Radiopure PEN for Rare-Event Searches

Brennan Hackett[1], Andreas Leonhardt[2]

[1]Max Planck Institute for Physics, Germany

[2]Physics Department, Technical University of Munich, Germany

MAX-PLANCK-INSTITUT FÜR PHYSIK

Low background materials for Rare-Event Searches

Radiopure

- produced radio-purely
- cleaned after production

Self-vetoing

- generating a signal for internal radioactivity, e.g., scintillation
- aiding detection mode of experiment

Scalable & available

- commercially available
- produceable on semi-industrial scale

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Long-term stable

- cryogenically stable
- mechanically resistant
- chemical resistant
- UV resistant

Multifunctional

- structural
- optically active
- bulk vs. thin application
- insulating vs. conductive

PEN

Polyethylene Naphthalate

Thermoplastic Polyester

- industrially produced e.g., food packaging
- commercially available as granulate or thin film

Teijin-DuPont TN-8065 SC granulate

Structural and resistant

- structural at cryogenic temperatures
- long-term stability in liquid argon
- resistant to chemicals, UV-resistant

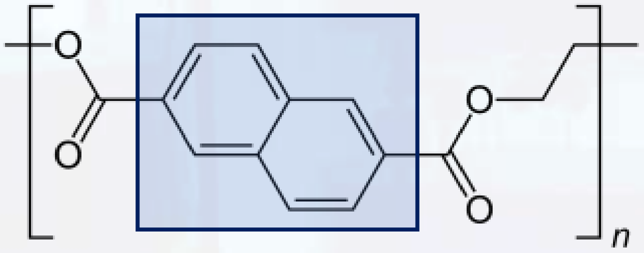
Mylar® Speciality Films Kaladex® 2000 PEN film

Y. Efremenko et al 2022 JINST 17 P01010 [iopscience]

Optically active

- intrinsically scintillating and wavelength-shifting in visible blue
- transparent above 400 nm

L. Manzanillas et al 2022 JINST 17 P09007 [iopscience]



naphthalene dicarboxylate groups (π, π)-excitation (eximer formation)*

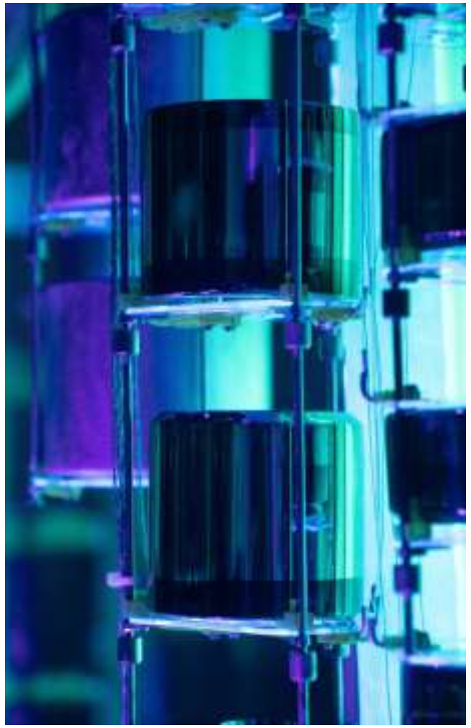
PEN is used by several current and future experiments

KamLAND2-Zen

PEN test balloon to hold ^{136}Xe-loaded liquid scintillator

S Obara et al 2020 J. Phys.: Conf. Ser. 1468 012136 [iopscience]

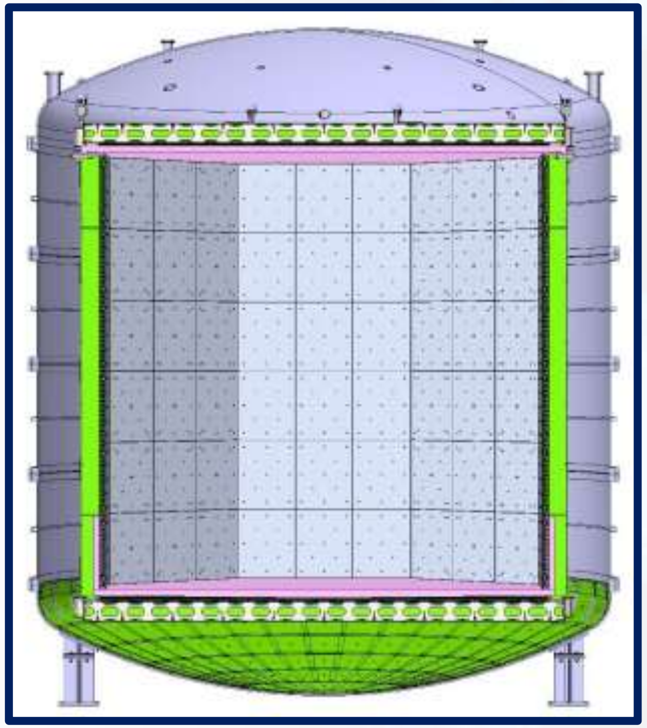
LEGEND-200



PEN holder plates for enriched Ge detectors

Y. Efremenko et al 2022 JINST 17 P01010 [iopscience]
Picture: M. Willers, LEGEND collaboration (2022)

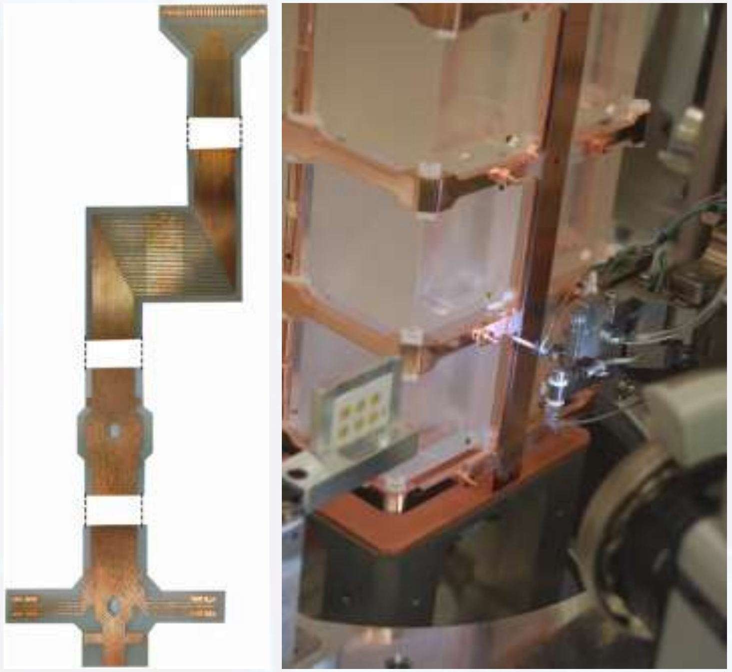
DarkSide-20k



Commercial PEN thin films on walls of outer liquid argon veto against neutrons

Choudhary, et al., LIDINE 2024 presentation [indico]

CUORE



Electrical connectors for cryogenic detectors made of copper on PEN substrate

C Brofferio, et al. 2013 NIM A Vol 718 211-212 [elsevier]
Right image: CUORE website [link]

