Development of stable extractive scintillating materials for quantification of radiostrontium in aqueous solutions

A. F. Seliman, V.N. Bliznyuk, T. A. DeVol

Environmental Engineering and Earth Sciences Department, Clemson University,
Clemson, South Carolina 29634-0919, USA.

LSC 2017
May 1-5, 2017

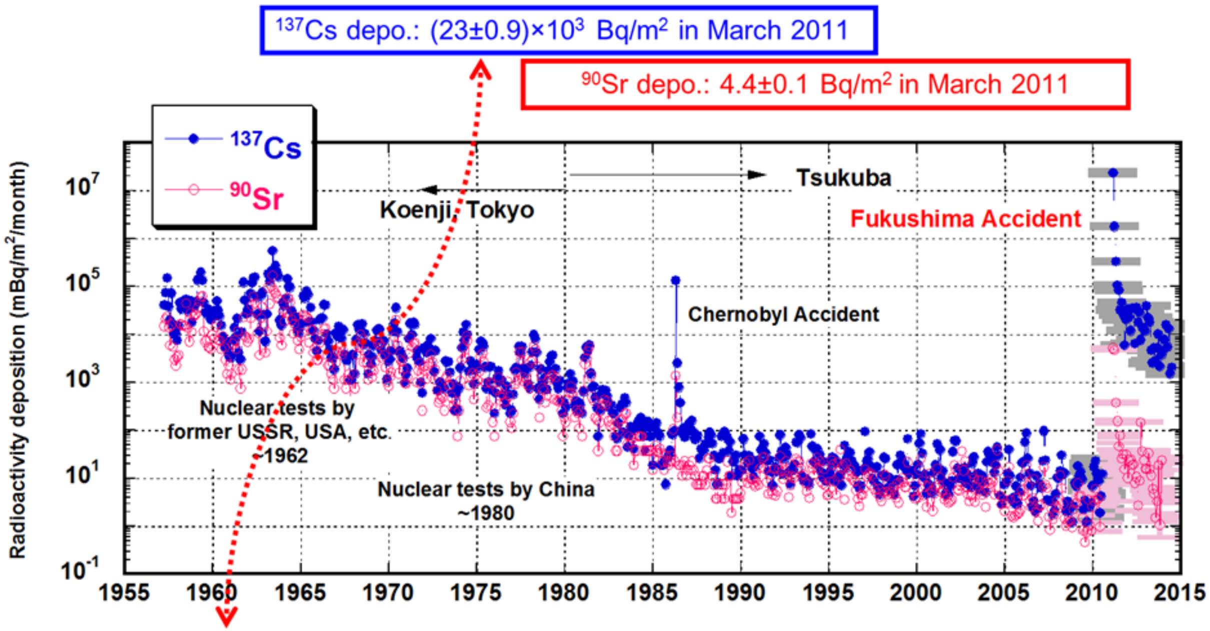
Radiostrontium in the Environment

Anthropogenic radionuclides produced from thermal fission of ^{235}U

^{89}Sr (β, $t_{1/2}$=50.52 d) | ^{90}Sr (β, $t_{1/2}$=28.9 y)

Sources: **Nuclear weapons testing conducted primarily in 1950s and 1960s**

Major nuclear incidents Fukushima Daiichi nuclear power incident of 2011 (Japan) and Chernobyl in 1986 (Ukraine)

