Boron-Doped Polysiloxane Organic Scintillators

M. Duce[1], C. Chandler[2], A. Sellinger[2], A. Erickson[1]

[1]Georgia Institute of Technology, [2]Colorado School of Mines

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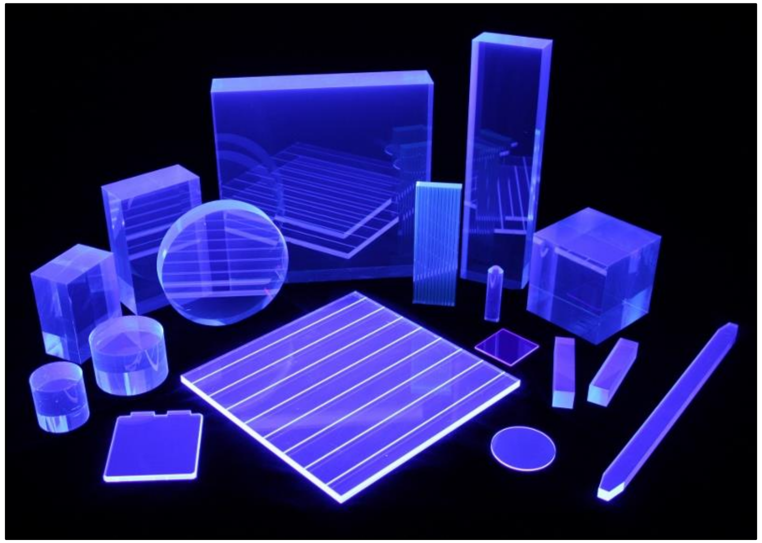
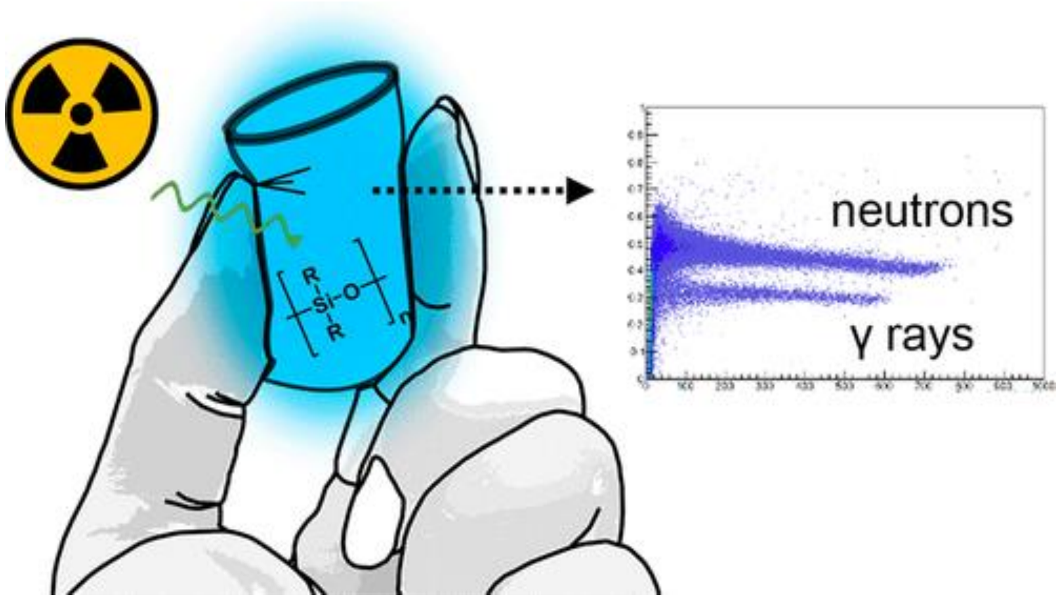
Motivation

- Scintillators respond to ionizing radiation by emitting photons
- Polysiloxanes are an alternative to thermoplastics like poly(vinyltoluene) PVT with reduced processing times and do not require overdoping





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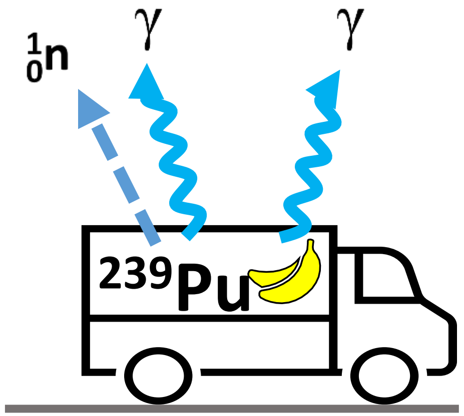
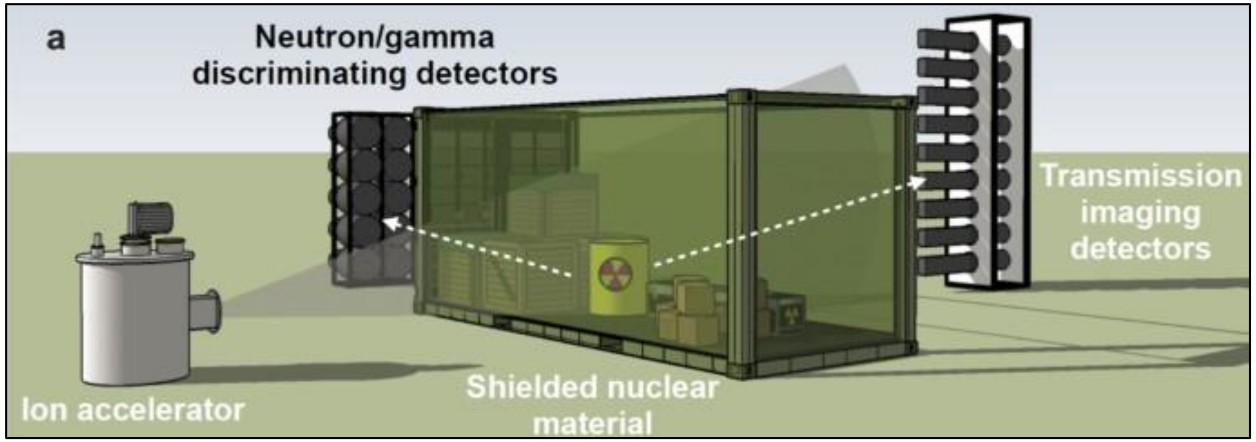
A. Lim, J. Arrue, P. Rose, A. Sellinger,, A. Erickson, ACS Appl. Polym. Mater., 2020, 2, 8, 3657-3662

Mission Relevance

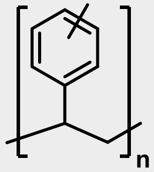
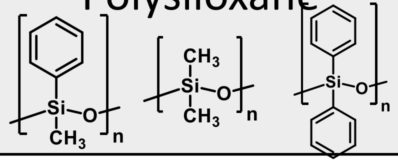
- Triple particle detection can support many detection applications





Rose, P., Erickson, A., Mayer, M, Nattress, J., Jovanic, I., Scientific Reports, 3016

PVT vs. Polysiloxane-based scintillators

	PVT 	Polysiloxane 
Transparency	Yes	Yes
Physical Properties	Hard, rigid	Variable
Radiation Hardness	No	Yes
Thermal Stability	No	Yes
Fabrication	5 days, air sensitive	3 hrs, in air
Cost	\$0.08/g	\$0.75 - \$16/g
PSD	@ 20%wt dopant	@ 5%wt dopant

Bertrand, G. H. V.; Hamel, M.; Sguerra, F. *Chem. Eur. J.* 2014, 20 (48), 15660–15685.
Quaranta, A. et al. *Nucl. Instrum. Methods Phys. Res., B.* 2010, 268 (19), 3155–3159.
Marchi, T. et al. *Sci. Rep.* 2019, 9 (1), 9154.
Prices from Sigma, Gelest, TCI America, and Nusil

National Nuclear Security Administration

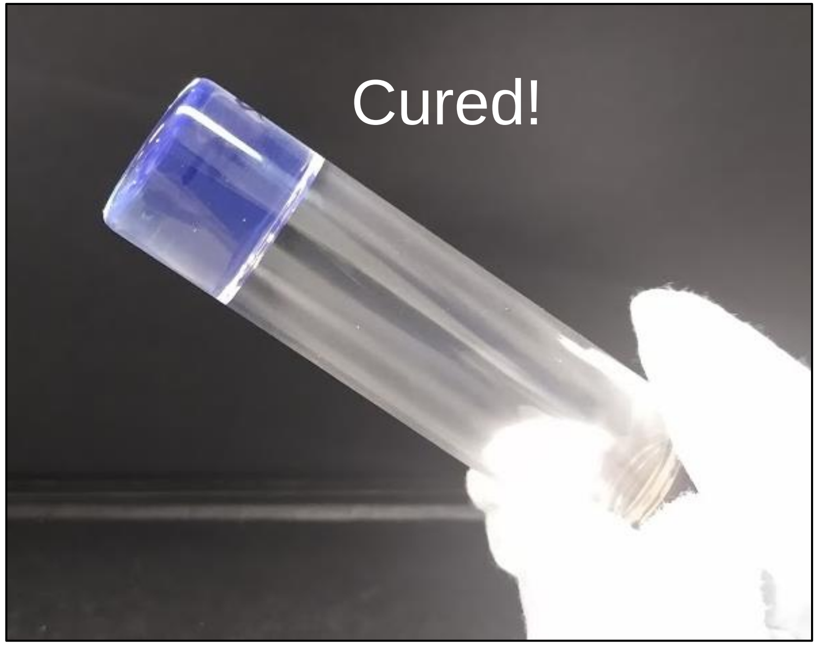
Fabrication – Colorado School of Mines


Prepare silanized vial (30-60 mins)


Add SFS, PPO


Add xylenes

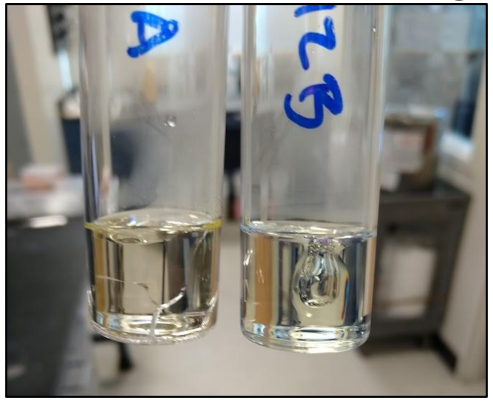

Solubilize and add Part A, mix, add Part B



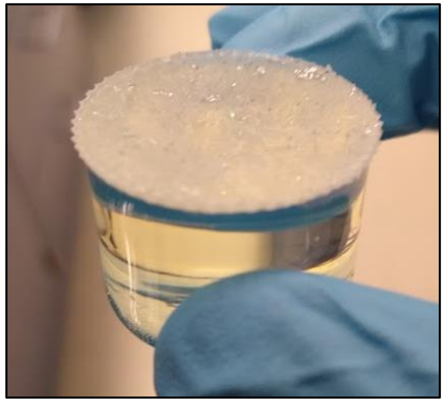
Vortex, then cure at 150 C for 3 hrs in air

Common Fabrication Challenges

Glass Cracked | **Internal Bubbling**

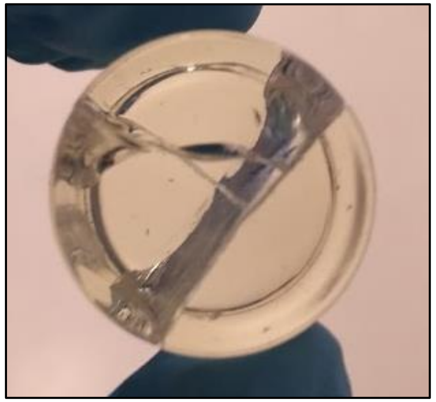


Dopant Precipitation on Surface

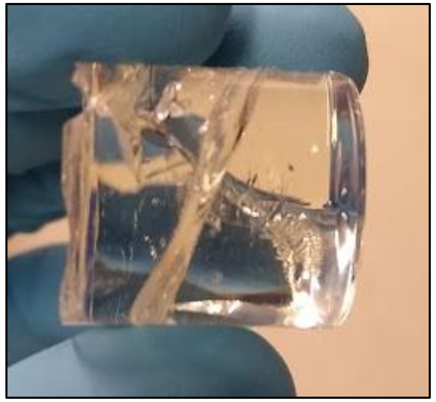


Internal Precipitation

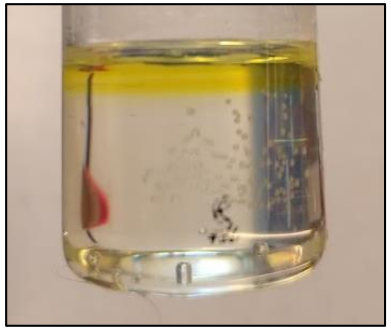
Cracked



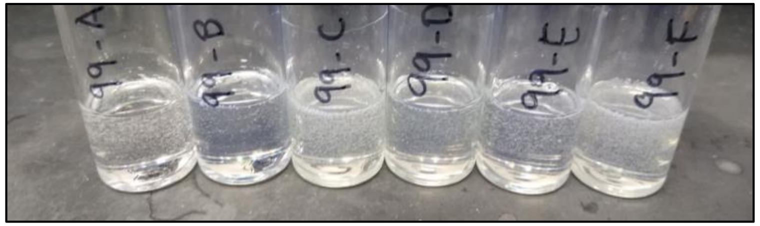
Cracked



Surface Coloration

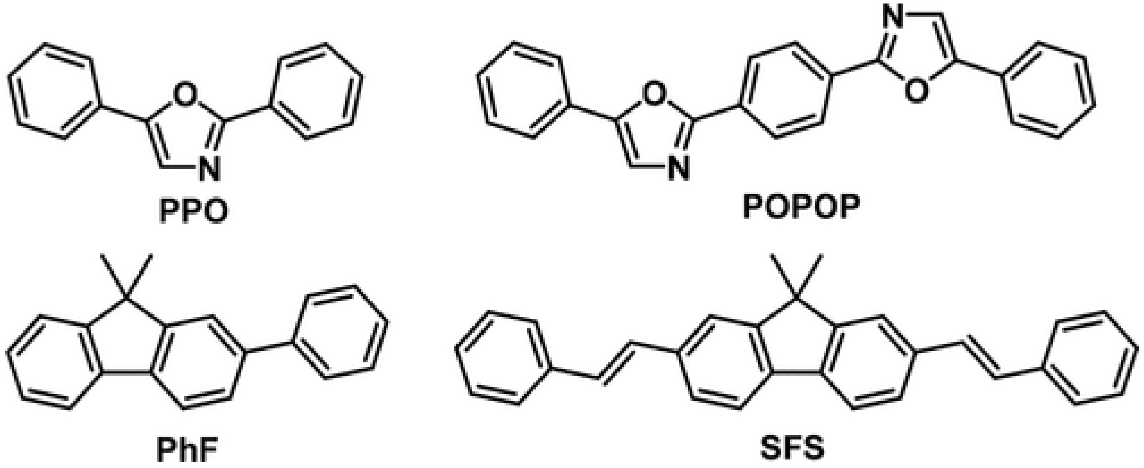


Air Bubbles Trapped



Primary Fluorophores

- Primary dopants (fluorophore):
  - 9,9-dimethyl-2-phenyl-9H-fluorene (PHF)
  - 2,5-diphenyloxazole (PPO) : Industry-standard fluorophore
- Secondary dopant (wavelength shifter):
  - 9,9-dimethyl-2,7-distyryl-9H-fluorene (SFS)