Production of PEN parts

Production of PEN parts for rare-event searches

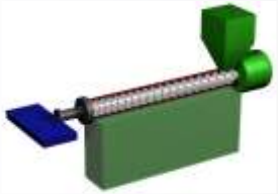
A

Commercially available thin films

Production of PEN parts for rare-event searches

A

Commercially available thin films



plastic sheet extruder

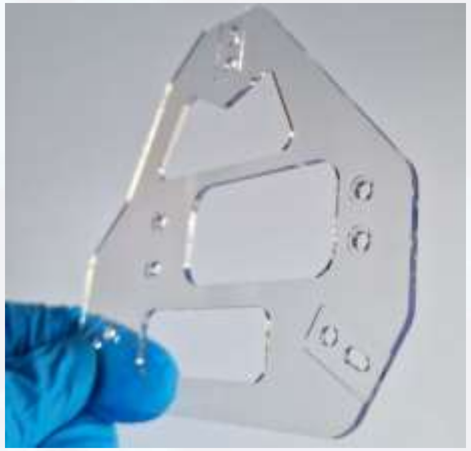
B

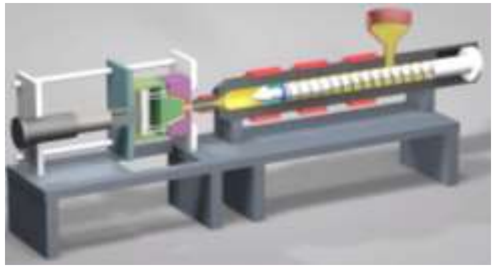
Commercial granulate

Extruded thin films

Injection molded PEN plates

Machined PEN pieces





Plastic injection molding machine

CNC machine

PEN holders for LEGEND-200

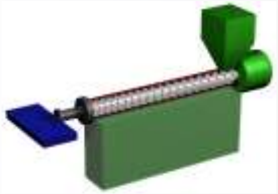
Production of PEN parts for rare-event searches

C

Synthesized granulate

B

C…ial gra…ulate



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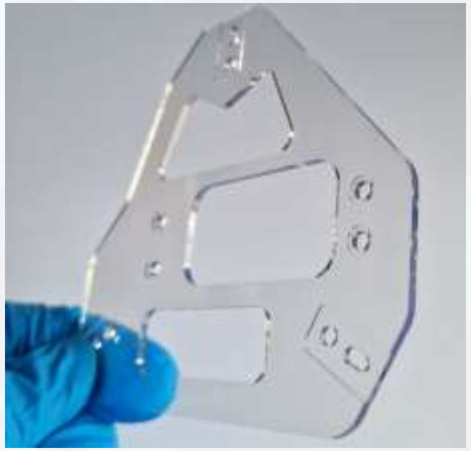
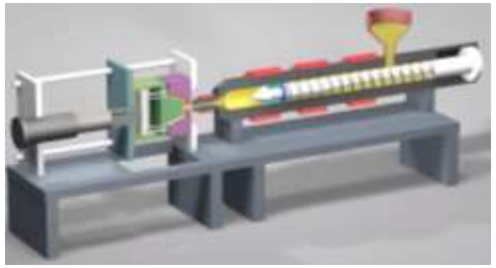


PEN holders for LEGEND-200



Plastic injection molding machine

CNC machine

A: Commercially available PEN thin films

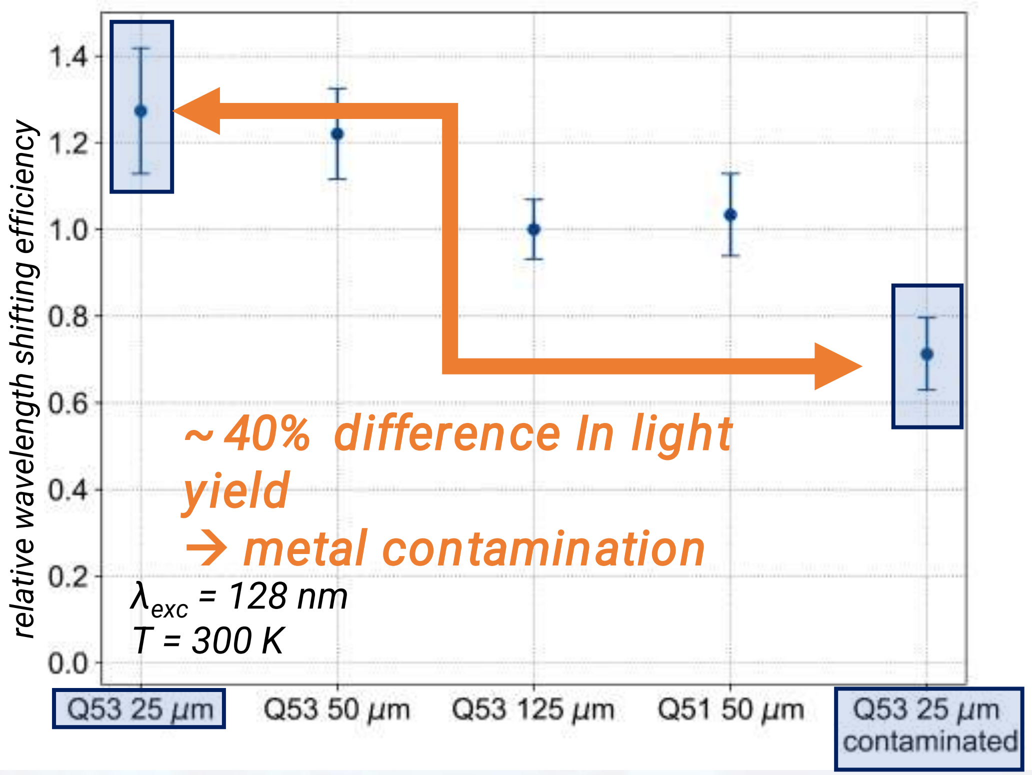
Advantages

- fast, cost-efficient installation
- large dimensions available

Challenges

- not optimized for optical use
- not optimized for radiopurity
- radioactive contamination possible
- variation between products & batches

Careful quality control and extensive surface cleaning are needed



Different available Teonex production grades and thicknesses
Source: Araujo, et. al, LIDINE 2023 Poster Contribution [indico]

B: Parts made from commercial granulate

Advantages

- production in a clean environment
- cleaning between each production step
- control of structure, e.g., amorphous
- custom shape of final parts

clean environment

Commercial granulate →  Injection molded PEN plates →  Machined PEN pieces

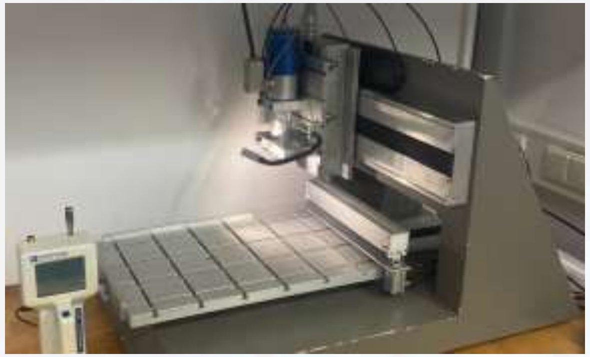
Commercial granulate	Injection molding	Injection molded PEN plates	CNC machining	Machined PEN pieces
sonicated in DI water and isopropanol	new barrel & screws, cleaned with DI water and isopropanol		in laminar flow hood, cleaned with DI water and isopropanol	sonicated in DI water and isopropanol,

LEGEND-200 PEN production

Commercial granulate cleaning

Injection molding machine in cleanroom

Images from:
Y. Efremenko et al 2022 JINST 17 P01010 [iopscience]



CNC machine placed in laminar flow hood

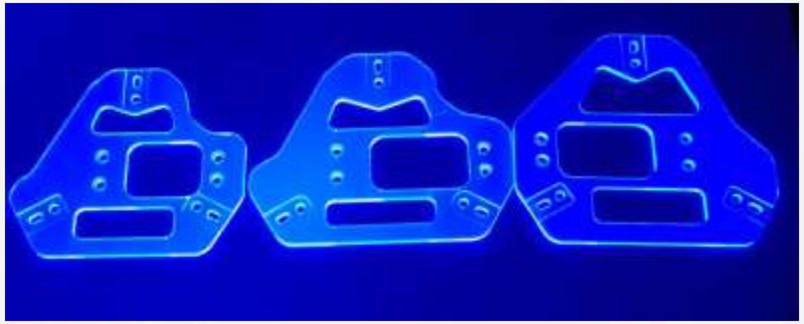
B: Parts made from commercial granulate

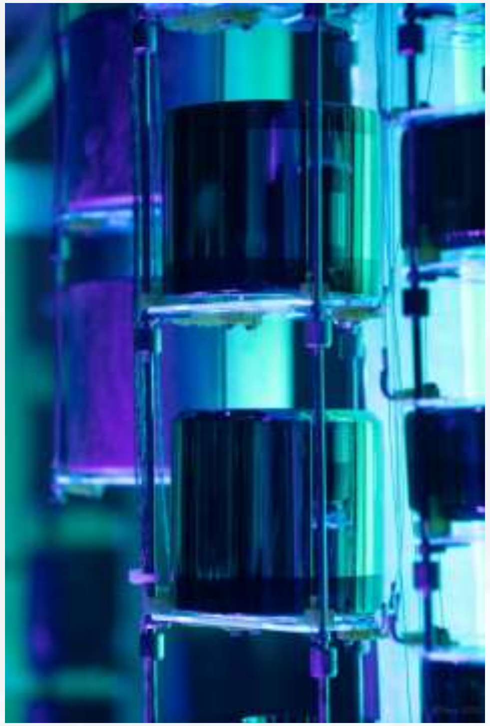
Challenges

- expensive machinery needed
- limited in shapes and dimensions
- granulate not optimised for radiopure, optical production