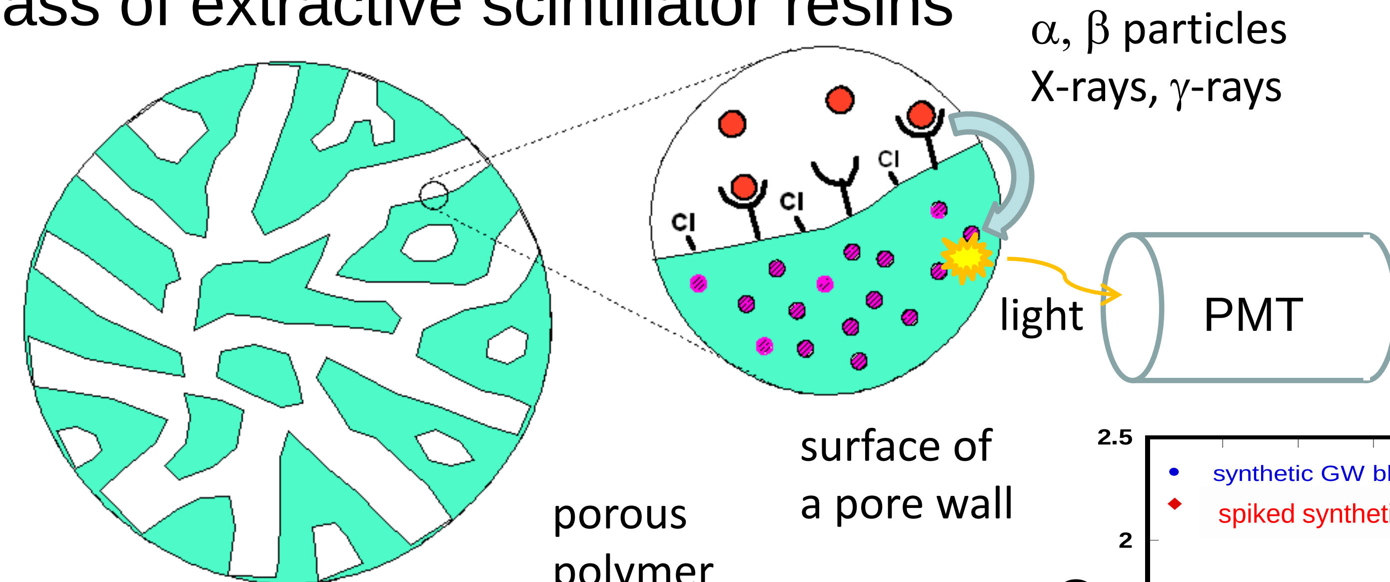


Need for portable inexpensive real-time operating detectors for in field detection of radionuclides

Y. Igarashi, M. Kajino, Y Zaizen, K. Adachi, M. Mikami, Progress in Earth and Planetary Science, 2:44, 2015.

Extractive Scintillating Materials

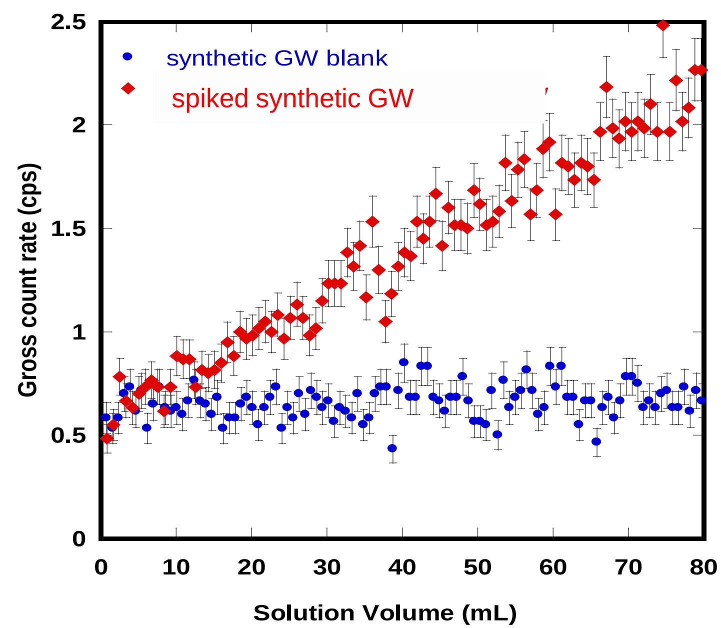
Objective: Design, synthesize, characterize a new class of extractive scintillator resins



porous polymer bead

surface of a pore wall

- Radioactive ion
- Radionuclide selective ligand
- functional groups
- fluor



V.N. Bliznyuk et al, *Polymer,* 2015, 56, 271

Research Objectives

Develop a simple and easy to handle for *in-field* detection methodology for monitoring ^{90}Sr in natural waters