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Detector Characterization

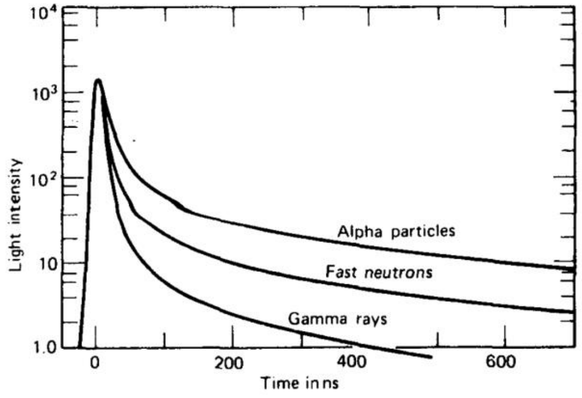
- Light yield
- Pulse shape discrimination (PSD)

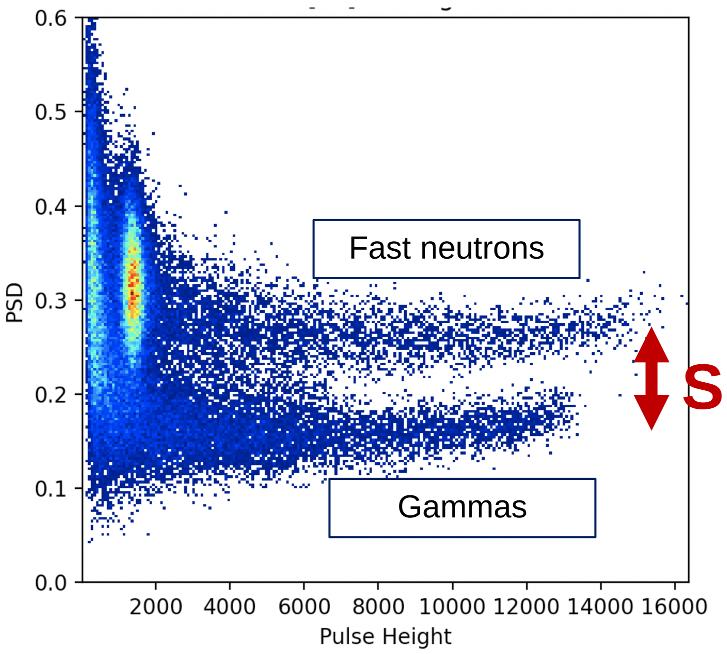
$$PSD = \frac{Q_{tail}}{Q_{total}}$$

- S = separation of neutron and gamma lobe
- Figure of merit (FoM)

$$FOM = \frac{S}{FWHM_\gamma + FWHM_n}$$

- “Efficient” FOM at 1.27





Knoll, Radiation Detection and Measurement
Zaitseva, N., Rupert, B., PaweLczak, I., Glenn, A., Martinez, H., Carman, L., Faust, M., Cherepy, N., Payne, S., NIM A, 2012

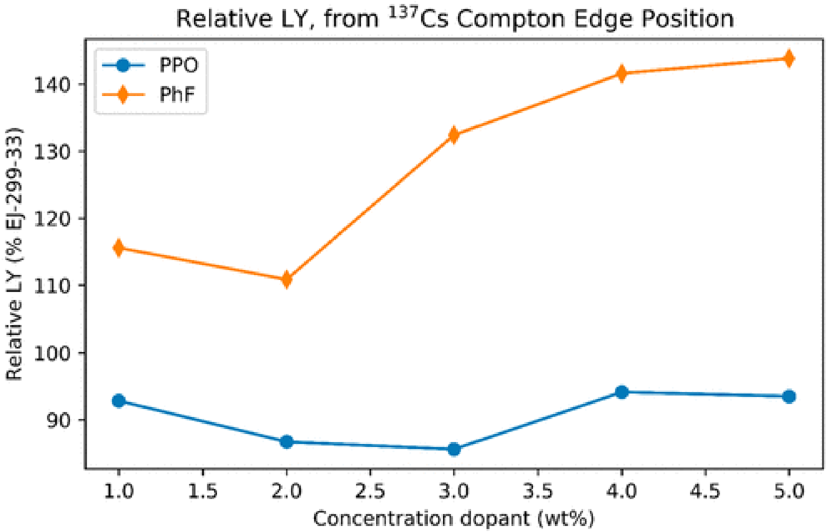
National Nuclear Security Administration

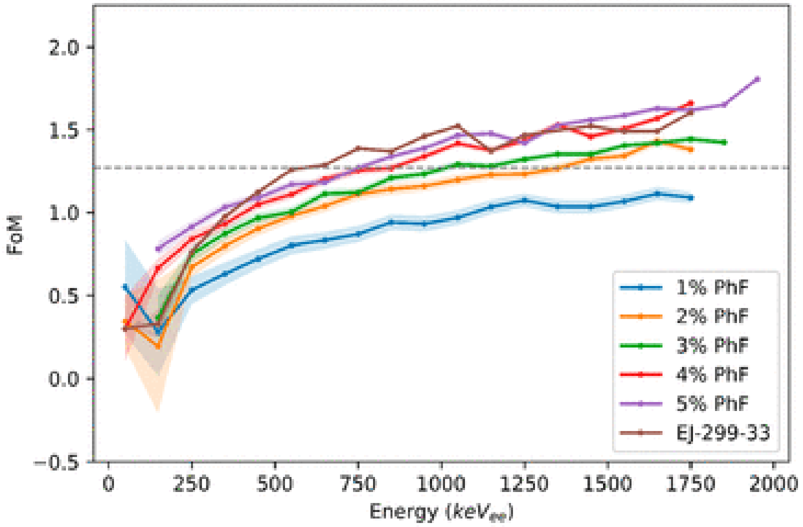
Previous Results

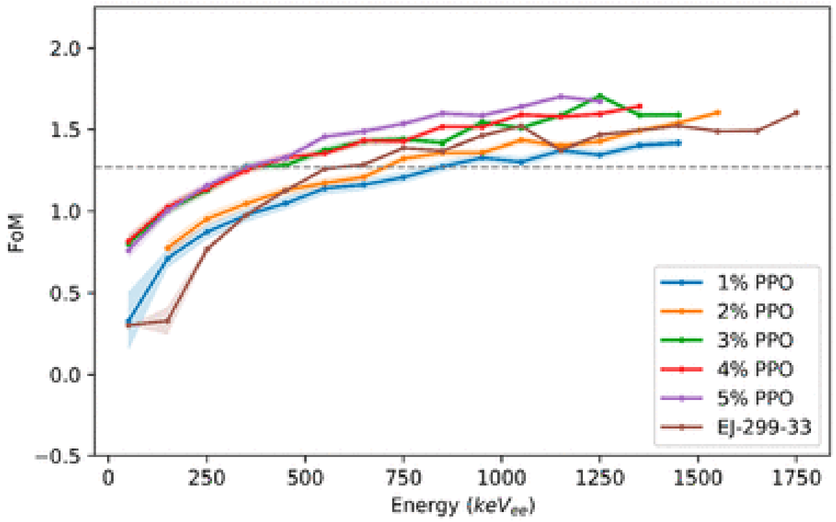
- Polysiloxane fabrication with Wacker Lumisil 579, PHF, PPO
  - FoM of 1.09 ± 0.03 with 5% PHF at 450keV
  - FoM of 1.33 ± 0.03 with 5% PPO at 450keV

	λ_{max}, PPO [nm]	λ_{max}, PhF [nm]
1 wt % in polysiloxanes	407	356
4 wt % in polysiloxanes	411	360
1 wt % in PVT	400	398
20 wt % in PVT	408	405

EJ200 max is 425







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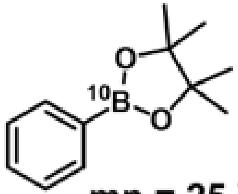
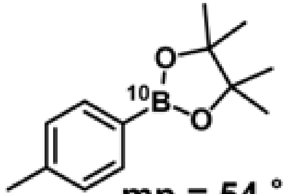
B-10 Enriched Molecules

3.75wt% phenylpinacolborane[1]



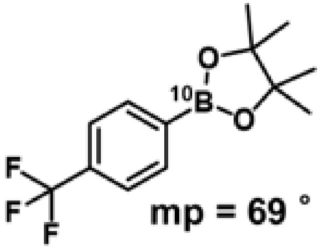
mp = 25 ° C

3wt% tolyl-



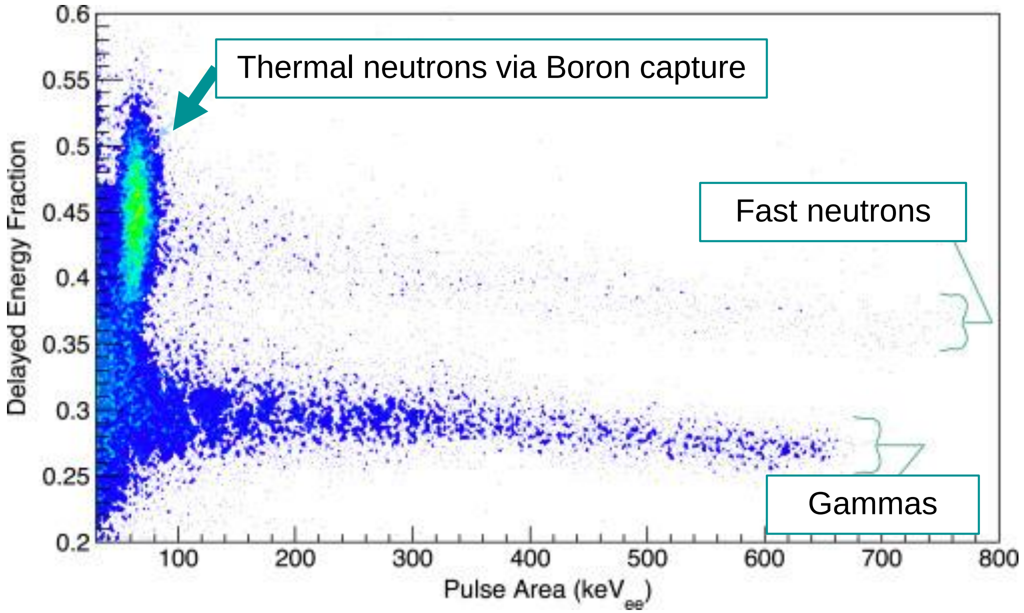
mp = 54 ° C

5wt% trifluoro-



mp = 69 ° C

$$^{10}B + n_{th} \rightarrow \begin{cases} ^{7}Li_{(1.01\ \mathrm{MeV})} + \alpha_{(1.78\ \mathrm{MeV})} \\ Q = 2.790\ \mathrm{MeV},\quad 6.3\% \\ \\ ^{7}Li^{*}_{(0.84\ \mathrm{MeV})} + \alpha_{(1.47\ \mathrm{MeV})} \\ \hookrightarrow {}^{7}Li^{*} \rightarrow {}^{7}Li + \gamma_{(478\ \mathrm{keV})} \\ Q = 2.310\ \mathrm{MeV},\quad 93.7\% \end{cases}$$

