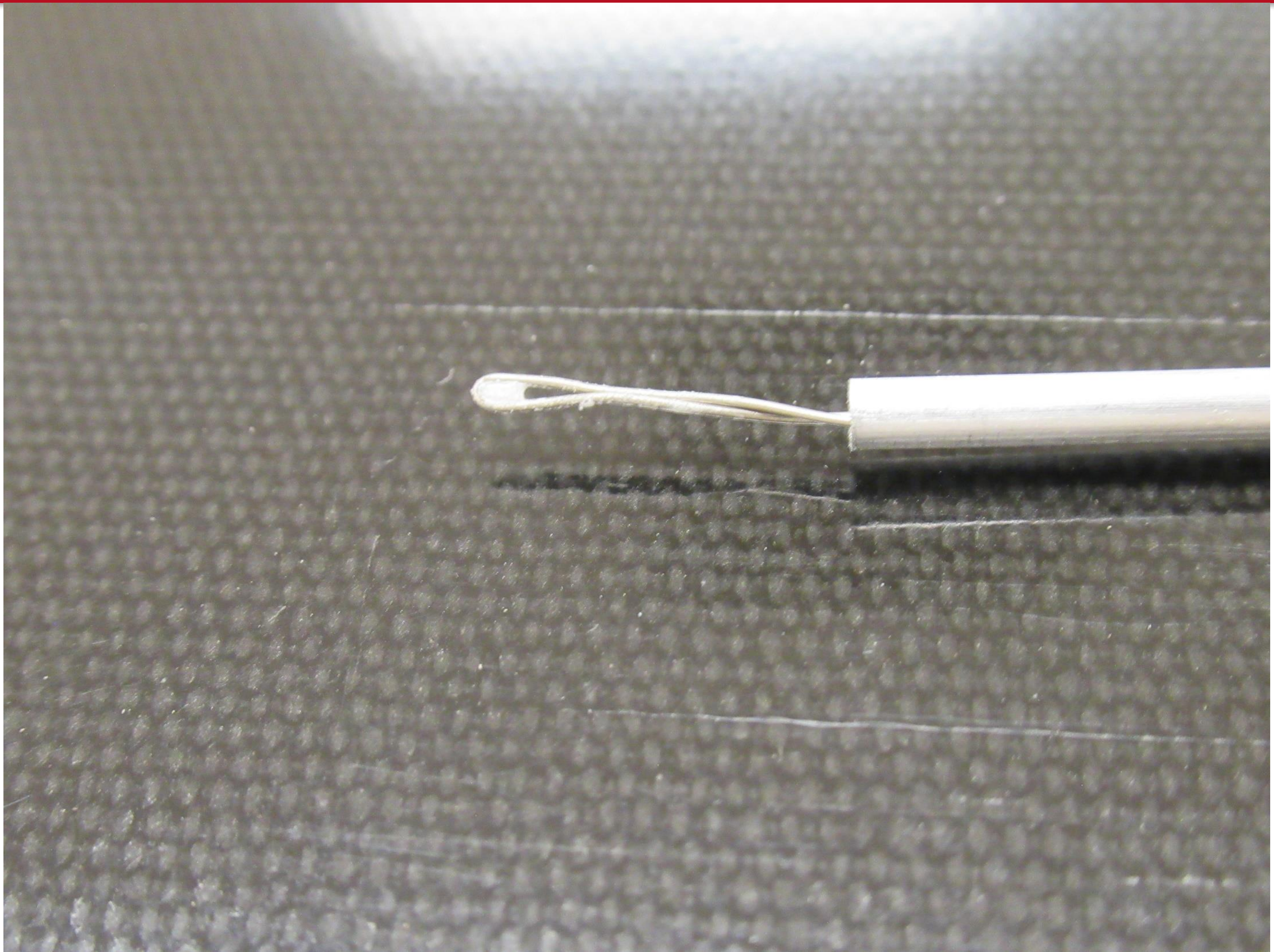


Zoom-in Na-22 peak region of fuel salt at post 10-days irradiation

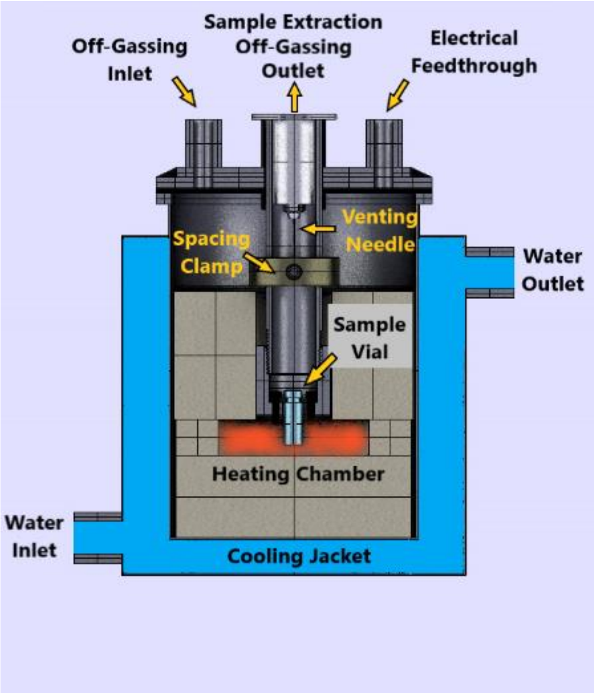
- Na-22 (1274.5 keV) neighborhood is cleared off any sign of interferences with current burn-up
- Fe-59 comes from impurity in salt