An extensive workforce is needed with strict procedures for cleaning

LEGEND-200 PEN production



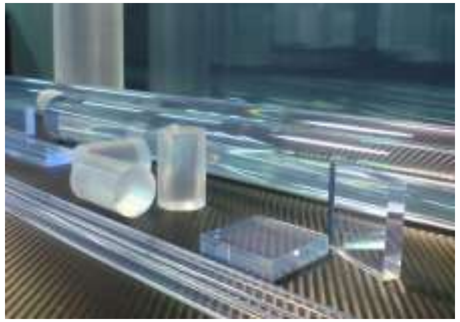


Final components machined for detector holders for LEGEND-200

Top image: Y. Efremenko et al 2022 JINST 17 P01010 [iopscience]

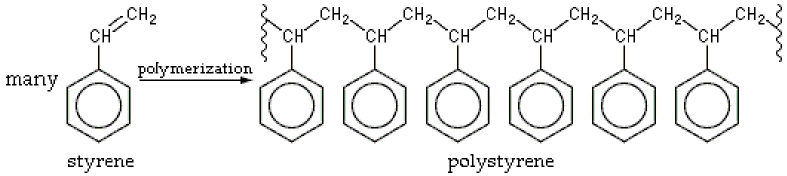
Bottom image: M. Willers, LEGEND collaboration (2022)

C: Synthesis of PEN polymer



Other plastic scintillators

- liquid monomer available, e.g., styrene
- mixed with fluor dopants and radical initiator
- heating or exposure to UV
- casting in desired shape



- more complicated
- higher temperature
- condensation of reaction by-products
- use of two catalysts

- no fluors needed
- adaptability

Synthesis of PEN

- "monomer" in form of diester or diacid derivative
- combined with ethanol glycol
- transesterification with acid catalyst
- polycondensation with oxide catalyst

C: Parts made from self-synthesized granulate

Advantages

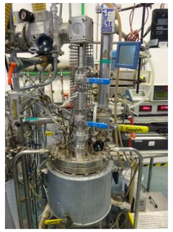
- modify reagents for improved optical performance
- eliminate additives (coloring, etc.)
- radiopure reagents
- full production chain in a clean environment

Challenges

- challenging synthesis
- semi-industrial scale

10-liter autoclave reactor at TITK

clean environment

Synthesis reagents →  Synthesized granulate →  Injection molded PEN plates →  Machined PEN pieces

C: Synthesis of glycol-modified PEN

Autoclave reactor

- 10-liter stainless steel
- nitrogen-flushed or vacuum

Improving radiopurity

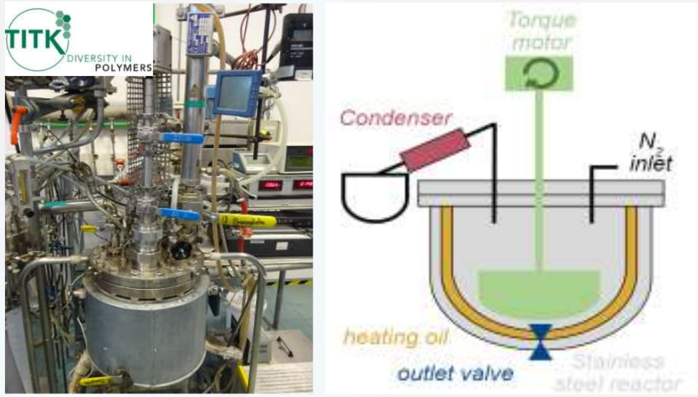
- sourced radiopure reagents
- purified by distillation
  or re-crystallization

Glycol-modification

- added cyclohexanedimethanol (CHDM)
- prevents crystallization

Catalysts

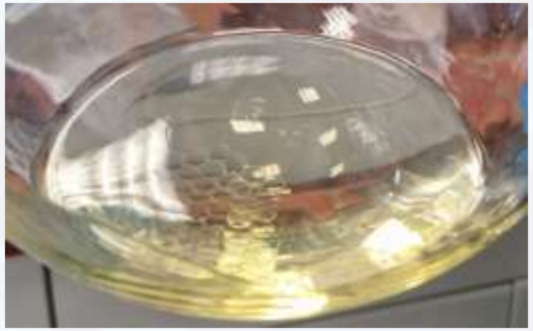
- magnesium acetate:
  - improved transparency
  - no neutron activation
- germanium dioxide:
  - Ge detector production
  - does not produce flakes in product