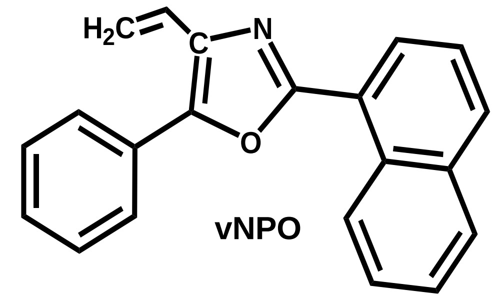
Approach	Preparation techniques	Extractant	Scintillator	Flow-cell type	Sensor code
1	Extract./scint. mixed beads	SuperLig® 620	Y_2SiO_5:Ce GS20** CaF_2:Eu	Heterog	SUPLiG-Y_2SiO_5:Ce SUPLiG-GS20 SUPLiG-CaF_2:Eu
2	Suspension polymerization	SuperLig® 620	vNPO*	Homog.	Polymer
3	Surface polymerization	SuperLig® 620	vNPO*	Homog.	Surf
4	Nanocomposite	SuperLig® 620	vNPO*	Homog.	HS

***: 2-(1-naphthyl)-4-vinyl-5-phenyloxazole; **: Cerium activated lithium silicate glass scintillators**

Methods and Instrumentation

Materials:

- Extractant: SuperLig®620 (IBC Technologies, Trade secret)
- Organic Scintillator: 2-(1-naphthyl)-4-vinyl-5-phenyloxazole (vNPO)
- Inorganic Scintillators: Y_2SiO_5:Ce, CaF_2:Eu, GS20



vNPO

Polymer Synthesis:

- Suspension polymerization:
  - Oil phase: 4-vinyltoluene, Divinylbenzene(DVB), Porogen, Benzoyl peroxide + SuperLig®620 (20%) + vNPO (3%)
  - Aqueous Phase: DDI water, NaCl, Polyvinyl alcohol (PVA), HPMC (methacel)
- Surface polymerization:
  - Ethanol, Toluene, DMF, NMP, 4-vinyltoluene, vNPO scintillator, AIBN initiator

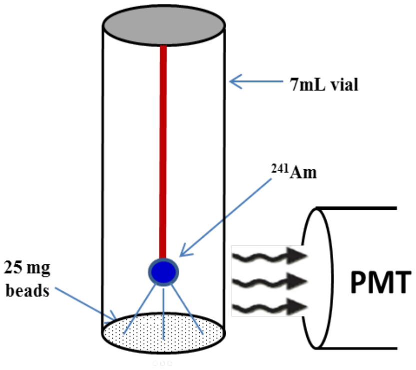
Flow scintillation analyzer
(Online detection)

Radiation detection:

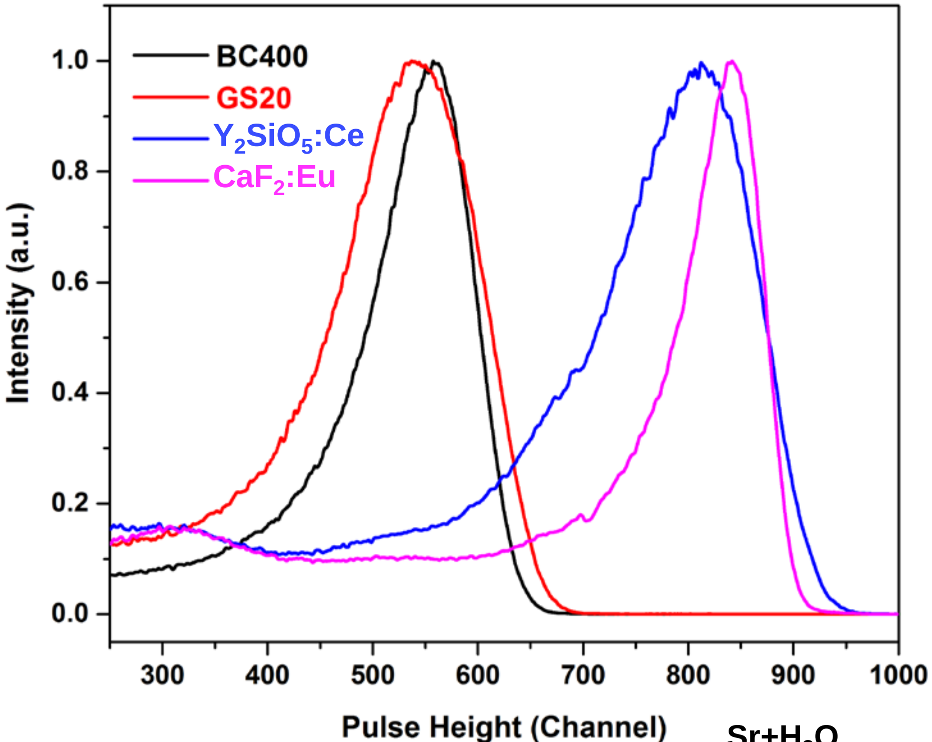
- **Liquid scintillation counting (**QUANTULUS , PerkinElmer)
- **Flow scintillation analyzer (**β-RAM 5, LabLogic Systems)

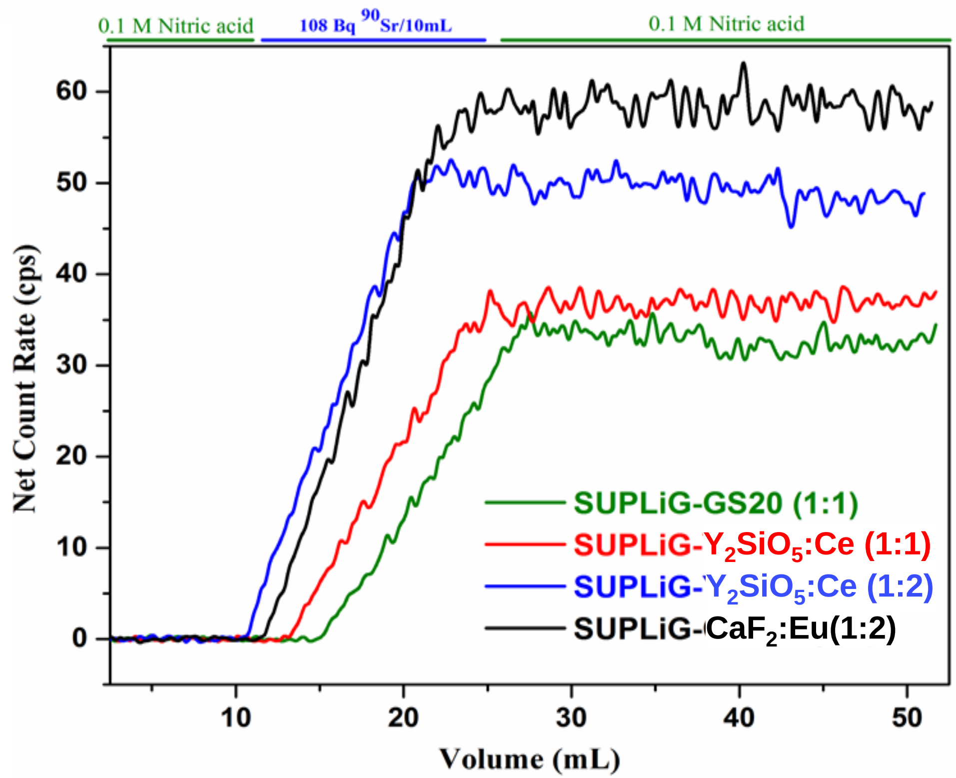
Liquid scintillation counting
(offline detection)