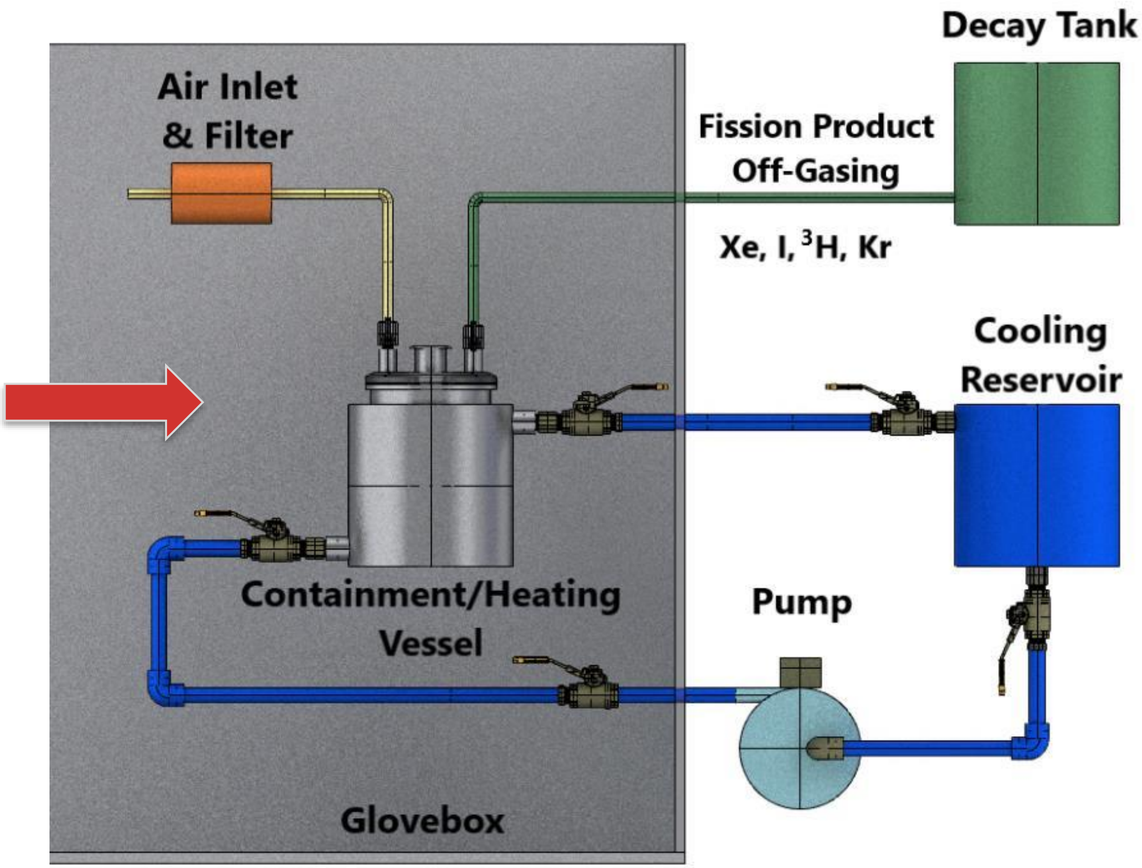


Fuel salt sample extraction practice



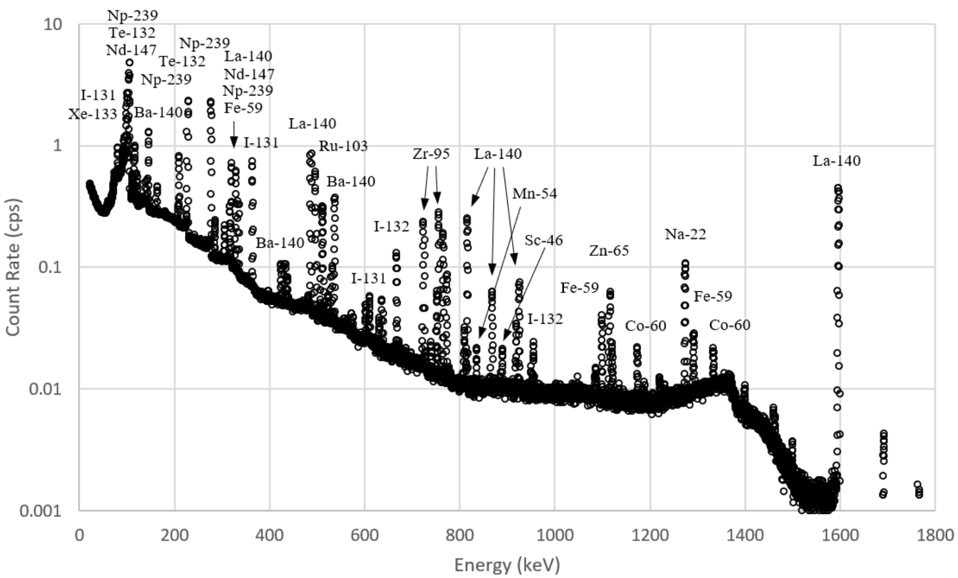
Our facility is capable of off-gassing study





Update: Irradiated fuel salt gamma spectrum analysis

Figure 3.7. Energy spectrum of irradiated salt capsule after 21 days (Plat+T5 with No filter)



Interference Peaks

- No significant interference peaks from observable radionuclides detected
- Eu-154 production negligible due to short irradiation time
- Gamma energies from other radionuclides:
  - Iodine-132 at 1272.8 and 1290.8 keV (0.168% and 1.13% intensity)
  - Nb-99 at 1269.5 keV (0.06% intensity)
- These energy peaks have very low intensity and emission rate
- With good resolution and low uncertainty overlap does not occur

Observed Energy Peaks after 3 days

Radionuclide Peak (identified by Genie)	Daughter product	Emitted Gammas of Interest (keV)
Sc-46*	Ti-46	1120.5
Mn-54*	Cr-54	834.85