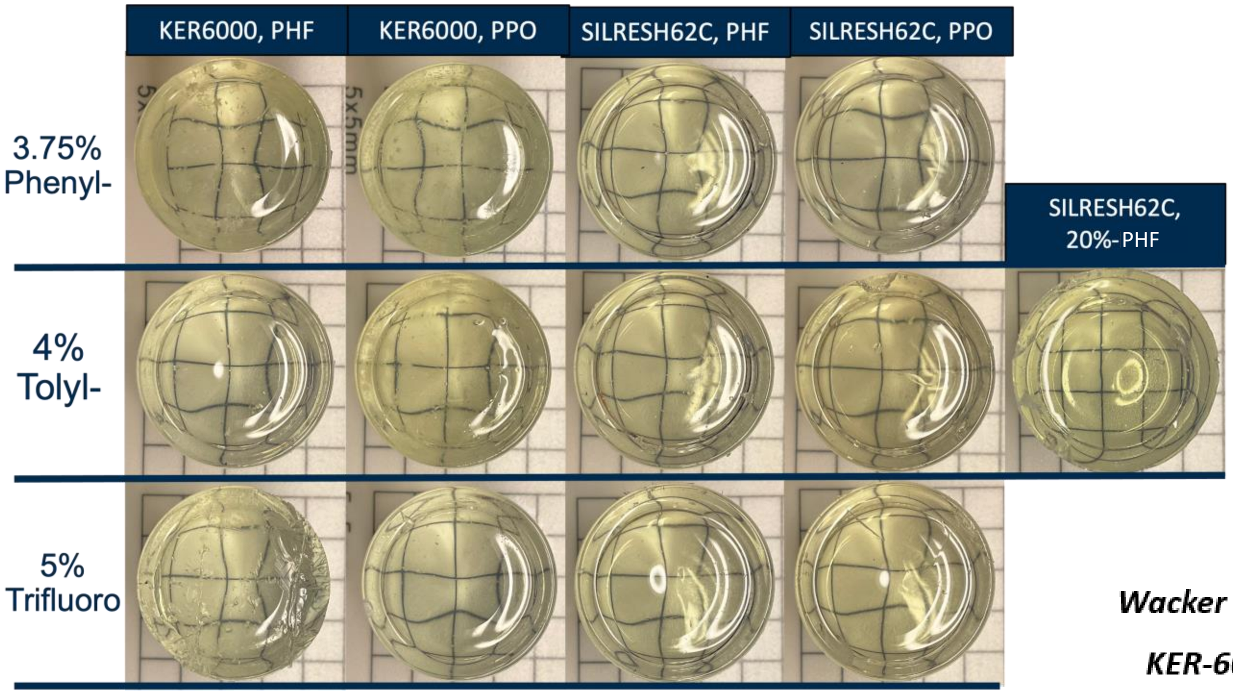


Previous work with phenyl B-10 enriched molecule for thermal neutron detection with PVT matrix, PPO, POPOP[1]

^{10}B has a neutron reaction cross section of 3837 barns (compared to ^{3}He: 5333 barns) at thermal neutron energies (25 meV)

A. Mahl, H.A. Yemam, R. Fernando, J.T. Koubek, A. Sellinger, U. Greife, NIM A, 2018, 880, 1-5

Boron-Loaded Matrices



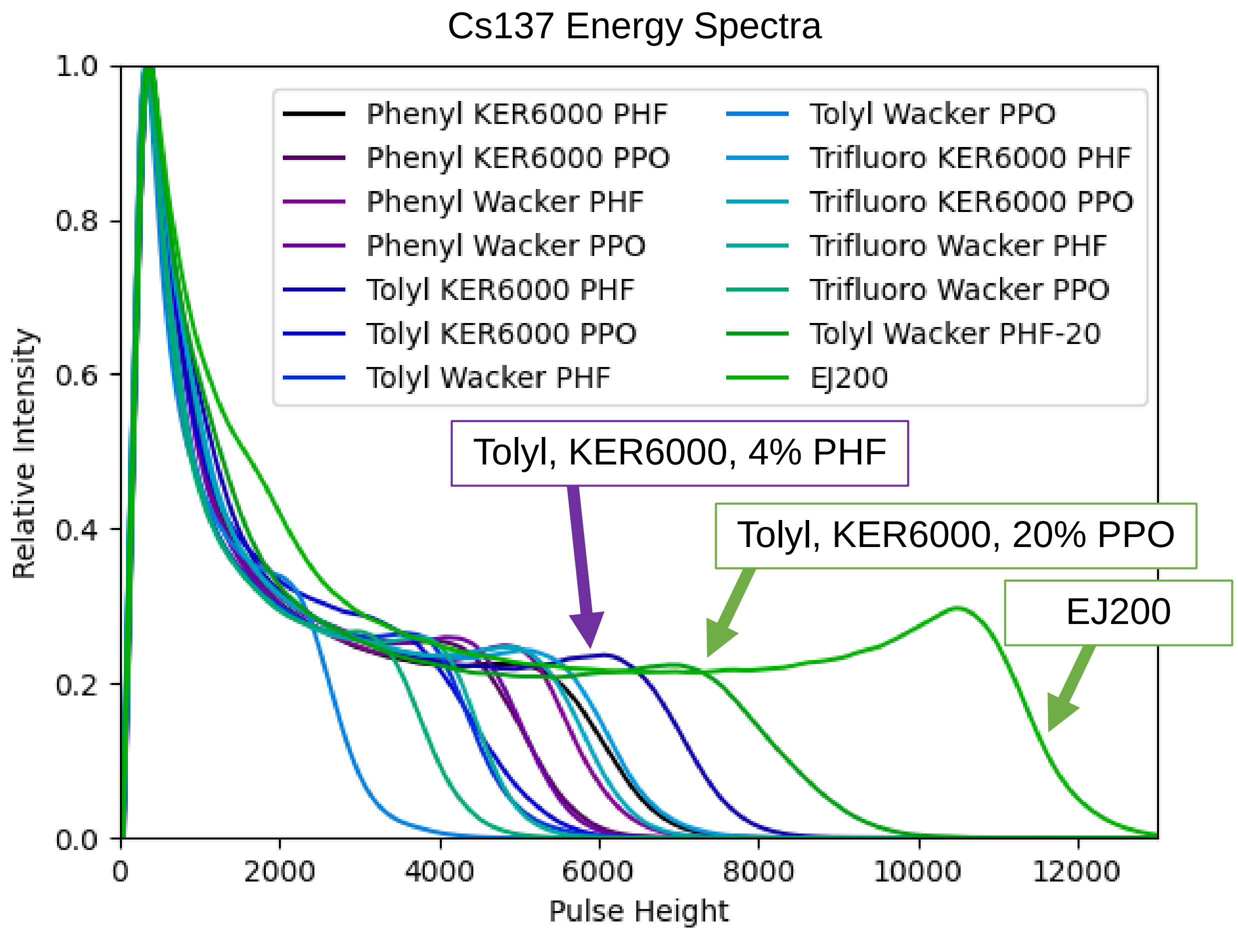
- Polymer resins used:
  - ~~Wacker Lumisil 579~~
    - ~~LED encapsulant~~
  - Shin-Etsu KER-6000
    - LED encapsulant
  - Wacker SILRES H62C
    - electronics encapsulant

	R.I.	Hardness	Mix	Cure
Wacker 579	1.53	25 Shore A	2-component	150 °C / 1 hr
KER-6000	1.51	22 Shore A	2-component	100 °C / 1 hr, 150 °C / 2 hr
SilRes H62C	1.50	65 Shore D	1-component	150 °C / 10 hr

Light Yield

- Cs-137 Measurements
  - Compton edge calculated per Safari et. al

	Light Yield (%EJ200, %Anthracene)			
B-10 enriched molecule	5% PHF	5% PPO	20% PHF	Matrix
5% Phenyl-	53, 34	45, 29		KER6000
	49, 31	45, 29		Wacker
4% Tolyl-	**62, 40**	39, 25		KER6000
	39, 25	23, 15	**71,45**	Wacker
5% Trifluoro-	55, 35	51, 33		KER6000
	39, 25	33, 21		Wacker



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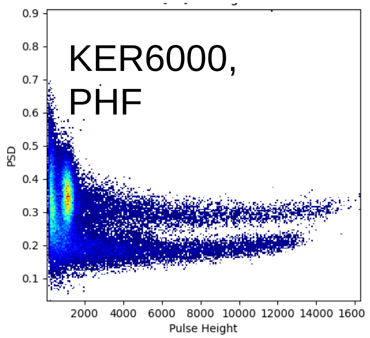
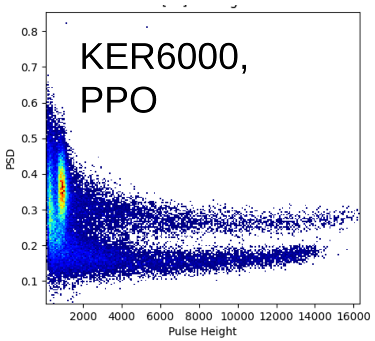
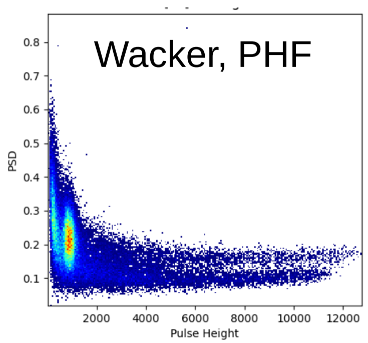
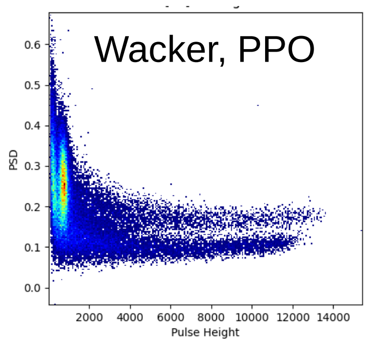
Safari, M.J., Davani, A., Afarideh, H, Radiation Physics and Engineering, 2016

PSD Plots

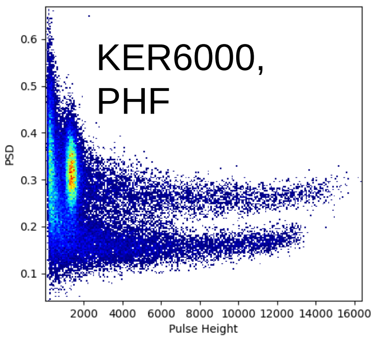


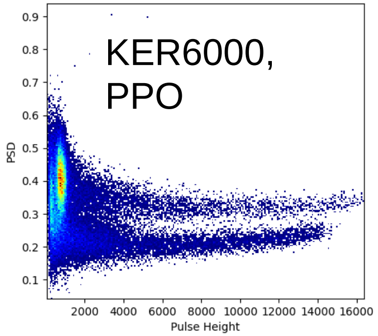


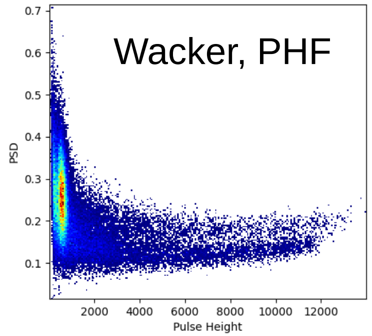


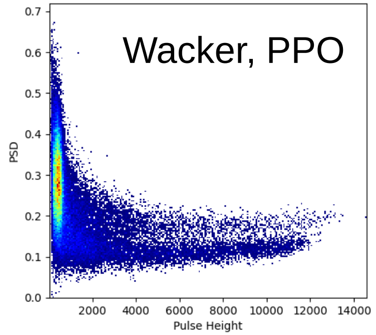


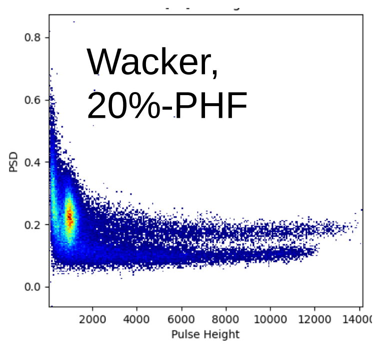
Phenyl-



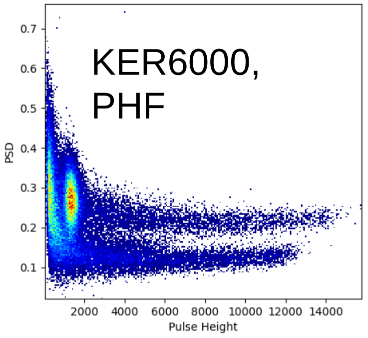


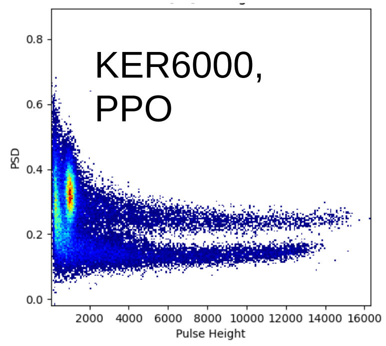


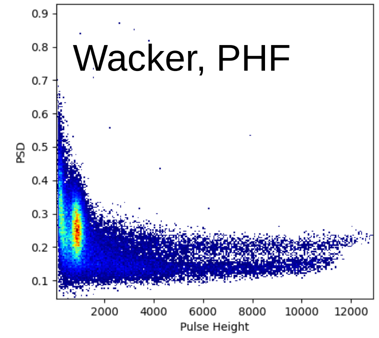


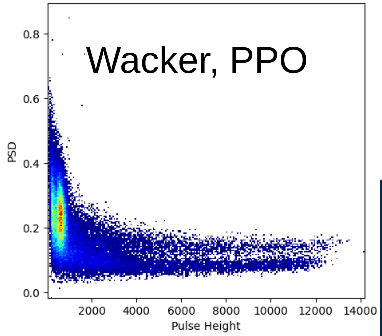


Tolyl-









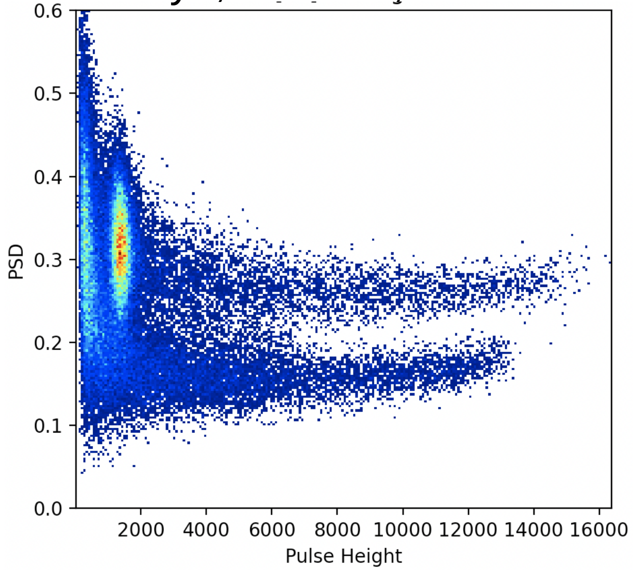
Trifluoro-

Figure of Merit $(\mathbf{n}, \gamma)$

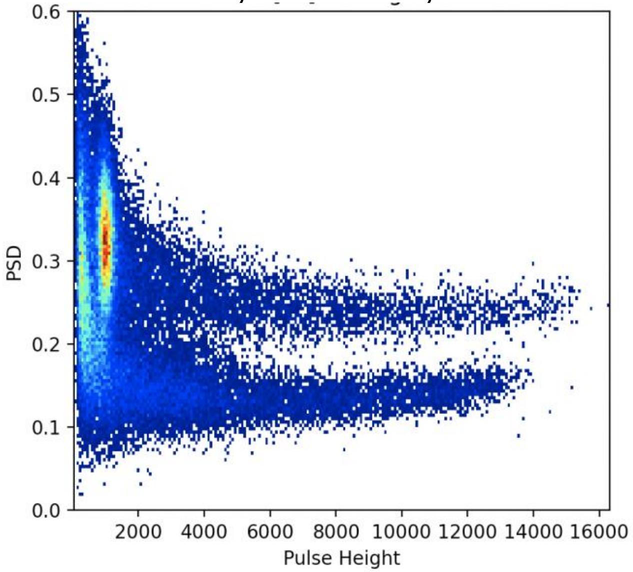
	FoM at 500keV			
B-10 enriched molecule	5% PHF	5% PPO	20% PHF	Matrix
5% Phenyl-	1.09	0.81		KER6000
	x			Wacker
4% Tolyl-	**1.17**	0.78		KER6000
	0.64	0.62	1.03	Wacker
5% Trifluoro-	1.10	**1.21**		KER6000
	c	0.69		Wacker