10-liter autoclave reactor at TITK

DMN before and after recrystallization

CHDM distillation setup



Residue after CHDM distillation

Comparison between PEN parts

A — Commercially available thin films

B — Commercial granulate

C — Synthesized granulate

increasing

- cost
- workforce
- R&D

more control over

- radiopurity
- optical properties
- adaptability

Comparison between PEN parts

A — Commercially available thin films

B — PEN-C

C — PEN-G

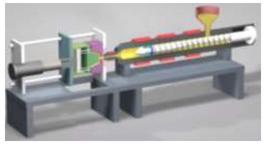
Topic of this talk

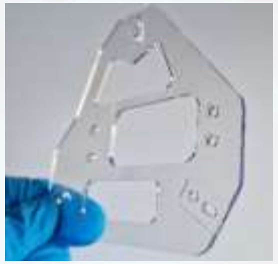
increasing
- cost
- workforce
- R&D

more control over
- radiopurity
- optical properties
- adaptability

Radiopurity of PEN

Comparison of radiopurity between PEN products





Commercial PEN pellets TN-6065S

^{228}Th = 0.23 mBq/kg
^{226}Ra = 0.25 mBq/kg
^{40}K = 1600 mBq/kg

sonicating in DI water & isopropanol

Injection molded PEN disks

^{228}Th = 0.09 mBq/kg
^{226}Ra = 0.03 mBq/kg
^{40}K < 0.24 mBq/kg

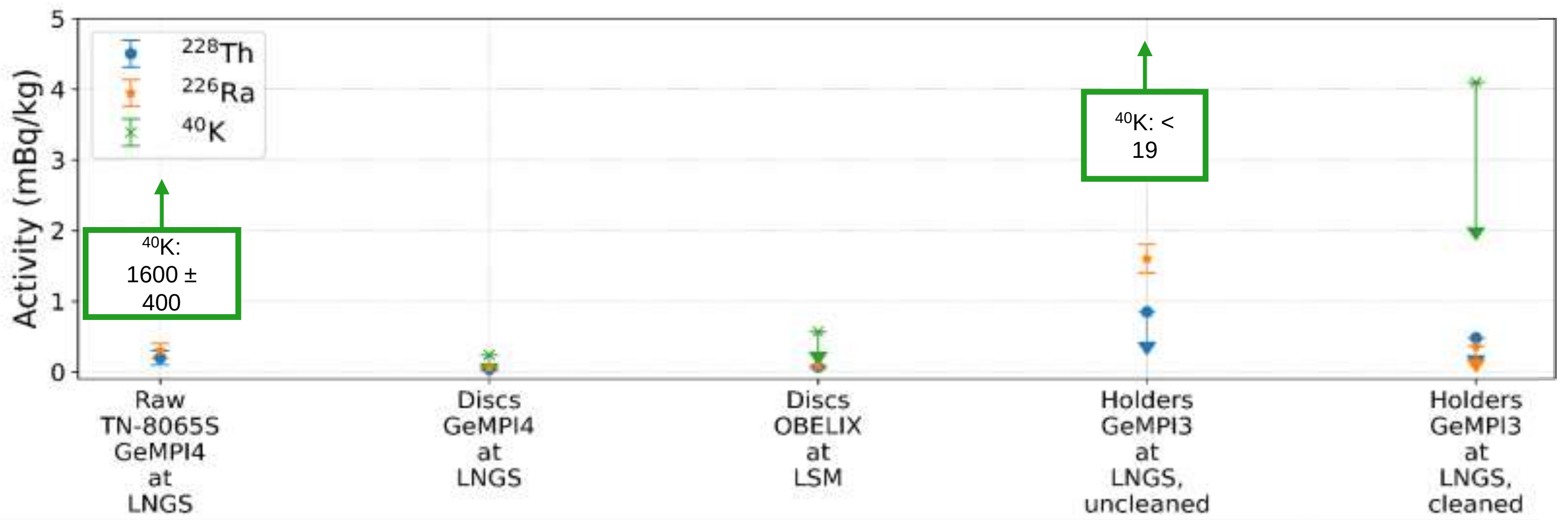
Uncleaned machined PEN holders

sonicating in DI water & isopropanol

Cleaned PEN holders

^{228}Th < 0.48 mBq/kg
^{226}Ra = 0.36 mBq/kg
^{40}K < 4.1 mBq/kg

Data from Y. Efremenko et al 2022 JINST 17 P01010 [iopscience] and M. Laubenstein, LEGEND



Radiopurity of PEN-C

- ^{40}K contamination removed by cleaning
- no introduction of ^{228}Th, ^{226}Ra during production

Cleaning PEN with nitric acid

Removal of surface contamination

- leaching of PEN holders in 5% nitric acid for 4 hours
- Leachates contain ^{232}Th and ^{238}U contamination

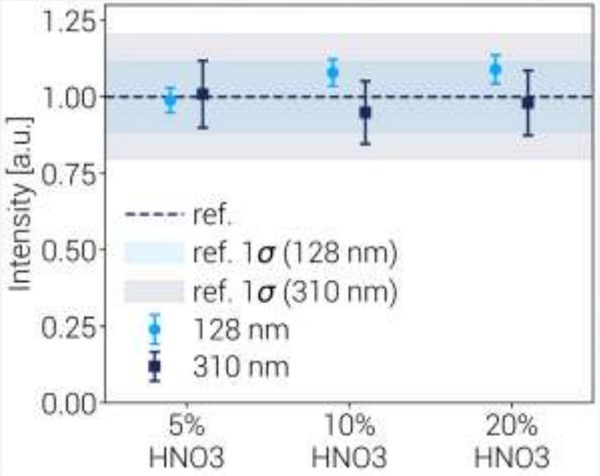
Optical Performance

- Nitric acid might deteriorate optically active surface
- VUV radiation is absorbed in first few hundred nanometers
  → sensitive to surface quality
- Check VUV performance after leaching

Sample Weight [g]		^{232}Th ppt	^{232}Th ± inst	^{238}U ppt	^{238}U ± inst
PEN #1	leach #1	0.071	0.013	0.09	0.04
0.7907	leach #2	0.004	0.005	0.0068	0.0017
PEN #2	leach #1	0.10	0.03	0.031	0.011
0.7136	leach #2	0.0045	0.0015	0.007	0.002

Description	Replicate	Sample wt [g]	^{232}Th ppt	^{238}U ppt
PEN #1	1	0.2745	< 1.13	< 1.98
	2	0.2481	< 1.30	< 2.08
	3	0.2655	< 1.22	< 1.94
PEN #2	1	0.2784	< 1.02	< 1.81
	2	0.1408	< 2.02	< 3.57
	3	0.2940	< 0.97	< 1.71

L-200 PEN data from Y. Efremenko et al 2022 JINST 17 P01010 [iopscience]; ICP-MS by M. Laubenstein



← 15 min leach

4 hours in 5% nitric acid did not show any degradation

Comparison of radiopurity between PEN products

Commercial reagents

Autoclave reactor

Synthesized granulate

PEN-G Synthesis

- autoclave reactor cleaned manually
- reagents not purified
- not performed in cleanroom

ICP-MS of synthesized PEN-G granulate	
Isotope	ppt (bulk)
Th-232	16.8 ± 5.1
U-238	62.7 ± 18.8
Comparison to L-200 PEN (bulk)	
Th-232	< 2
U-238	< 2

L-200 PEN data from Y. Efremenko et al 2022 JINST 17 P01010 [iopscience]
ICP-MS by M. Laubenstein

Granulate from PEN-G synthesis

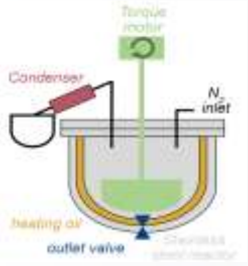
- baseline for future improvements
- significant uranium & thorium content

Comparison of radiopurity between PEN products

Commercial reagents

Distillation & recrystallization setup

Purified reagents



new autoclave cleaned with nitric acid

Synthesized granulate

clean environment

Clean PEN-G Synthesis

- In cleanroom environment
- new glassware & reactor
- purified reagents

Synthesis with purified reagents

Improved color

Synthesis with purified reagents

- improved color of granulate
- molded test pieces in production
- ICP-MS of reagents in progress

Optical Performance

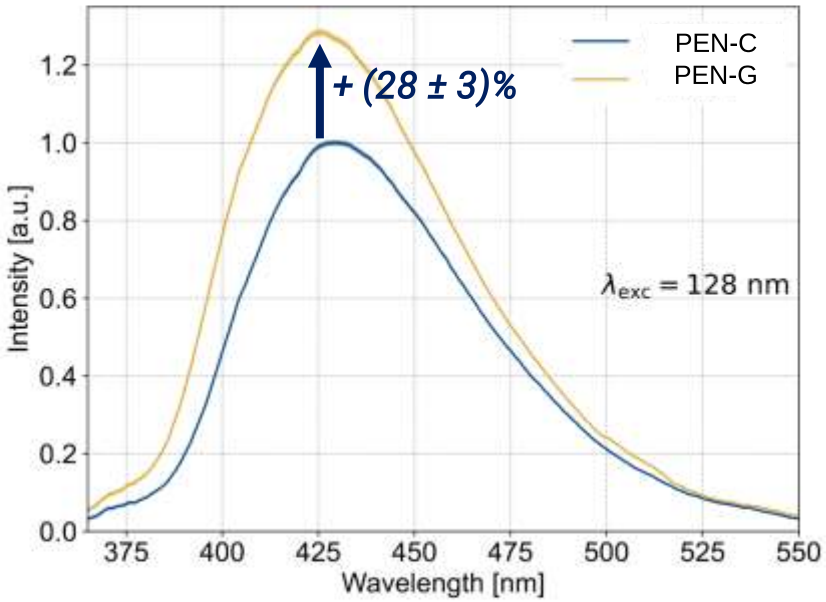
Optical performance of PEN-C and PEN-G

Comparison of Wavelength Shifting

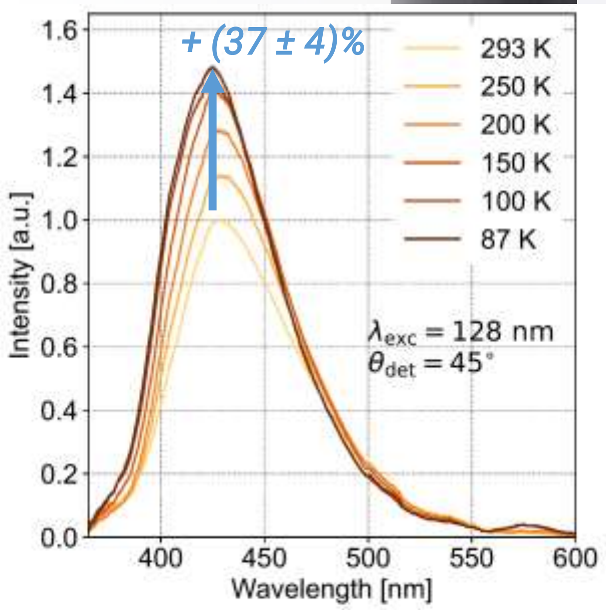
- molded from commercial and synthesized granulate
- surfaces sanded for higher light output