Co-60*	Ni-60	1173.23; 1332.49
Zn-65*	Cu-65	1115.5
Br-82	Kr-82	1173.4; 1180.2; 1317.5
Zr-95	Nb-95	724.2; 756.7
Nb-95	Mo-95	765.8
Tc-99m	Ru-99	140.5
Nb-99	Mo-99	1228.9; **1269.5**; 1303.7
Mo-99	Tc-99	739.5; 1017; 1056
Ru-103	Rh-103	210.7; 213.4
Ru-105	Rh-105	316; 469; 1251.9; 1321.28
Rh-105	Pd-105	319.23
Sb-124	Te-124	645.8; 1101
I-131	Xe-131	722.9
Te-132	I-132	228.2
I-132	Xe-132	667.7; 772.6; **1272.8; 1290.8**
Xe-133	Cs-133	80; 233.2
Nd-147	Pm-147	91.1; 531.01
Ba-140	La-140	162.7; 304.85; 537.3
La-140	Ce-140	328,8; 487.0; 815.8; 1097; 1303.5
Ce-141	Pr-141	145.4
Ce-143	Pr-143	1160.6; 1324.48
Ce-144	Pr-144	133.5
Pm-149	Sm-149	285.95
Np-239	Pu-239	38.7; 91.1; 120.5; 531.0

* Asterisk represents peaks due to impurities in irradiated sample gasket cap

Update: Irradiation #2

Total Salt Mass Irradiated: 6.065 grams; **Tracer (Na-22) Activity:** 1.5 µCi (decay corrected)
Time Irradiated: 1 hour at 450 kW