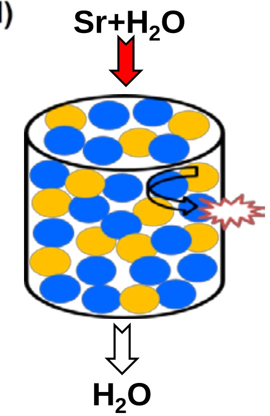
Luminosity measurement



Approach 1: Heterogeneous Flow-Cell

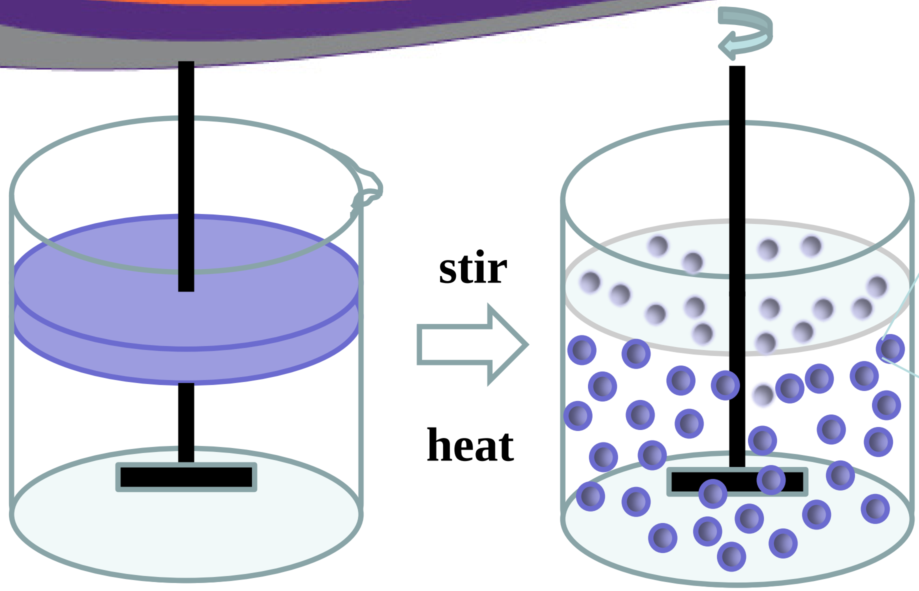


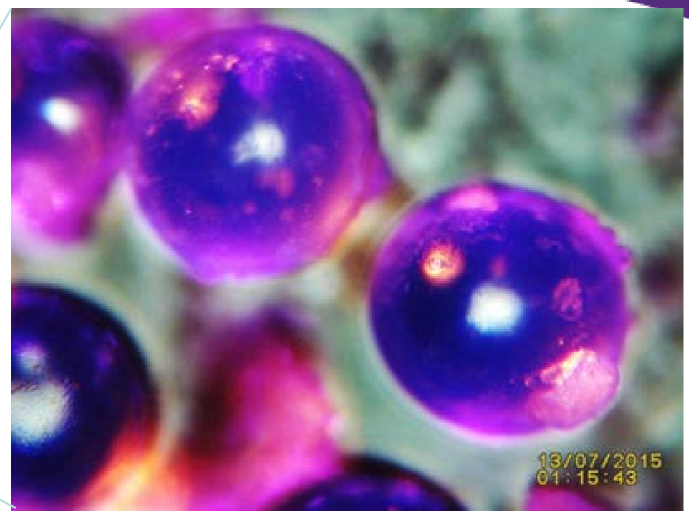




Sample	Loading Efficiency (%)	Detection Efficiency (%)
SUPLiG-GS20 (1:1)	100	30.6±1.0
SUPLiG-Y_2SiO_5:Ce (1:1)	100	34.1±1.0
SUPLiG-Y_2SiO_5:Ce (1:2)	100	46.2±1.2
SUPLiG-CaF_2:Eu (1:2)	100	54.3±1.3