Wavelength shifting efficiency of PEN-G exceeds PEN-C at RT and 87 K

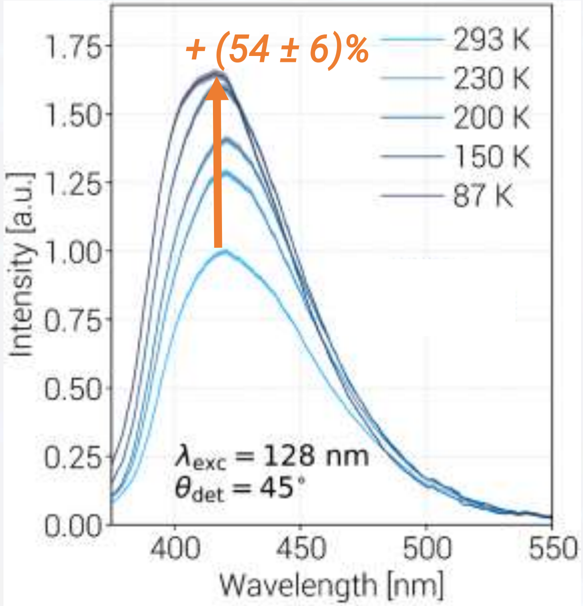
PEN-C vs. PEN-G at RT



PEN-C
300 K – 87 K



PEN-G
300 K – 87 K



Light output of smooth PEN-C

sanded PEN-C

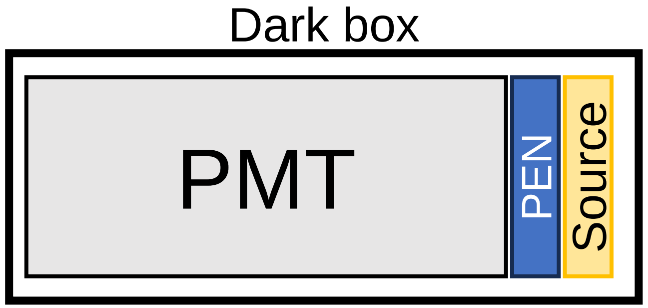
PEN-C results published in Andreas Leonhardt et al 2024 JINST 19 C05020 [iopscience]

Optical performance of PEN-C and PEN-G

Comparison of Scintillation

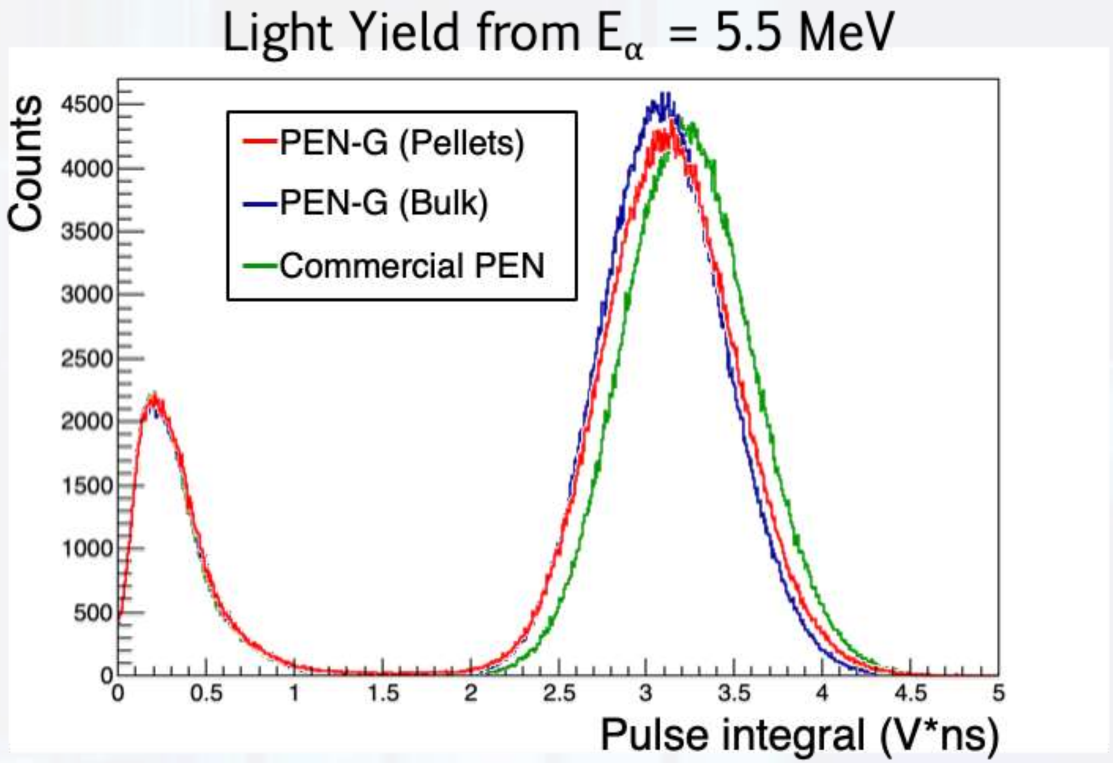
- molded from commercial and synthesized granulate
- excitation with ^{241}Am and ^{207}Bi source

Scintillation yield of PEN-G comparable to PEN-C



left to right: EJ-200, PEN-C, PEN-G (4 mm thickness)

Sample	Peak pulse integral [V*ns]		Light yield [ph/MeV$_{ee}$]
	E_α = 5.5 MeV	E_β ~ 1.0 MeV	
EJ-200	11.31 ± 0.07	20.6 ± 0.2	10,000 (ref.)
PEN-C	***3.23 ± 0.03***	***6.8 ± 0.1***	***3,300***
PEN-G	***3.13 ± 0.02***	***7.2 ± 0.1***	***3,500***

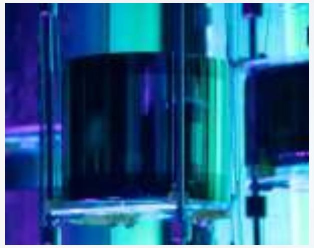


Summary & Outlook

Polyethylene Naphthalate

Radiopure ✓ **Long-term stable** ✓ **Scalable & available** ✓

Self-vetoing ✓ **Multifunctional** ✓



commercial films

- successfully used in several experiments
- strong variation in product
- risk of bulk contamination
- commercially available

commercial granulate

- successful implementation in LEGEND-200
- clean machining procedure
- removal of granulate surface contamination
- limited control of product parameters

synthesized PEN

- necessary for future rare-event search experiments
- full control over product parameters
- improved optical properties
- techniques for radiopure production developed

Backup

Cleaning PEN with nitric acid

Removal of surface contamination

- leaching of PEN holders in 5% nitric acid for 4 hours
- Leachates contain ^{232}Th and ^{238}U contamination

Optical Performance

- Nitric acid might deteriorate optically active surface
- VUV radiation is absorbed in first few hundred nanometers
  → sensitive to surface quality
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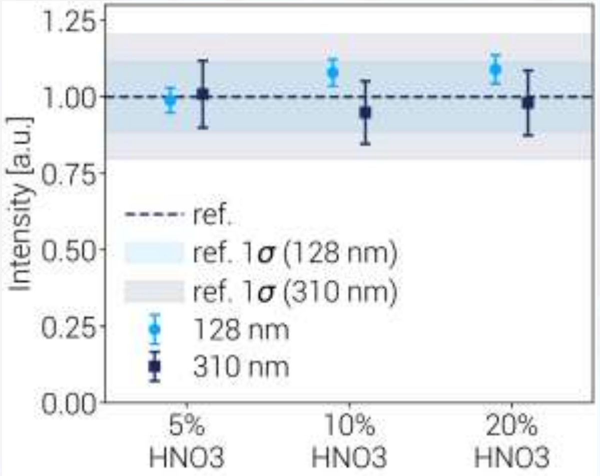