Irradiation #2

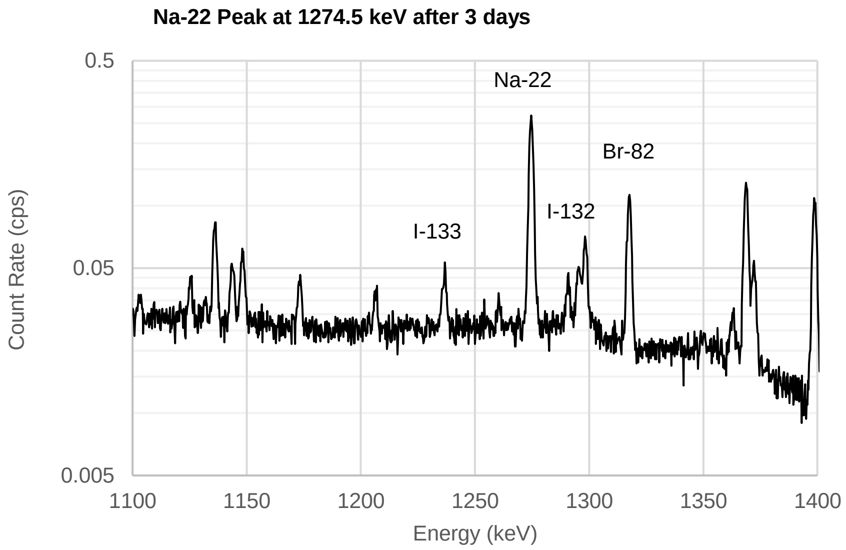
- Na-22 tracer peaks detected in all 7 samples (8 mg to 400 mg)
- Increasing count time improves results
- Reducing background reduces deadtime improving resolution
- Recommended actions:
  - Increase tracer amount
  - Reduce background through filter, smaller samples, longer decay period

9 days post-irradiation

No Cap T5 no Pb	
Bottle#	7
Count Date:	9/3/2023
Elapsed (d):	177
Decay factor:	0.879
Live Time (s):	54000.0
Peak Counts:	3379
Net Rate (cps):	0.063
Rate Uncert (%):	3.40
*Peak Eff (pcm):	9.010
Eff Uncert (%):	1.35
Activity (µCi):	0.0214
Uncert (%):	3.7
Dead Time	0.67%
Sample Mass	0.0792
Mass Uncert(%)	
Total Salt Mass (g)	6.30
*Percent error	3.89%

22 days post-irradiation

No Cap T5 no Pb	
Bottle#	7
Count Date:	9/15/2023
Elapsed (d):	189
Decay factor:	0.871
Live Time (s):	86400.0
Peak Counts:	5566
Net Rate (cps):	0.064
Rate Uncert (%):	2.50
*Peak Eff (pcm):	9.010
Eff Uncert (%):	1.35
Activity (µCi):	0.0222
Uncert (%):	2.8
Dead Time	0.06%
Sample Mass	0.0792
Mass Uncert(%)	
Total Salt Mass (g)	6.0668
*Percent error	0.03%



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Update: Irradiation #3

Total Salt Mass Irradiated: 7.27 grams
Tracer (Na-22) Activity: 7.91 µCi (decay corrected)
Time Irradiated: 1 hour at 450 kW

Irradiation #3

- Na-22 tracer peaks detected for all 6 samples (28 mg to 6000 mg)
- Sample 3-6 represents original salt vial with samples 1-5 removed
- Uncertainty and activity/mass accounting error consistently lower
- 0.1-inch Pb filter and 0.25-inch aluminum cap used to reduce deadtime
- Count rate uncertainty for longer 12-hour counts 0.6% or below
- Count rate uncertainty for 5 hour counts <1%
- Larger salt sample (6 grams) did not significantly improve results

2-Hour Count

Irradiation-Bottle # (days after irrad)	Sample Mass (g)	Activity (uCi)	Activity Error	Estimated Total Mass (g)	Actual Total Mass (g)	Percent Error
2-5 (10 days)	0.395	0.1281	15.17%	5.24	6.065	13.57%
3-2 (3 days)	0.420	0.4645	1.5%	7.16	7.267	1.48%
3-2 (9 days)	--	0.4615	0.85%	7.21	--	0.84%
3-5 (6 days)	0.454	0.490	0.89%	7.33	--	0.90%
3-5 (10 days)	--	0.495	0.16%	7.25	--	0.16%
3-6 (6 days)	6.149	6.767	1.10%	7.19	--	1.09%
3-6 (10 days)	--	6.686	0.41%	7.30	--	0.41%