x = GMM cannot converge

4% Tolyl-, 5% PHF, KER6000



5% Trifluoro, 5% PPO, KER6000



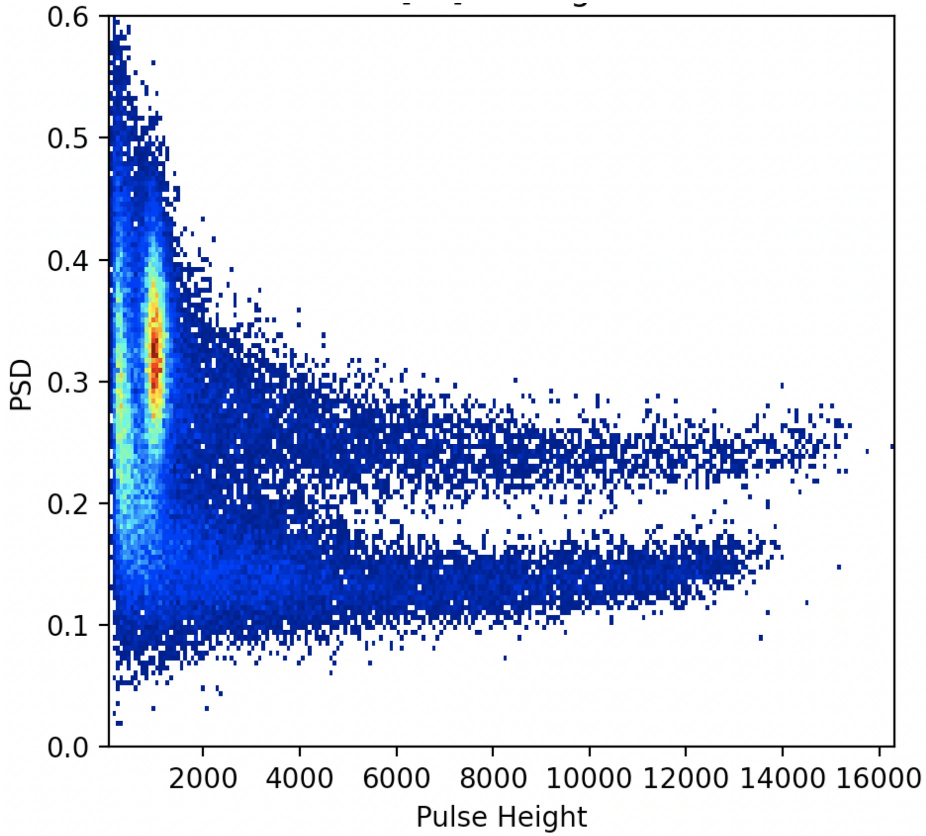
- Efficient PSD at 1.27 FoM

Figure of Merit $(\mathbf{n_{th}}, \gamma)$

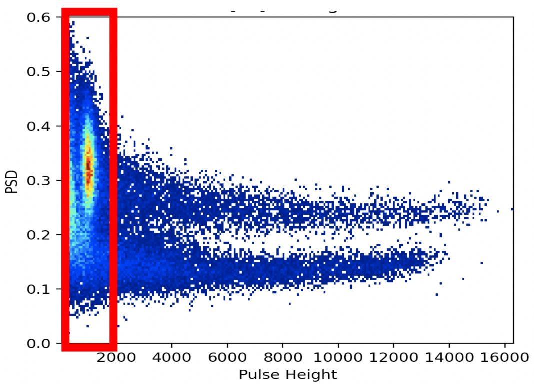
	FoM at 500keV			
B-10 enriched molecule	5% PHF	5% PPO	20% PHF	Matrix
5% Phenyl-	0.48	0.48		KER6000
	0.34	0.38		Wacker
4% Tolyl-	0.47	0.47		KER6000
	0.29	0.36	0.32	Wacker
5% Trifluoro-	0.48	**0.54**		KER6000
	0.33	0.33		Wacker

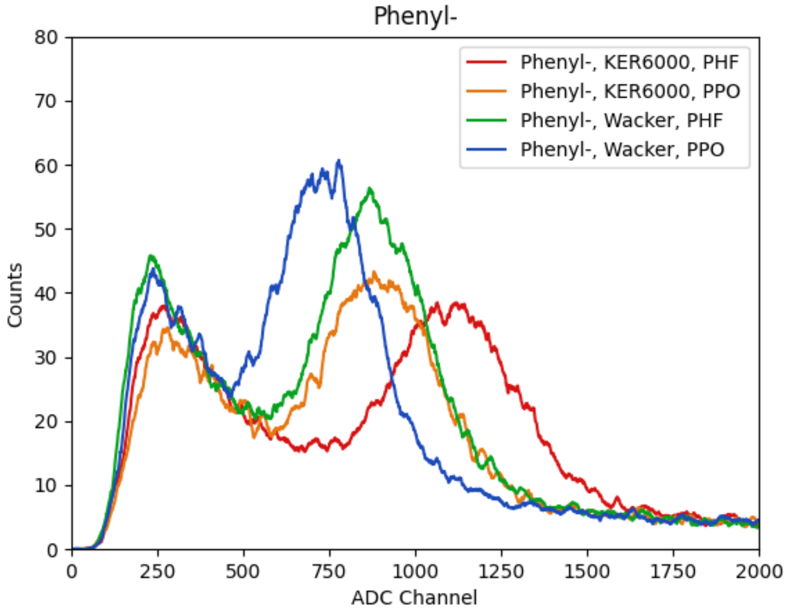
- EJ309-B: 0.65 FoM

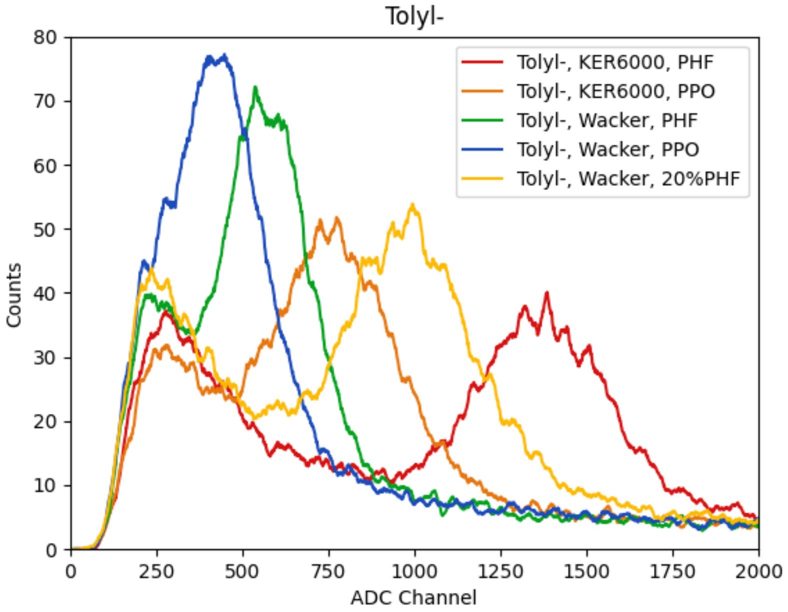
4% Trifluoro-, 5% PHF, KER6000

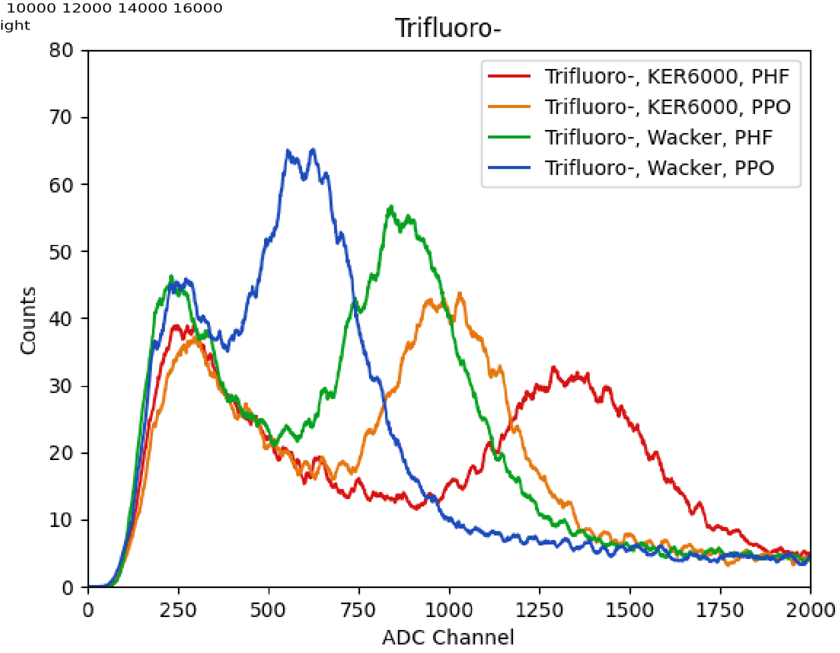


Energy Spectra



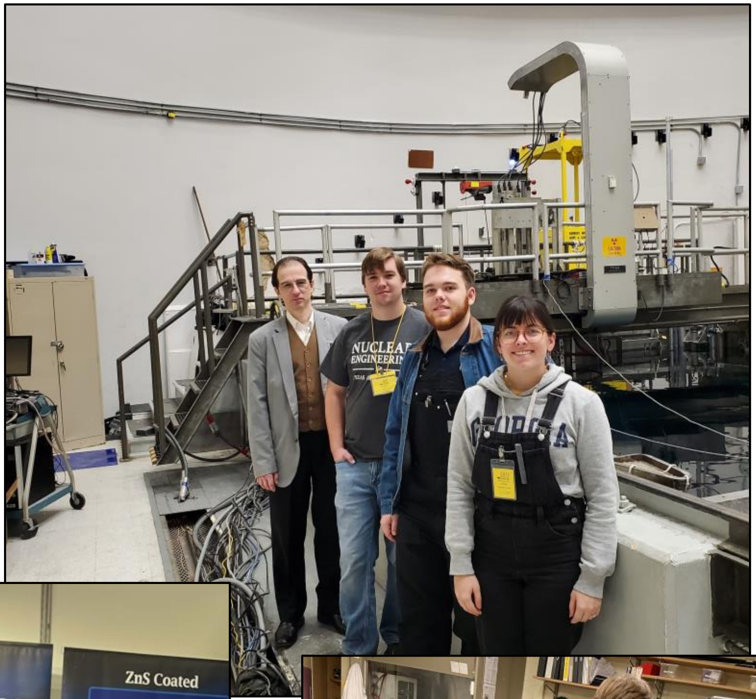






ETI Impact

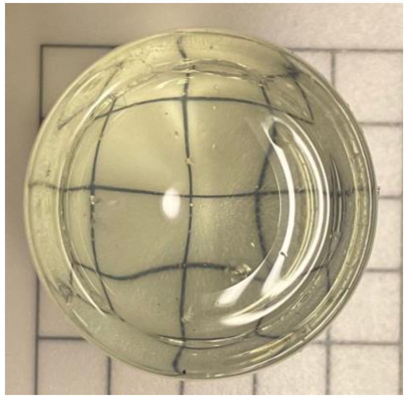
- Internship at LBL supporting the EOS demonstrator
- Presentation at IEEE MIC/NSS 2022
  - Arrue, J., Chandler, C., Duce, M., Sellinger, A., Erickson, A., “Boron Doped Polysiloxane Organic Scintillators for Thermal and Fast Neutron Detection Via Pulse Shape Discrimination”
- Collaboration with Colorado School of Mines
- Ex-Core measurements with Texas A&M



Conclusion

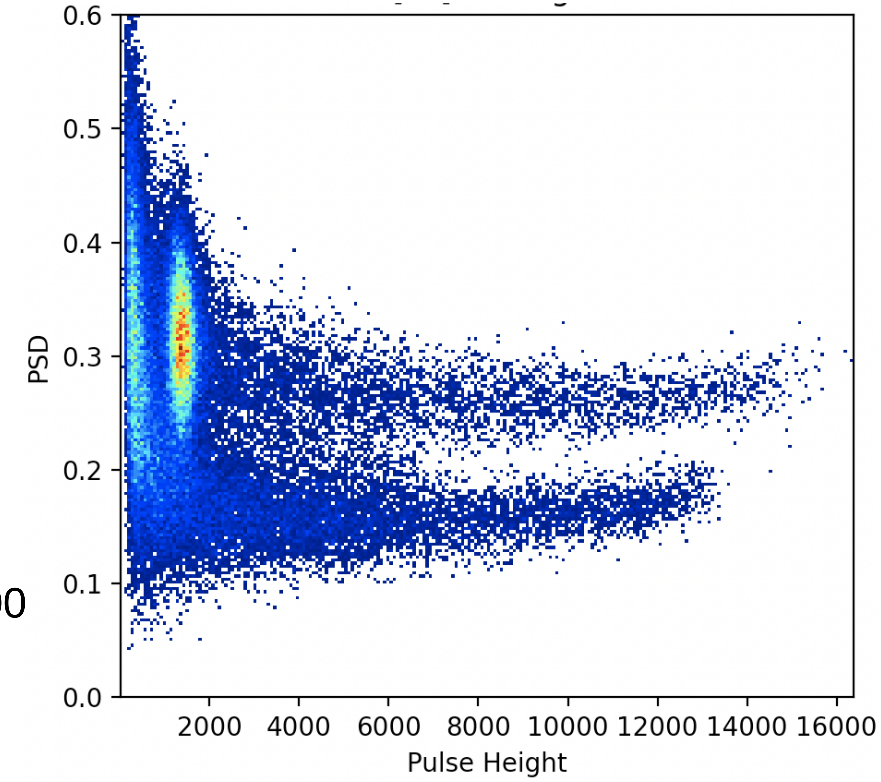
- Boron-enriched molecule doped did not diminish FOM(n, γ) from previous polysiloxane trials
- Best FOM$(n_{th}, \gamma) = 0.54$ 83% of EJ309-B
- Best light yield 62% of EJ200

- Successful triple particle detection!