Approach 2: Suspension Polymerization



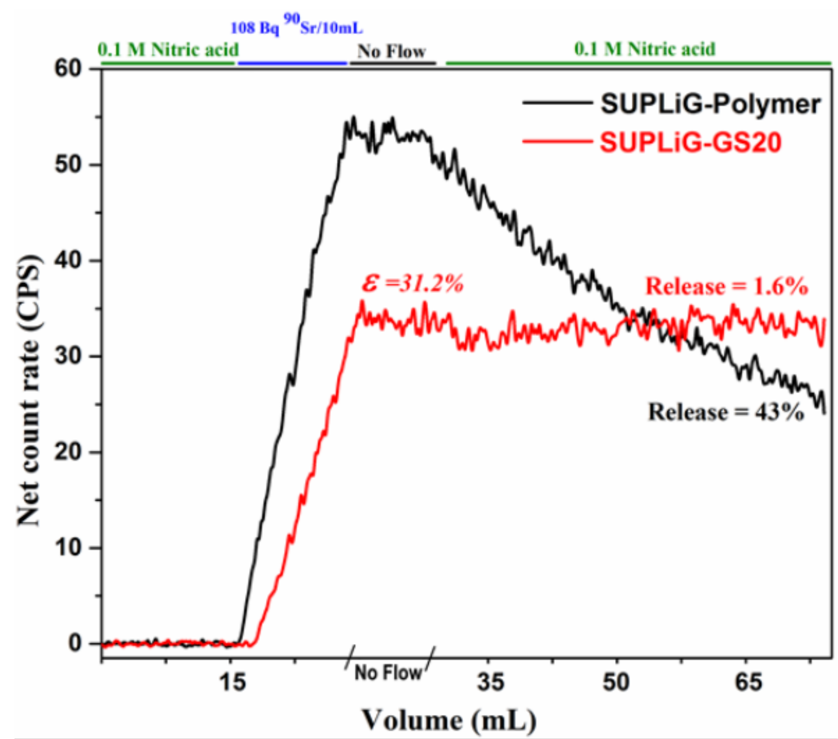


Oil Phase:

Methylstyrene + Divinylbenzene(DVB) + Porogen + AIBN + SuperLig®620 (20%) + vNPO (3%) (fluor)

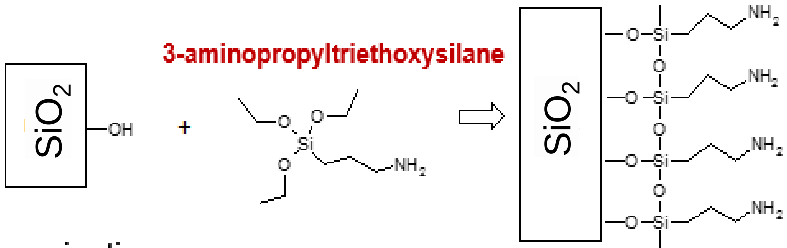
Aqueous Phase:

DDI water + NaCl + Polyvinyl alcohol (PVA) +HPMC (methacel)

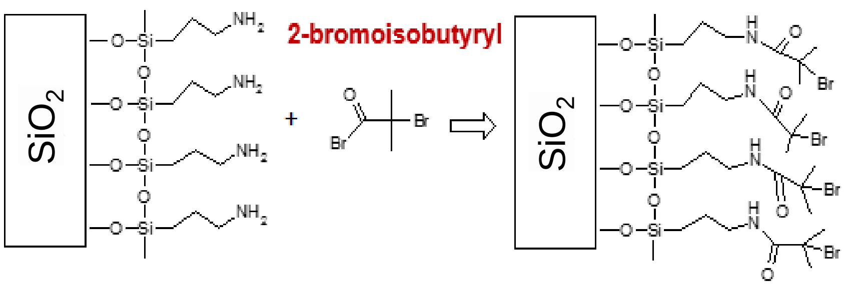


Approach 3: Polymer Brush

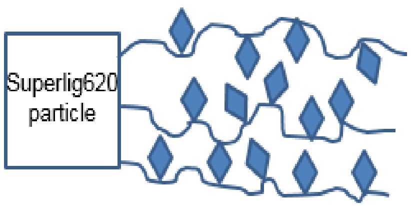
1) amination through silane chemistry

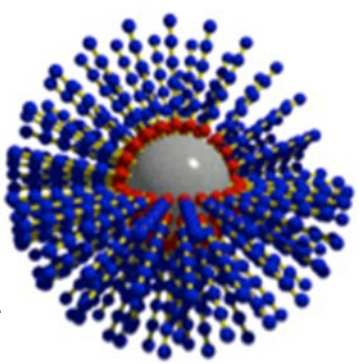


2) bromination;