← 15 min leach

4 hours in 5% nitric acid did not show any degradation

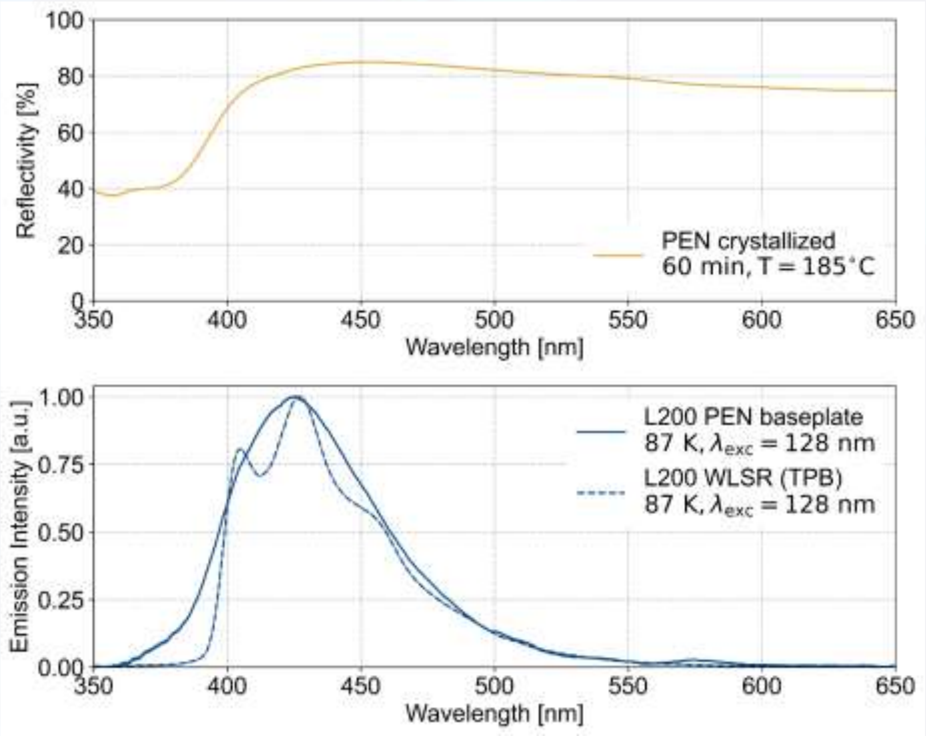
R&D for PEN

Crystallized PEN as single-part WLSR

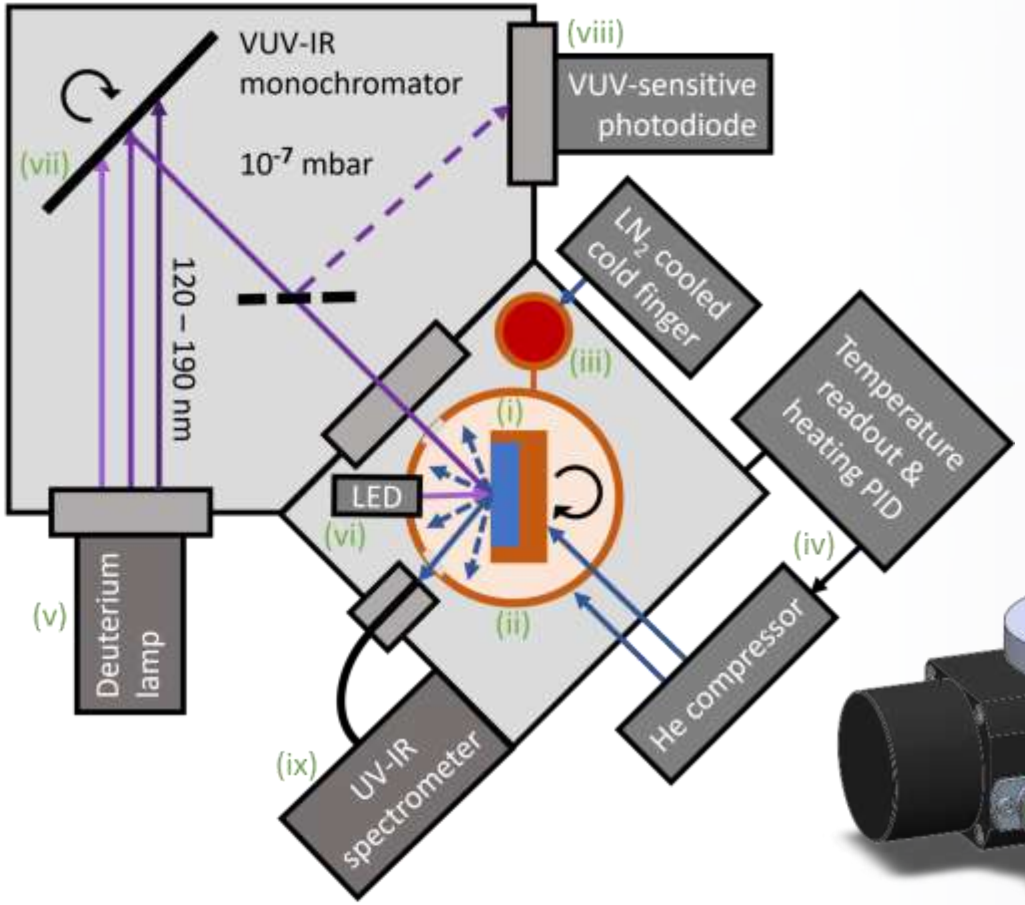
- eliminates reflector + wls coupling
- structural, long-term stable material
- can be produced in crystalline state easily

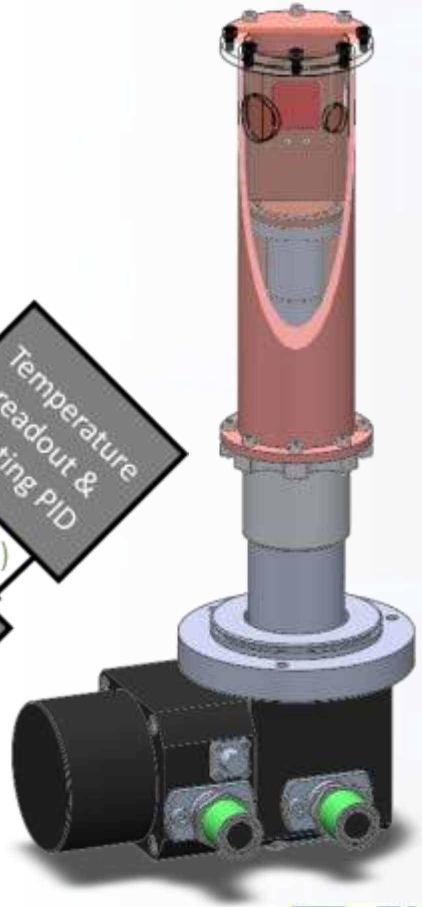
PEN enclosures for Ge detectors

- shield from ^{42}K beta-decay electrons
- tested at TUM LAr teststand enriched with ^{42}Ar
- talk by M. Schwarz at LRT2024