4% Tolyl-, 5% PHF, KER6000

4% Tolyl-, 5% PHF, KER6000



Thank you

- LANNS Group
  - Alex England
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  - Natalie Cannon
  - Matthew Dunbrack
  - Jana Shade
  - Pierre O’Driscoll
  - Anna Schafer
  - Dr. Anna Erickson
  - Dr. Yuguo Tao
- Caleb Chandler, Dr. Allen Sellinger

LANNS
LABORATORY FOR ADVANCED NUCLEAR NONPROLIFERATION AND SAFETY

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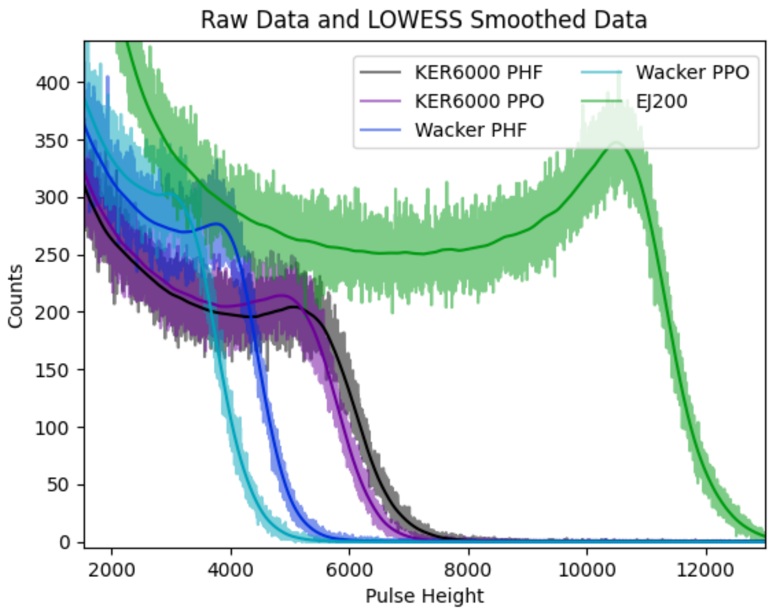
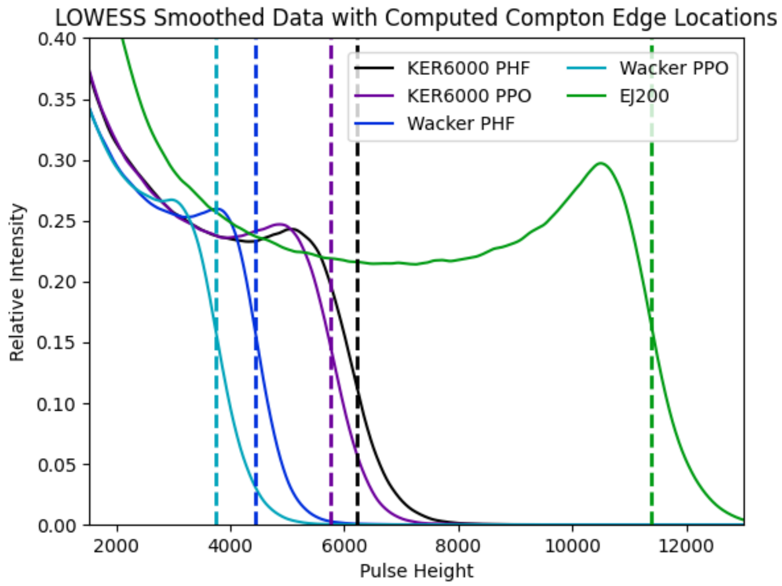
Nevada National Security Site · Oak Ridge National Laboratory · Pacific Northwest National Laboratory · PPPL Princeton Plasma Physics Laboratory · Sandia National Laboratories · SRNL Savannah River National Laboratory