12-Hour Count

Irradiation-Bottle #	Sample Mass (g)	Activity (uCi)	Activity Error	Estimated Total Mass (g)	Actual Total Mass (g)	Percent Error
2-5 (15 days)*	0.395	0.116	4.35%	5.81	6.065	4.17%
3-2 (7 days)	0.420	0.451	1.38%	7.378	7.2669	1.39%
3-2 (10 days)	--	0.453	1.11%	7.358	--	1.12%
3-5 (6 days)	0.454	0.498	0.87%	7.204	--	0.86%
3-5 (12 days)	--	0.496	0.41%	7.237	--	0.41%
3-6 (9 days)	6.149	6.722	0.43%	7.236	--	0.43%
3-6 (11 days)	--	6.661	0.48%	7.302		0.48%

* Bottle 2-5 was counted for a total of 15 hours

Sample bottle with Al cap and Pb filter

Summary

- Two separate salt samples (6.1 g and 7.3 g) were successfully irradiated at the OSU Nuclear Reactor (3.96 x 10^{16} n/cm^2 total fluence), gamma spectra of fission products with added Na-22 tracer was acquired for short and long term data
- No interference peaks identified for short term spectrum (3-7 days).
- Tracer burnup was minimal and consistent with ORIGEN results.
- A thin piece of lead between the source and detector was effective in reducing deadtime, 121 keV Eu-154 is blocked, but higher energy of Eu-154 at 1004.7 keV is still unobscured for spectrum correction
- Uncertainties and error related to count rate identified as main contributor to error. Mass measurements and geometry less of a concern when carefully managed.
- Increasing the Na-22 tracer activity level in the salt greatly improves peak resolution and reduces uncertainty and error well below 1%.
- Successfully demonstrated total mass accounting using the radioactive tracer dilution method

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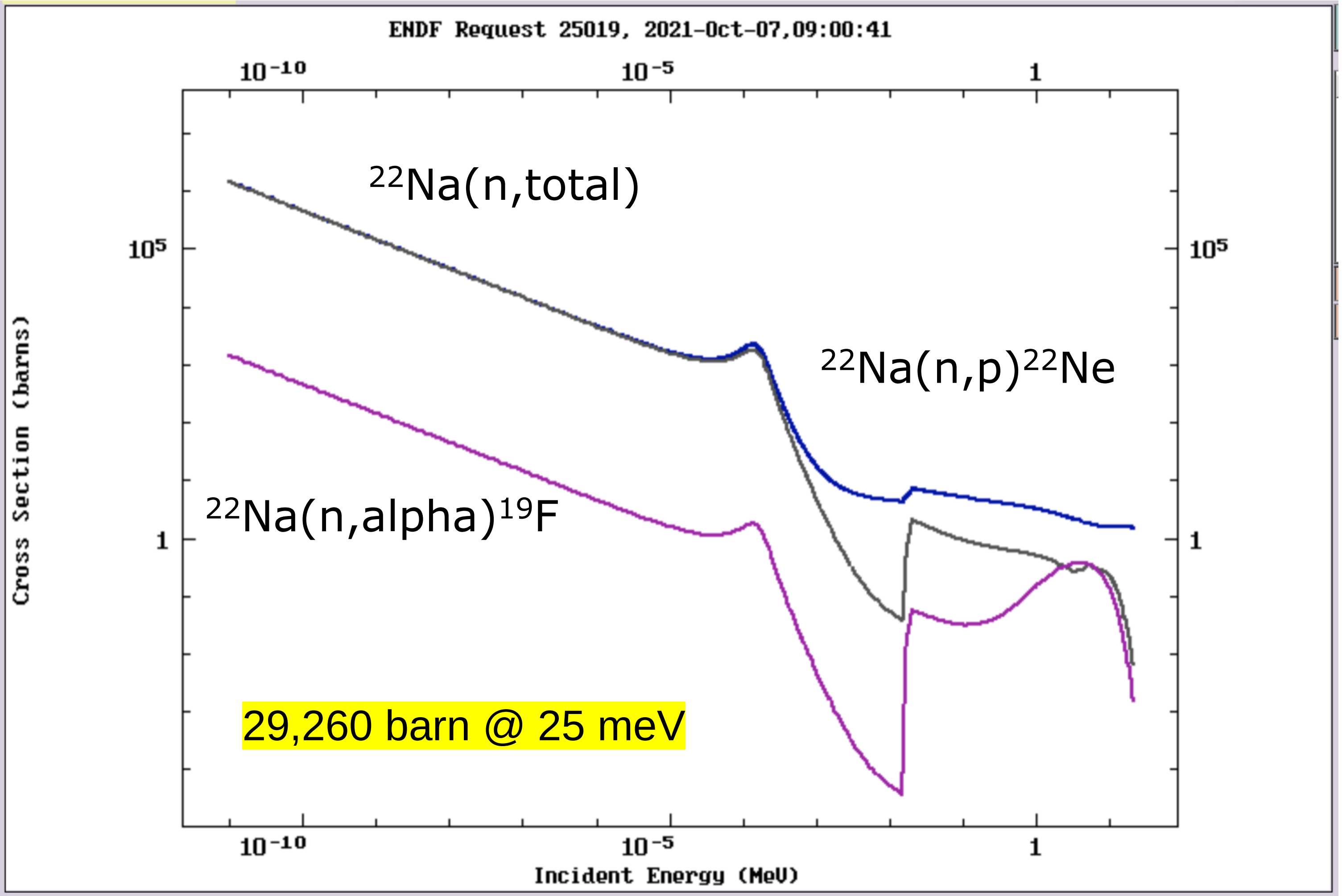
Thank you for your attention!