Cryogenic VUV spectrofluorometer





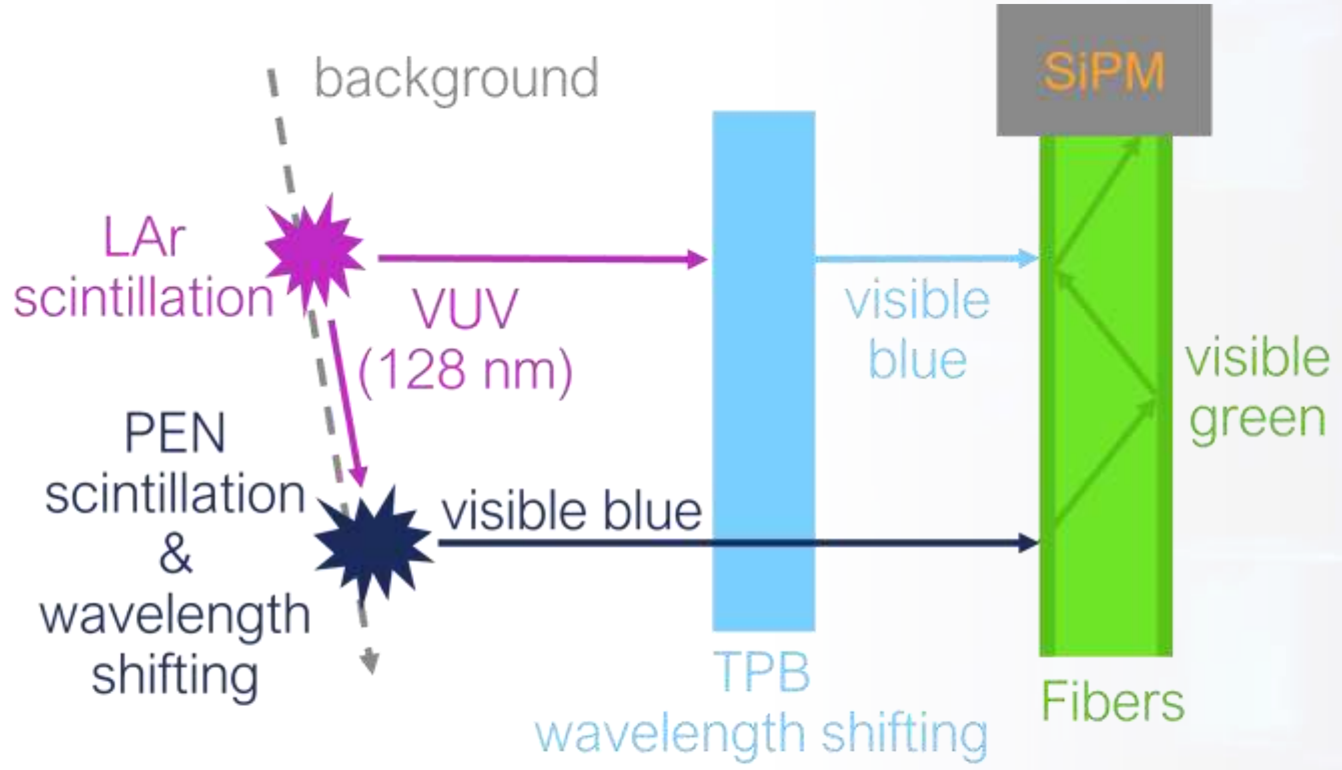
Sample held at temperatures between 300 K - 33 K.

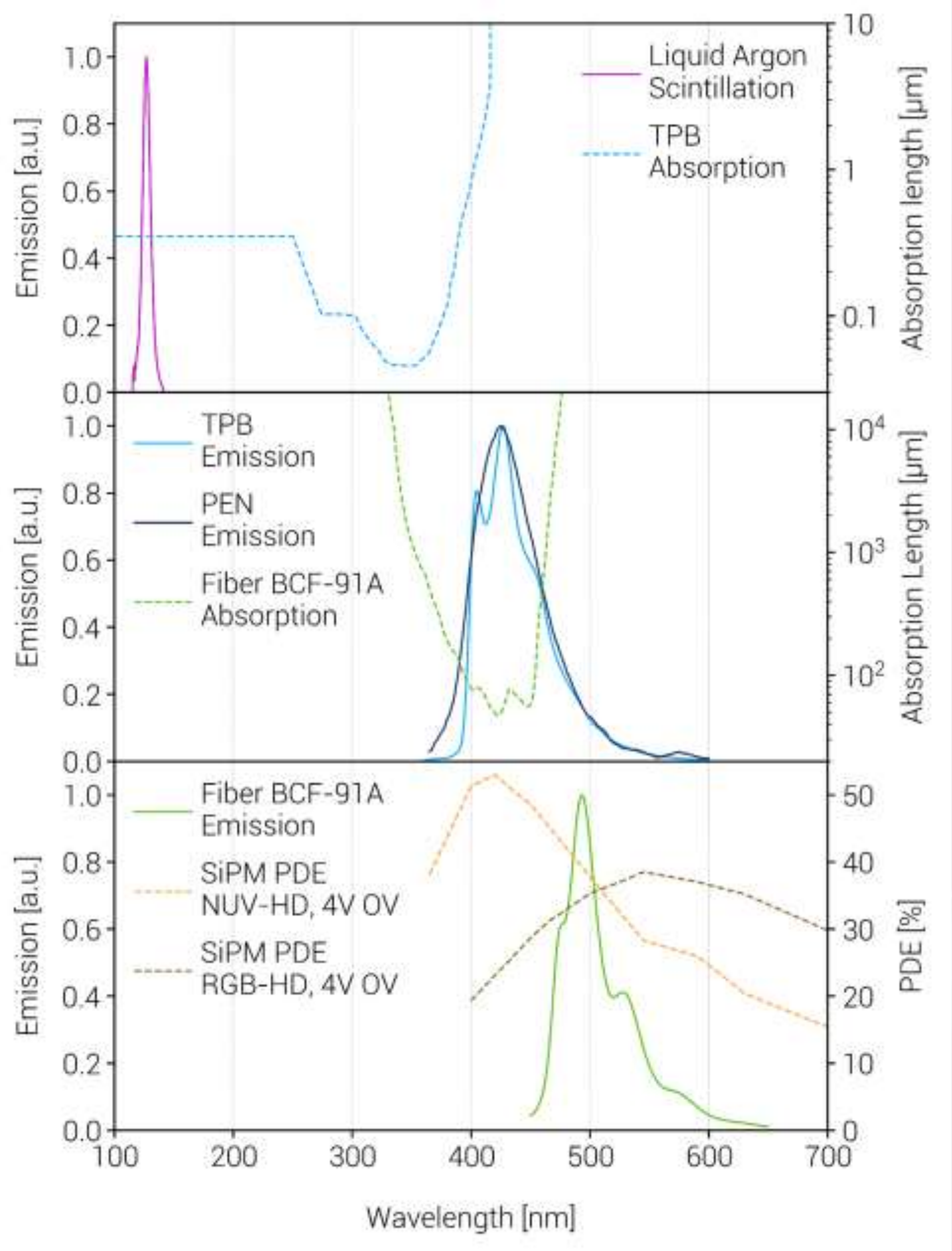
- Excited by
  - deuterium lamp (120 nm - 190 nm)
  - LED (310 nm or 420 nm).