NNSA National Nuclear Security Administration

Consortium for Enabling Technologies & Innovation

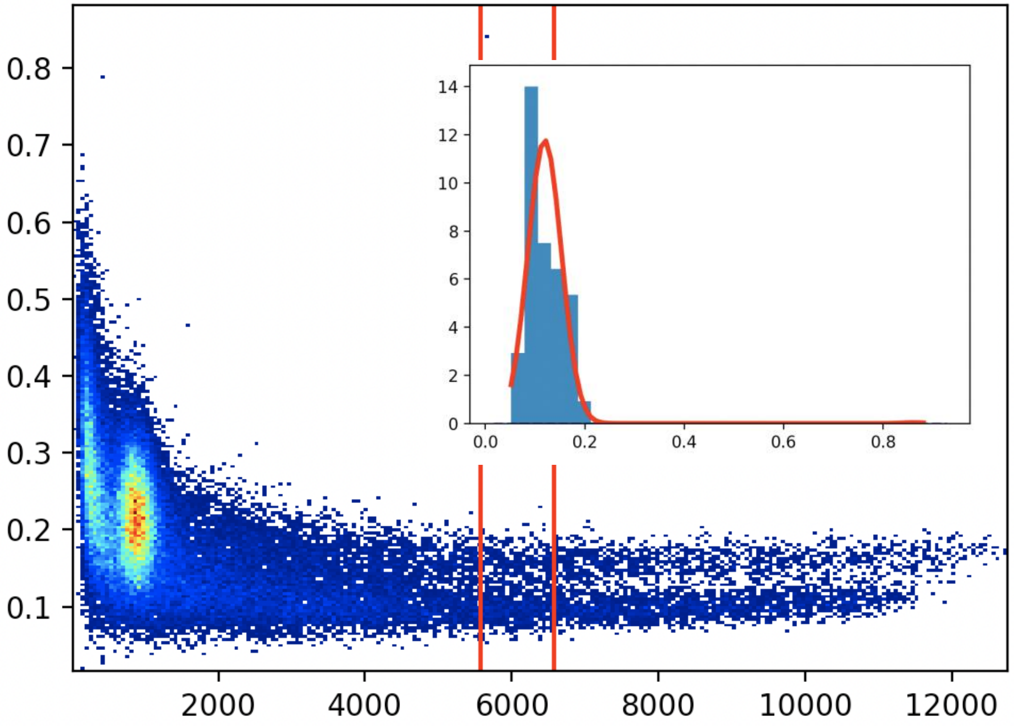
Light Yield – Compton Edge



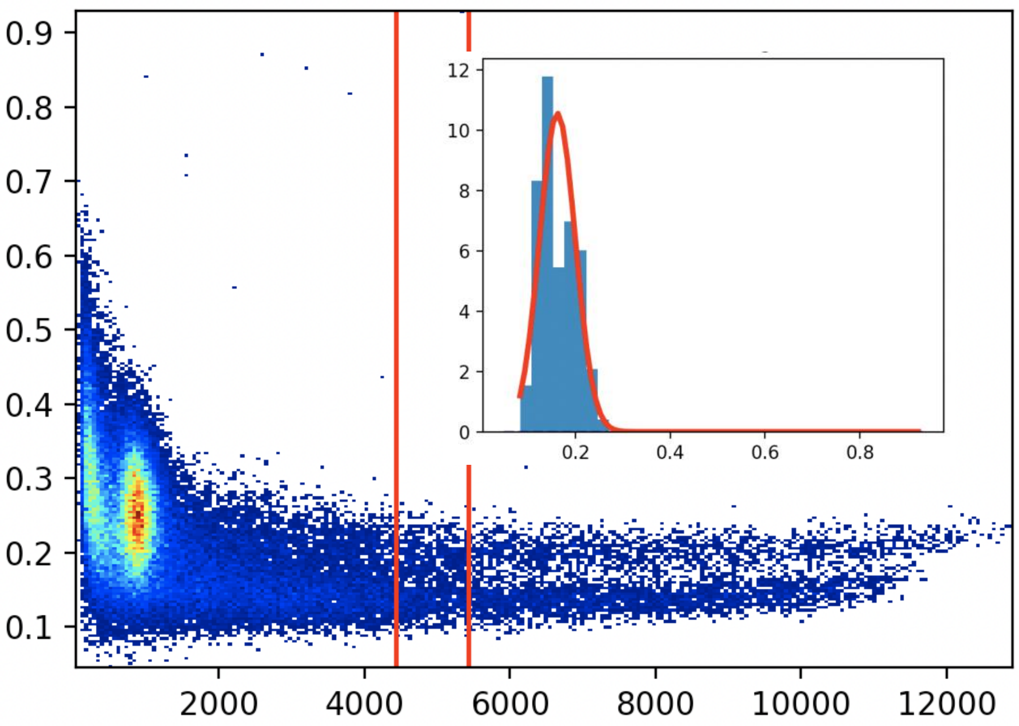


Non-convergable FoM

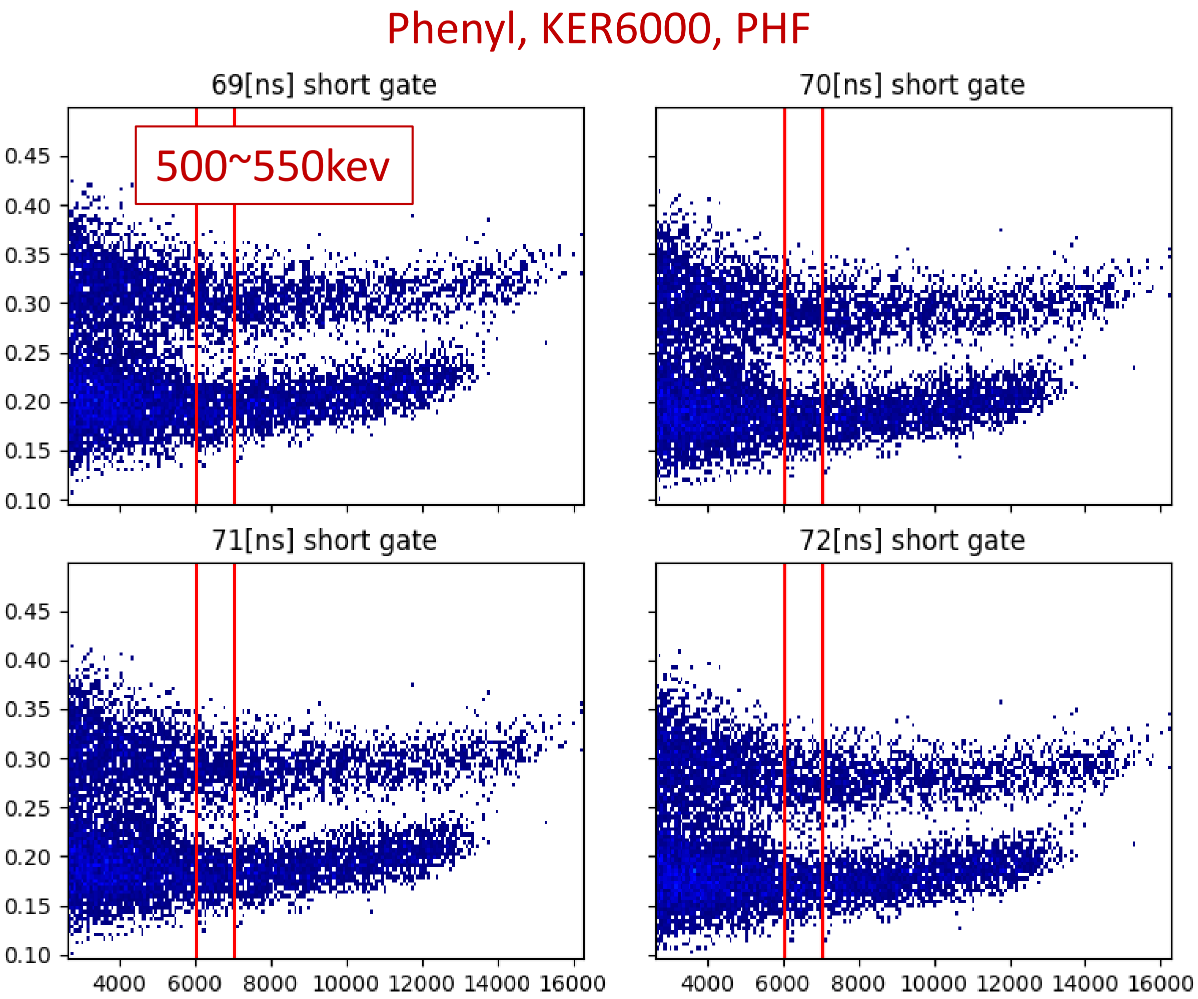
Phenyl, Wacker SILRES, 5% PHF

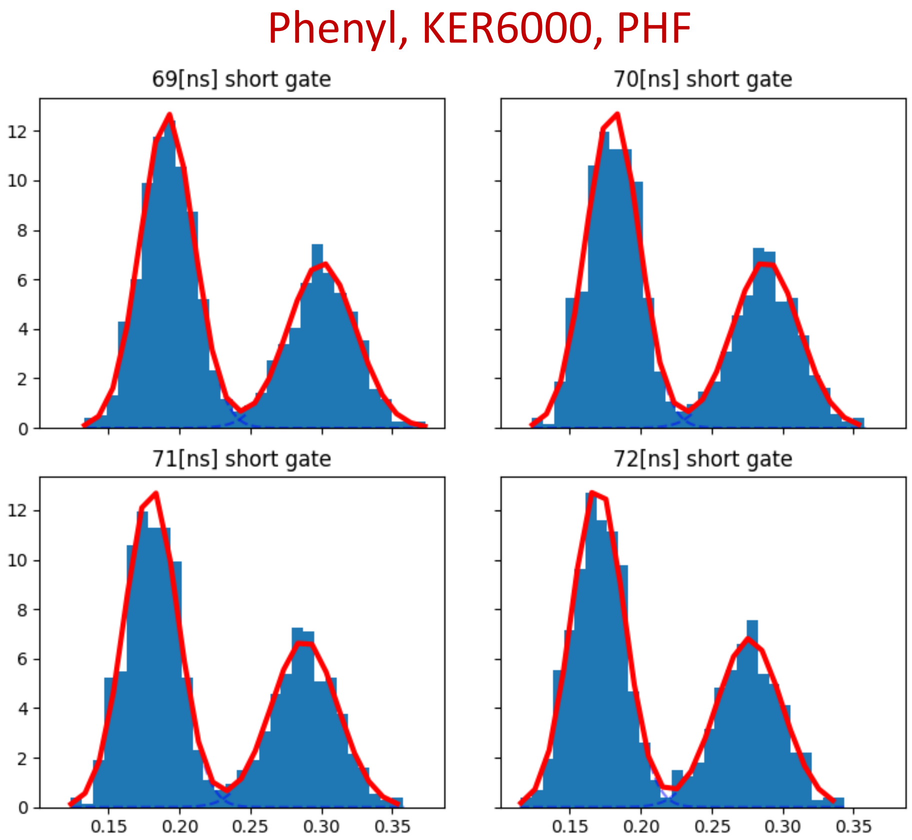


Trifluoro, Wacker SILRES, 5% PHF



FoM Calculation: GMM

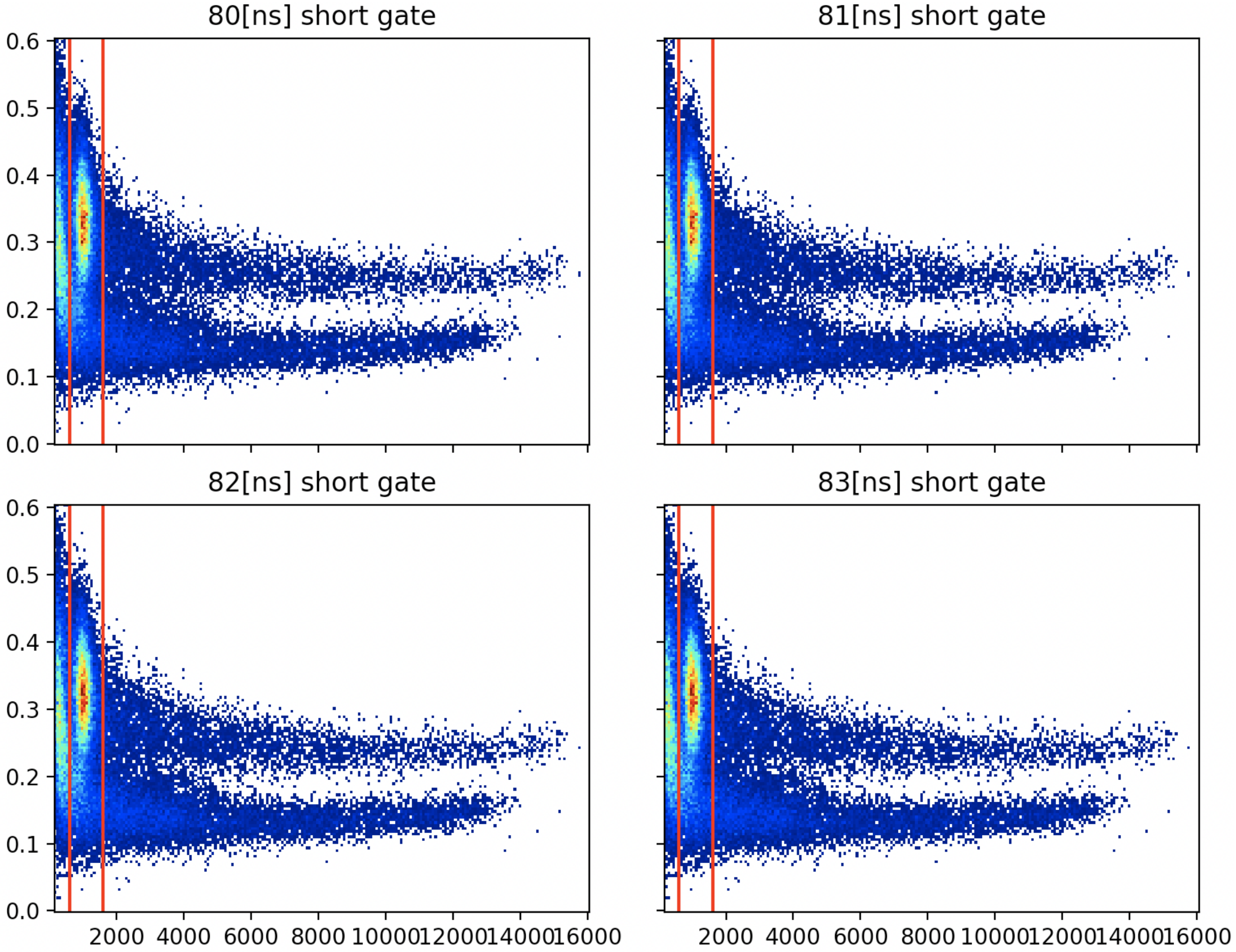




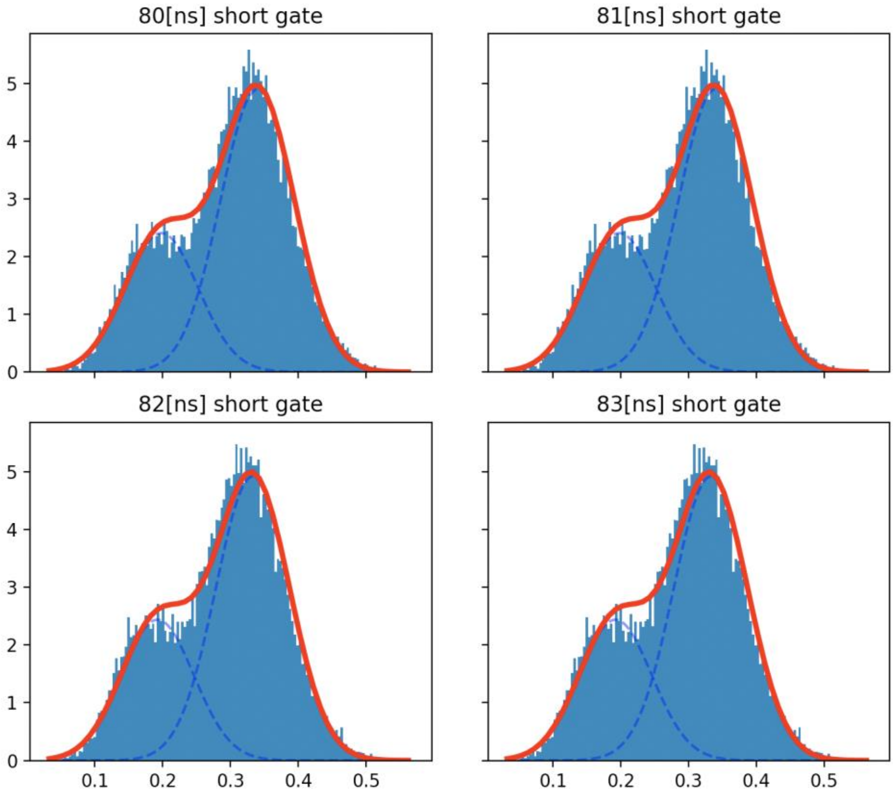
Gate	Means	Stds	FWHMs	FoM	R^2
69	0.191, 0.300	0.019, 0.024	0.044, 0.064	**1.08**	**0.96**
70	0.180, 0.288	0.019, 0.023	0.044, 0.055	**1.09**	**0.95**
71	0.180, 0.288	0.019, 0.023	0.044, 0.055	**1.09**	**0.95**
72	0.170, 0.275	0.018, 0.023	0.043, 0.055	**1.09**	**0.93**

FoM (nth, g) Calculation: GMM

Trifluoro, KER6000, PPO



Trifluoro, KER6000, PPO



Gate	Means	Stds	FWHMs	FoM	R^2
82	0.192, 0.333	0.054, 0.055	0.126, 0.129	**0.55**	**0.98**

Ion quenching in boron-doped organic scintillators

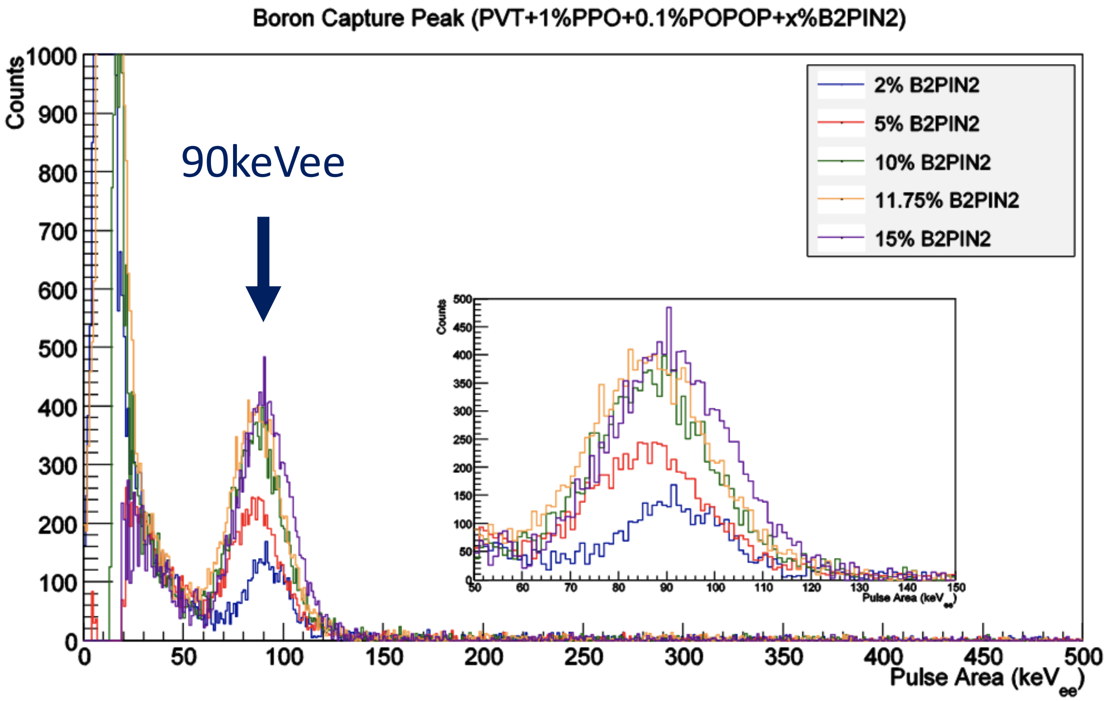


Figure 3: Number of counts versus calibrated pulse area (keV$_{ee}$) for ^{10}B thermal neutron reaction spectra with gamma response subtracted via cadmium shielded measurement. The keV$_{ee}$ sample scale adjusts all samples to the ^{137}Cs Compton edge position of each sample (light yield adjustment) to make changes in alpha quenching apparent.