Challenges with tracer burn-up

- Na-22 has a significant neutron absorption cross-section



https://www.nndc.bnl.gov/

Radioisotope Selection

Two or more gamma lines in one isotope might be used to verify each other or in case one has an interference

May add two isotopes to validate each other or in case one has an interference

Na-22 is the best option

	Na-22	Co-60	Na-24	Br-82
Decay mode	β+	β-	β-	β-
Main gamma energy/keV	1274.54	1173.23; 1332.50	1368.63; 2754.01	554.35; 619; 776.52;1044
Half life	2.6018 y	1925 d	14.977 h	35.28 h
Comments	Not a fission product	Selective bounding?	$T_{1/2}$ too short	$T_{1/2}$ too short

Challenges: Off-gas Constituents

Table 1
Potential species in the cover gas of an MSR.

Type of cover gas constituent	Example species
Mists, aerosols, and particles	Salt residues, graphite debris for graphite-moderated fluoride systems, corrosion products, and noble metals (e.g., Ru, Pd, Rh)
Gases and volatile species	^3HF, HF, F_2, Cl_2, Br_2, I_2, Ar, interhalogens (e.g., ICl, IF_5, IF_7), volatile halides, and the decay products (e.g., Cs, Ba, Rb, Sr, La, Br, I, Se, Te) (Ostvald et al., 2009)
Tritium	$^3H_{2(g)}$, $^3HH_{(g)}$, $^3HF_{(g)}$, $^3HF_{(l)}$, and possibly $^3HHO_{(g)}$ and/or $^3H_2O_{(g)}$
Short-lived fission gases and their daughters	^{139}Xe $t_{1/2} = 39.5$ s, ^{137}Xe $t_{1/2} = 3.83$ min, ^{135m}Xe $t_{1/2} = 15.3$ min, ^{135}Xe $t_{1/2} = 9.1$ h, ^{133m}Xe $t_{1/2} = 2.19$ d, ^{133}Xe $t_{1/2} = 5.25$ d, ^{90}Kr $t_{1/2} = 32.3$ s, ^{89}Kr $t_{1/2} = 3.18$ min, ^{88}Kr $t_{1/2} = 2.84$ h
Longer-lived radionuclides	^{129}I $t_{1/2} = 1.57 \times 10^7$ y, ^{79}Se $t_{1/2} = 6.5 \times 10^4$y, ^{85}Kr $t_{1/2} = 10.7$ y, ^{36}Cl $t_{1/2} = 3 \times 10^5$ y

Source: *Andrews, Hunter et al. "Review of molten salt reactor off-gas management considerations." Nuclear Engineering and Design* ***385*** *(2021): 111529.*