Surface effect from condensation of water/ice below 150 K mitigated by cryo-shield and UV LED cross-check.c

A novel cryogenic VUV spectrofluorometer for the characterization of wavelength shifters
Andreas Leonhardt et al 2024 JINST 19 C05020
[iopscience]

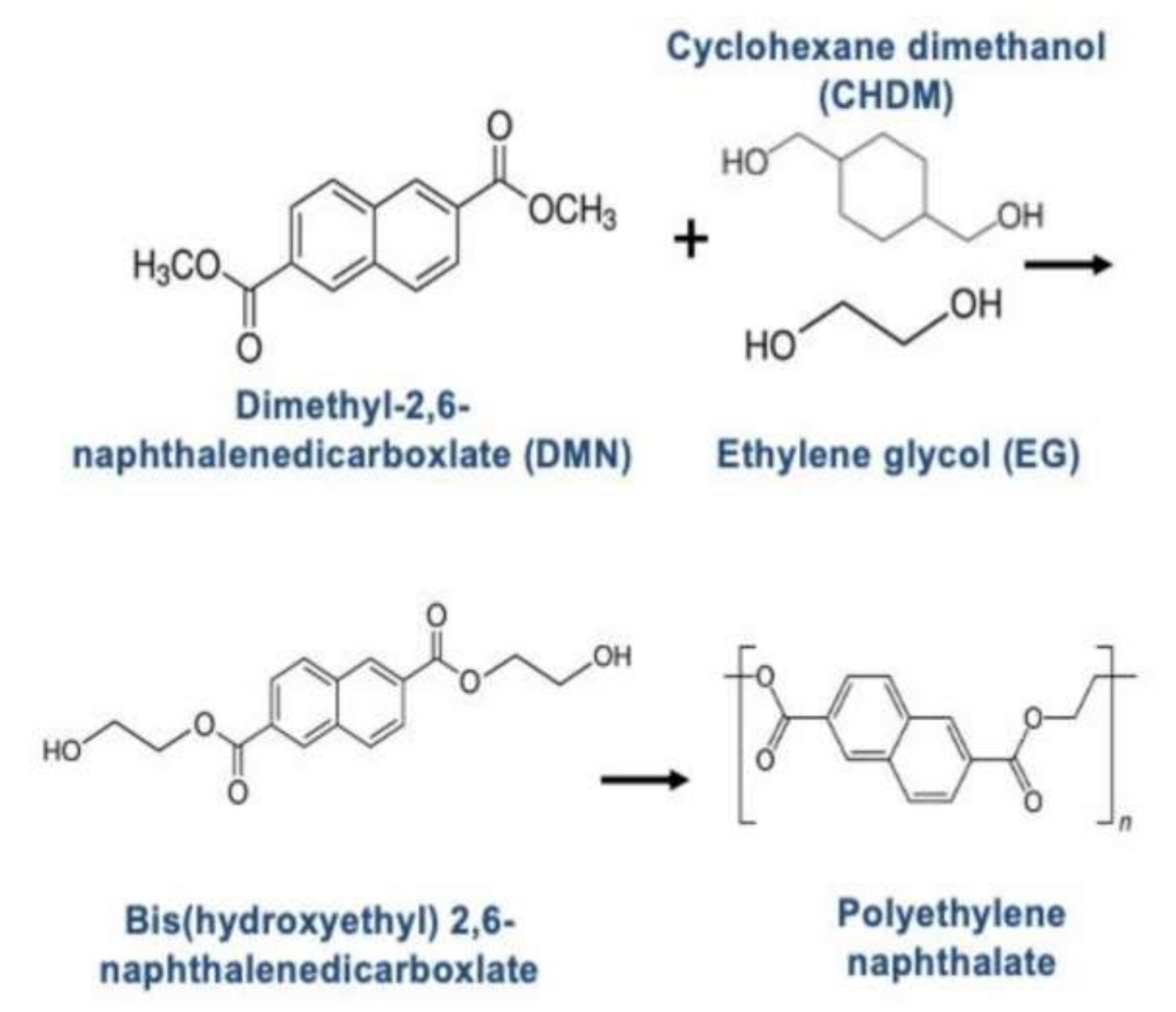
PEN in the LEGEND light path





PEN-G Synthesis

Detailed in B. T. Hackett, PhD Thesis, University of Tennessee (2022):
„Improving Sensitivities in 0νββ Decay Searches
by Utilizing PEN as a Structural Scintillating Material"



Sample	Intrinsic viscosity
Commercial PEN	0.47 g/dL
PEN-G #1	0.52 g/dL
Standard PET	~0.6 g/dL
PEN-G #2	0.6 g/dL

Comparison of radiopurity between PEN products

ICP-MS		
Element	Unit	PEN Teonex Q51 25 μm (contaminated)
Zn	ppm	4.1 +/- 1.2
In	ppm	15.4 +/- 4.6
W	ppm	20.4 +/- 6.1

Source: S. Nisi & F. Ferella, LEGEND internal

Gamma Screening		
Element	Unit	PEN Teonex Q51
K-40	mBq/kg	< 2.0 (90% C.L.)
Ra-226	mBq/kg	< 1.4 (90% C.L.)
Th-228	mBq/kg	< 3.6 (90% C.L.)

Source: B. Majorovits, Final Symposium of the Sino-German GDT Cooperation, 2015 [indico]

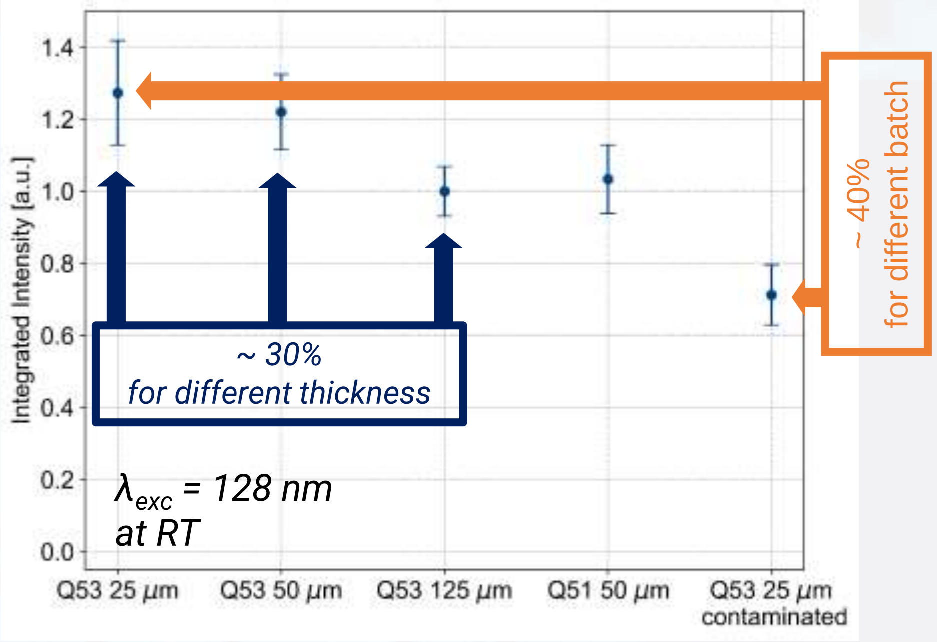
Radiopurity of commercial PEN films

- depends on production site and batch
- unclear if bulk or surface contamination

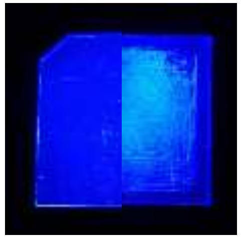
Optical performance of commercial PEN films

Light Yield of PEN relative to TPB					
PEN sample	***Relative LY***	Reflector	Surface	Temp.	Source
Teonex Q83 125 µm	***~ 50%***	no	sanded	RT	*Araujo, MSc Thesis (2019), TUM [researchgate]*
Teonex Q53 125 µm (Goodfellow)	***(75 ± 7)%***	Tetratex	sanded	87 K	Araujo et al Eur. Phys. J. C 82, 442 (2022) [springer]
Teonex Q53 125 µm *(Millipore Sigma)*	***(24.7 ± 0.8)%***	ESR (adhesive)	smooth	87 K	*Y. Abraham et al 2021 JINST 16 P07017 [iopscience]*
Teonex Q53 125 µm *(Goodfellow)*	***(34.0 ± 1.1)%***	ESR (no adhesive)	smooth	87 K	*Y. Abraham et al 2021 JINST 16 P07017 [iopscience]*
Teonex Q51 25 µm	***(47.2 ± 5.7)%***	ESR (no adhesive)	smooth	87 K	Boulay et al Eur. Phys. J. C 81, 1099 (2021) [springer]

Table adapted from *Araujo et al Eur. Phys. J. C 82, 442 (2022) [springer]*



Teonex Q53 125 µm



PEN-C extruded films 70 µm

PEN film	Relative Light Yield
Teonex Q53	100 %
Extruded (smooth)	***(28 ± 2) %***
Extruded (sanded)	***(125 ± 4) %***

Optical Performance varies extremely by

- production grade (Q51, Q53, Q83)
- reflector backing (+ adhesive)
- vendor, batch, etc.