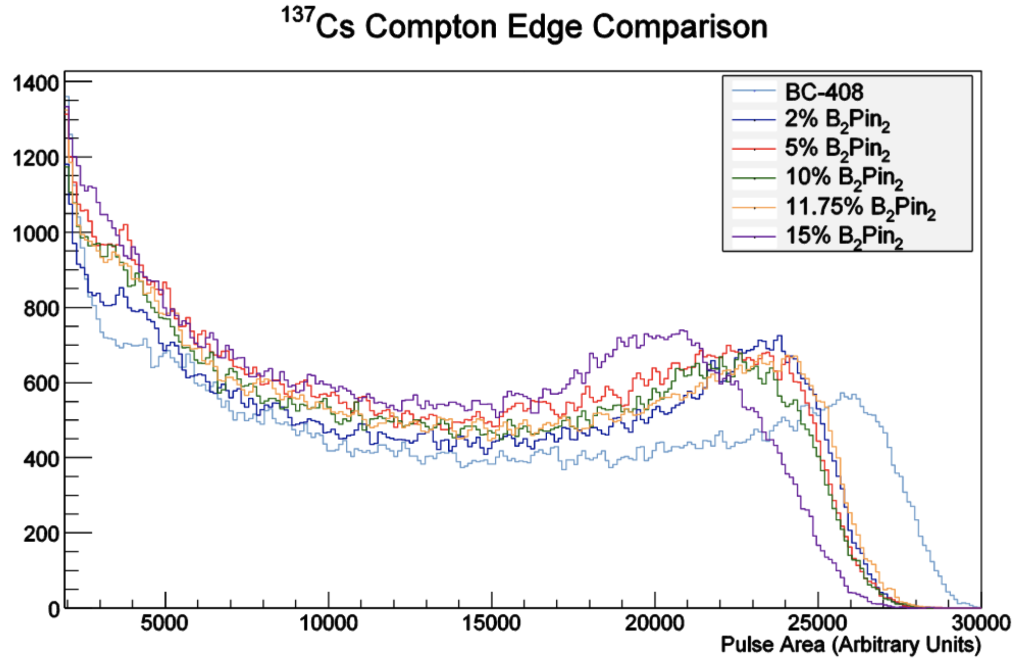
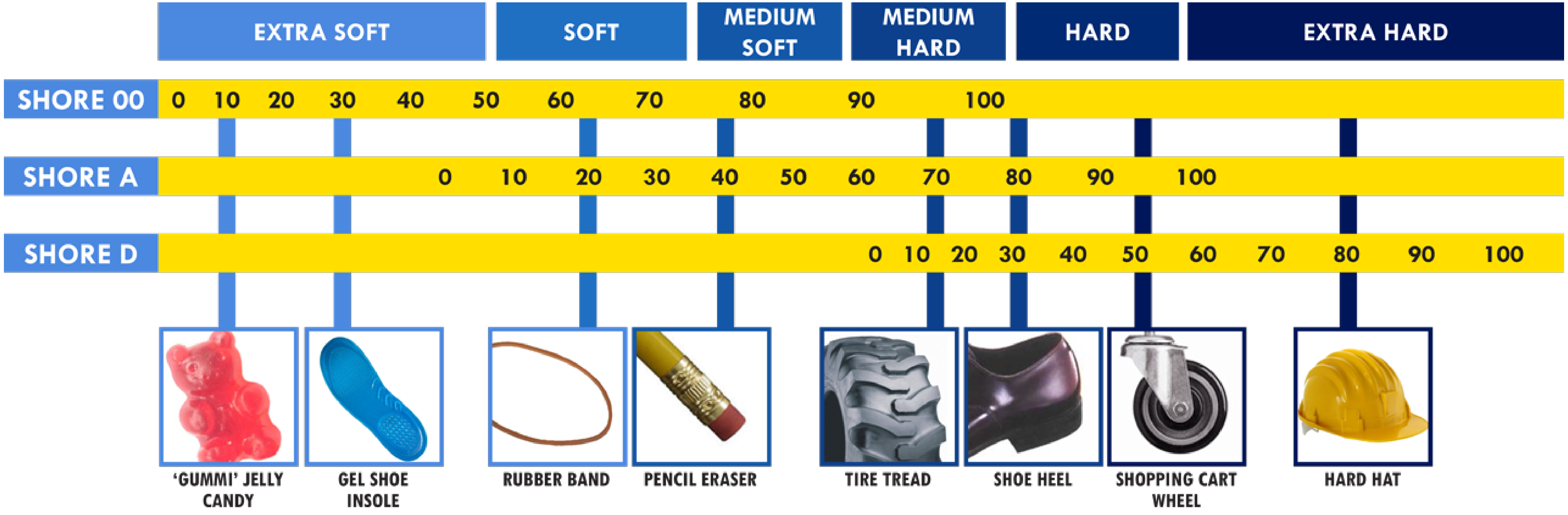


Figure 2: Number of counts vs uncalibrated pulse area in scintillating PVT based samples as measured through exposure to a ^{137}Cs γ-source using the same PMT bias value.

Adam Mahl*,2 Henok A. Yemam*,1 John Stuntz,1 Tyler Remedes,2 Alan Sellinger,1 Uwe Greife 2, et al, Bis(pinacolato)diboron as an additive for the detection of thermal neutrons in plastic scintillators, NIM A, Volume 816, 21 April 2016, Pages 96-100,
https://doi.org/10.1016/j.nima.2016.01.073, 2016

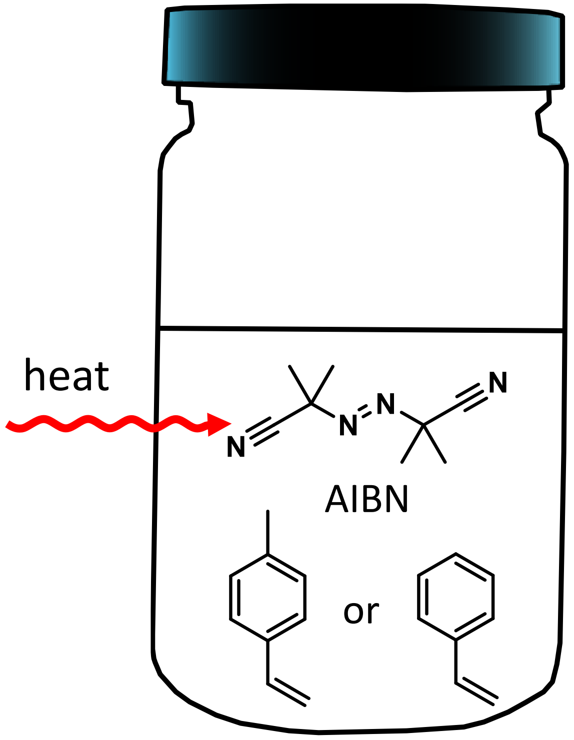
Shore Hardness Scale

	R.I.	Hardness	Mix	Cure
Wacker 579	1.53	25 Shore A	2-component	150 °C / 1 hr
KER-6000	1.51	22 Shore A	2-component	100 °C / 1 hr, 150 °C / 2 hr
SilRes H62C	1.50	65 Shore D	1-component	150 °C / 10 hr



Vinyltoluene Scintillator Fabrication

Plastic scintillators are fabricated via a **thermally initiated radical bulk polymerization**

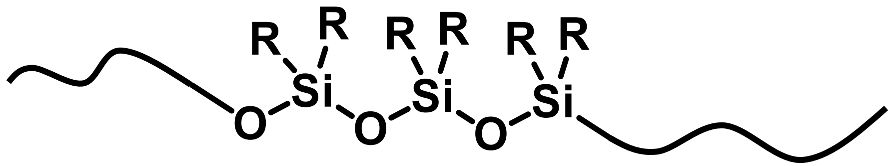


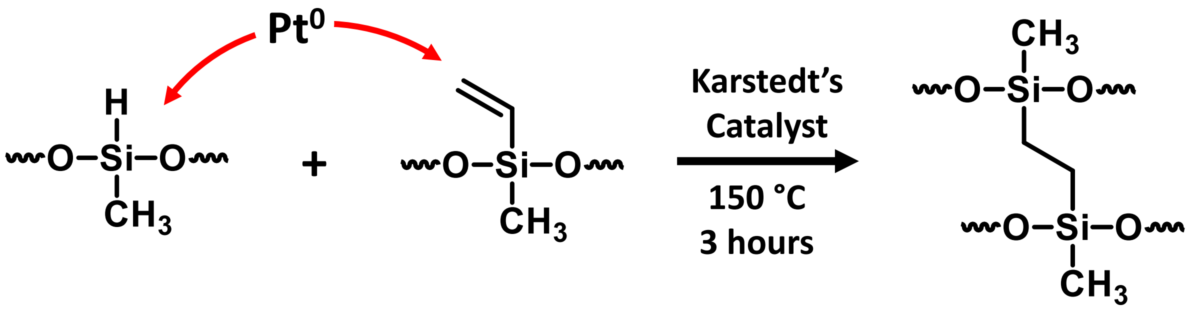
- Dissolve dopants in monomer
- Bubble with argon
- Polymerize in vacuum oven
  - 4 days at 80 °C
  - 1 day at 90 °C

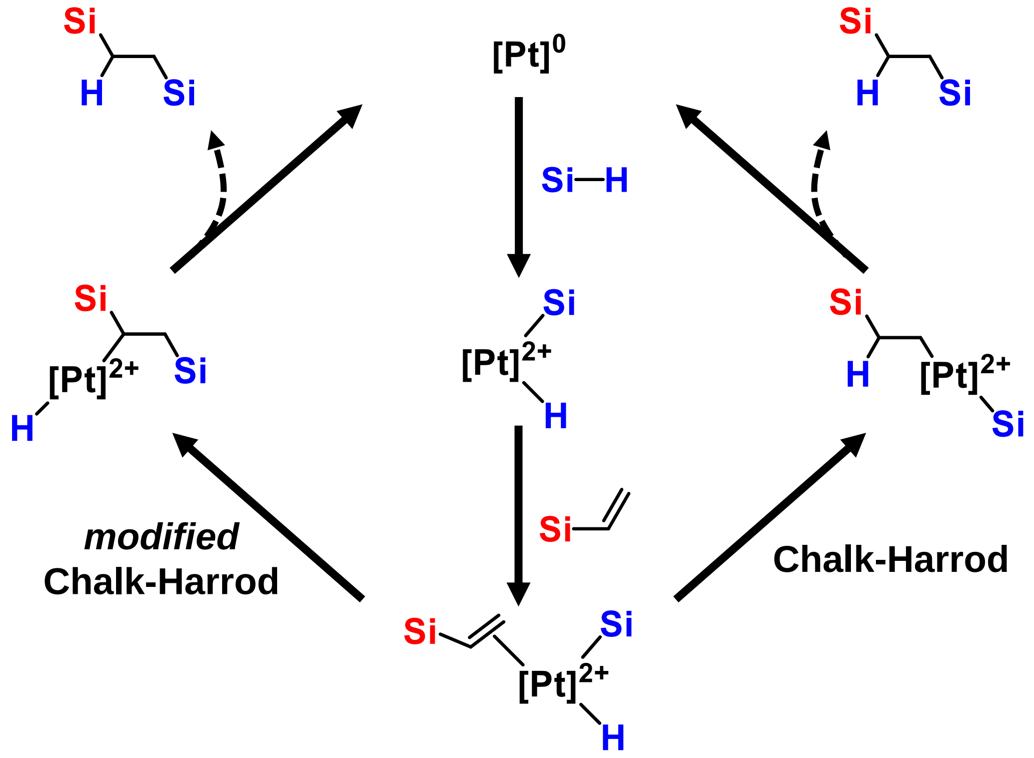
  → **5 days**

Siloxane-based Scintillator Fabrication

- Hydrosilylation: common and well studied method of to cross-link into solid
- Linking of vinyl- and SiH
- 2-part mix and heat cure procedure
- Not air sensitive!
- Macromonomer resins are not volatile!



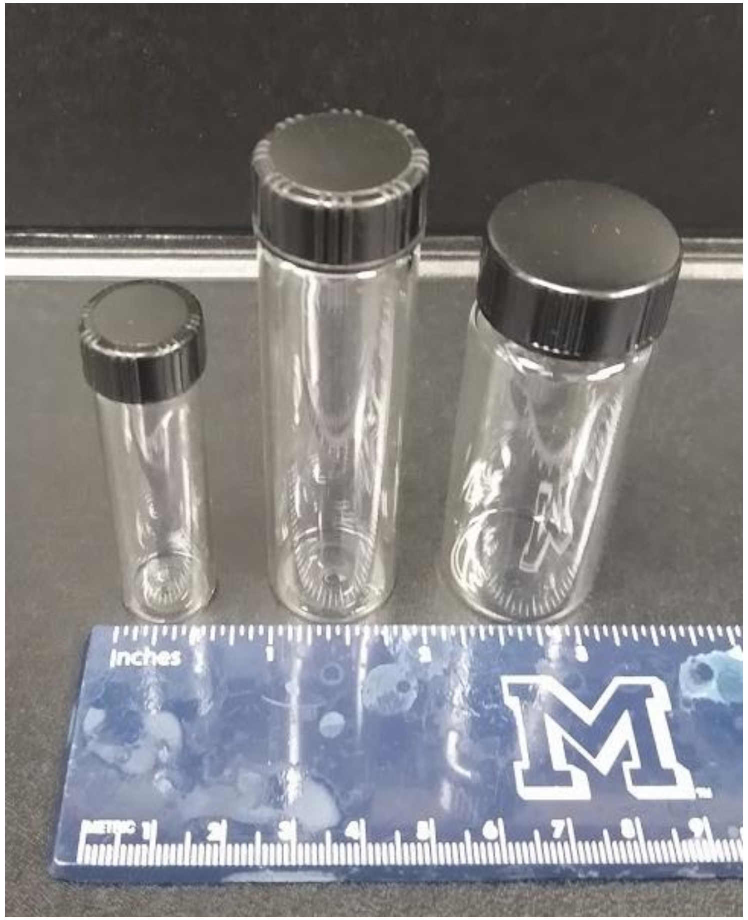




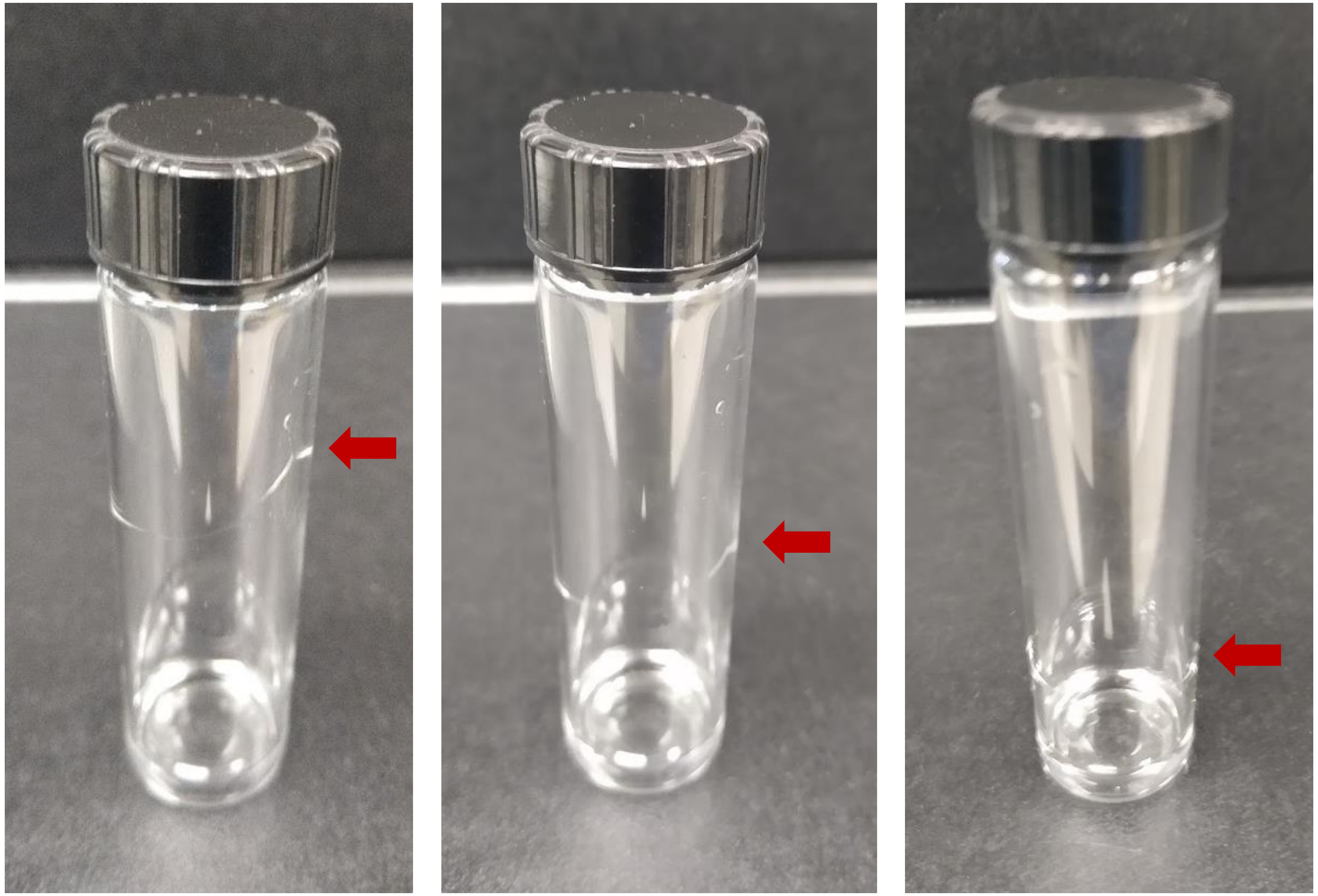
Hofmann, R. J.; Vlatković, M.; Wiesbrock, F. Polymers, 2017, 9 (10), 534.
Sakaki, S.; Mizoe, N.; Sugimoto, M. Organometallics, 1998, 17 (12), 2510–2523.
Comprehensive Handbook on Hydrosilylation; Marciniec, B., Ed.; Elsevier, 1992.
Mazurek, P.; Vudayagiri, S.; Skov, A. L. *Chem. Soc. Rev.* 2019, 48 (6), 1448–1464

Silanization of Vials

Several different vial sizes can be used



When silanized, methanol runs down vial wall in distinctive rings

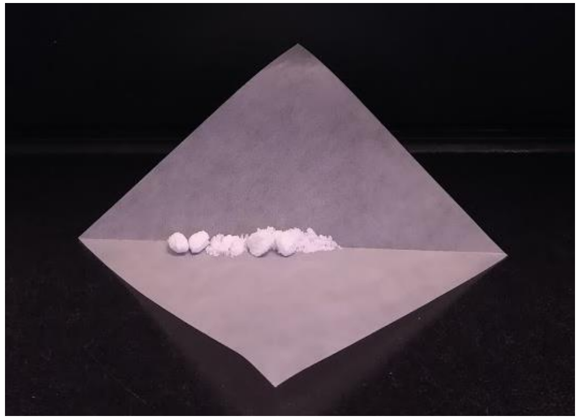


Preparation of Silicone Scintillators (*Thermal)*

Silanized vial

Add SFS

Add PPO



SFS is fluorescing in solid state, PPO is not

Add Xylenes

Preparation of Silicone Scintillators (*Thermal)*

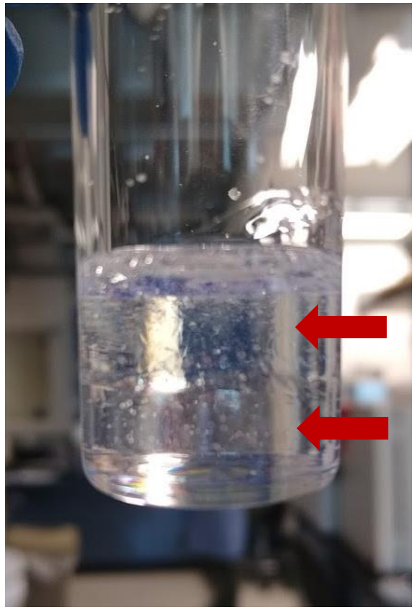
Gentle heating, to help solubilize

Dissolved!

Add Part A, two layers form

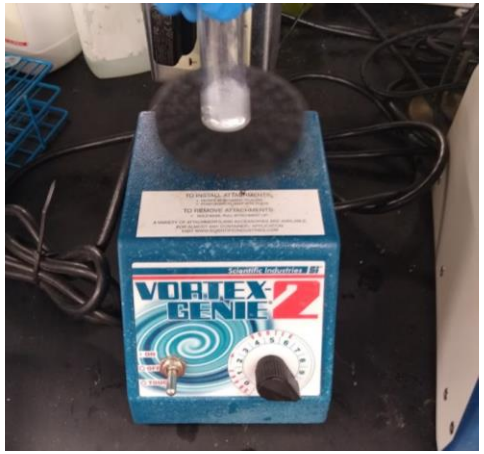
Mix

Add Part B, two layers form

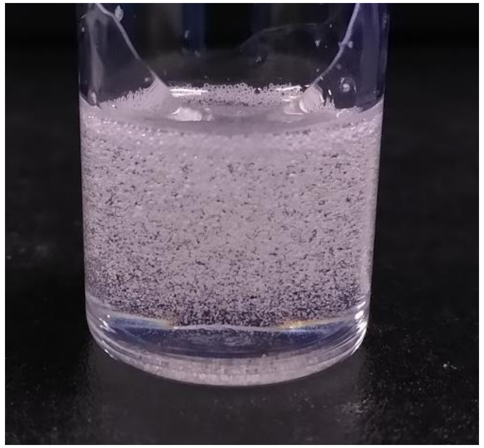


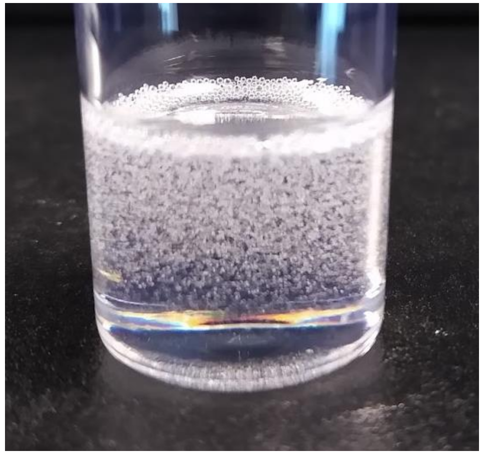
Preparation of Silicone Scintillators (*Thermal*)

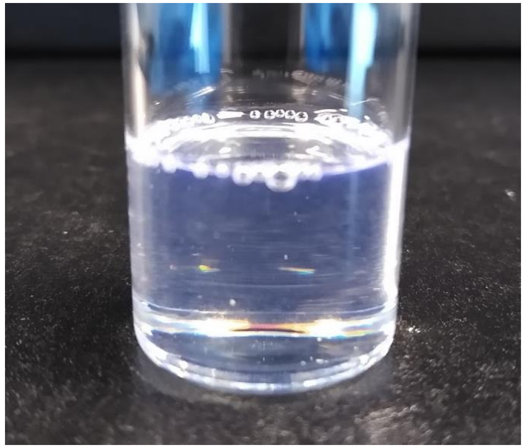
Vortex



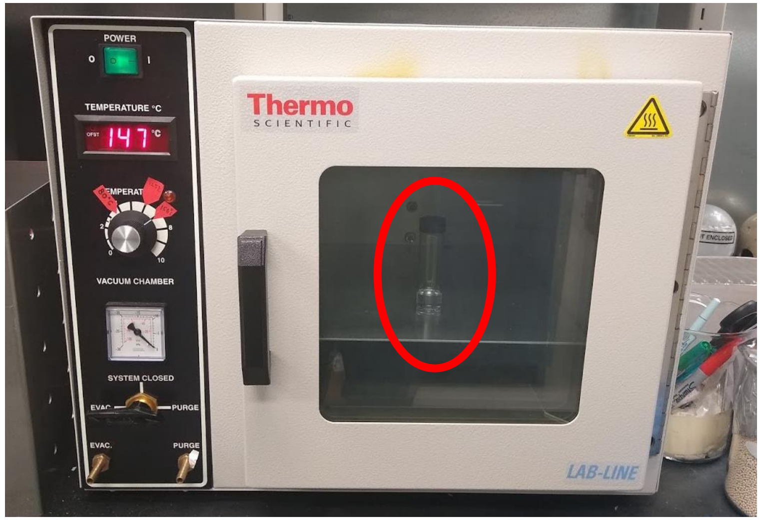
Wait for bubbles to dissipate – mild heat can help



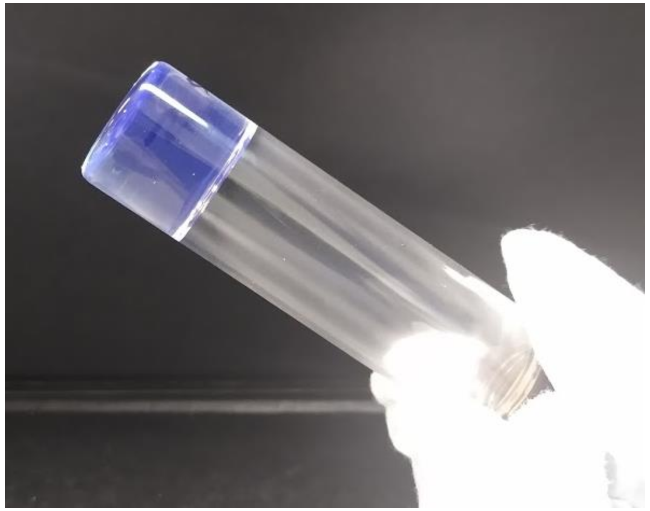




150 C, 3 hrs, Sealed in Air



Cured solid!



Preparation of Silicone Scintillators (*Thermal)*

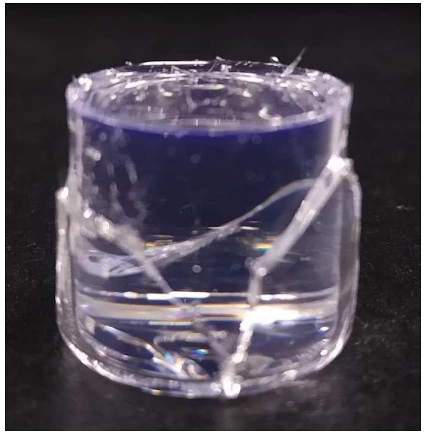
Cap Off

Hit here, once covered!

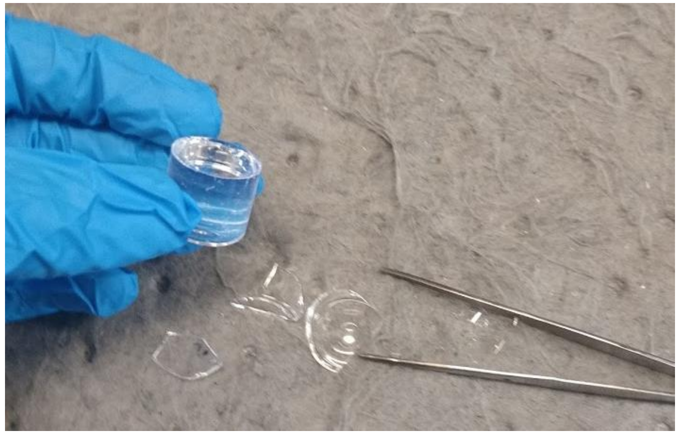
Cover sample to contain glass

Initial Break

Stuck Glass

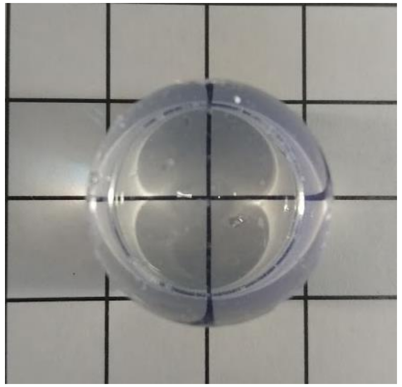


Extricate!

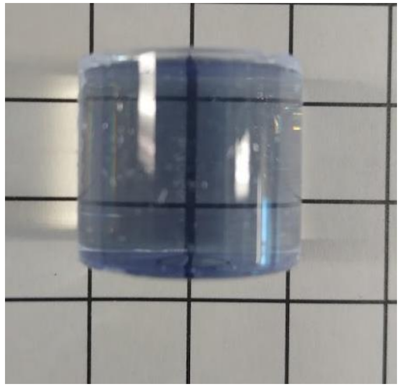


Preparation of Silicone Scintillators (*Thermal*)

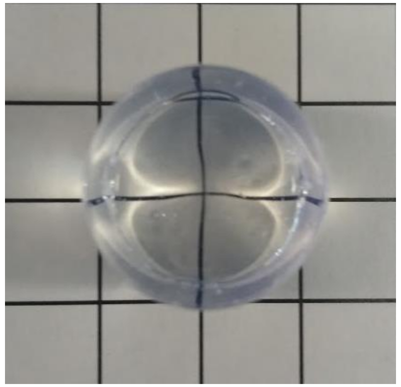
Top (meniscus)



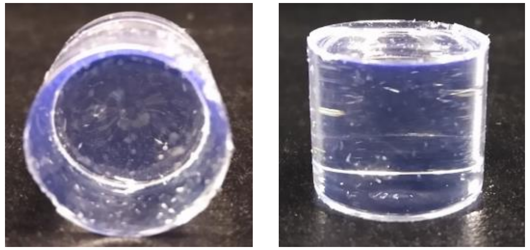
Side



Bottom



Lab Light (Fluorescent)



TLC Lamp (365 nm)