3) ATRP of vinyltoluene-co-vNPO

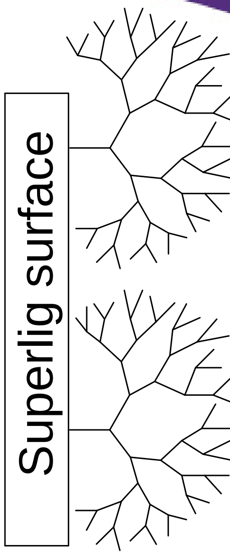




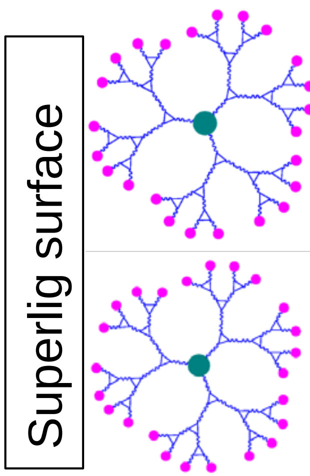
SI-ARGET-ATRP; vinyltoluene
Cu(II)/TPMA; $Sn(EtH)_2$

"Grafting from" growth of polymer dendrons

PVT-co-CMS-co-vNPO dendron

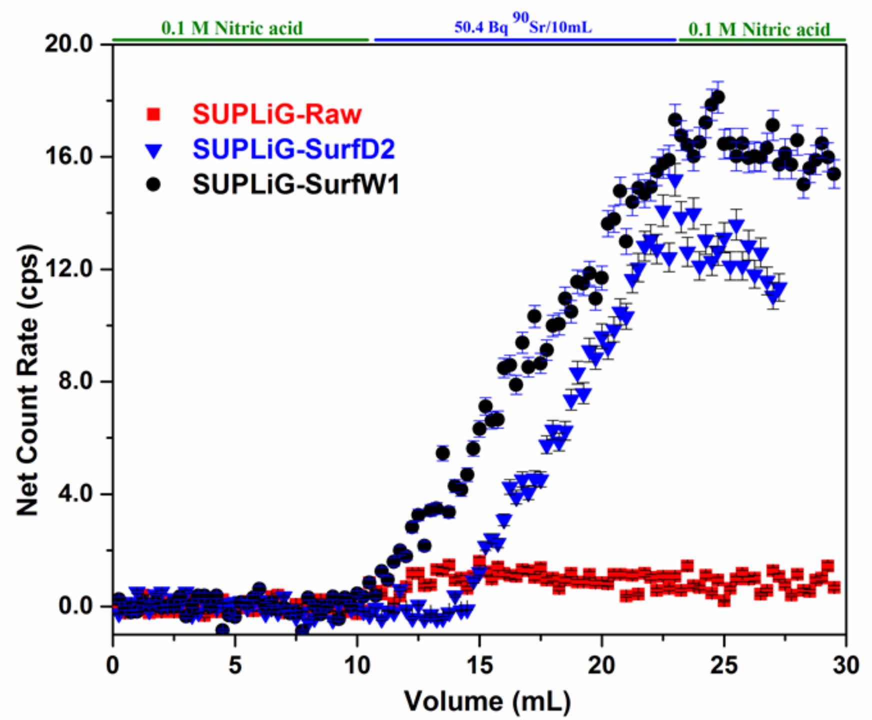


"Grafting to" of polymer dendrons with terminated epoxy groups

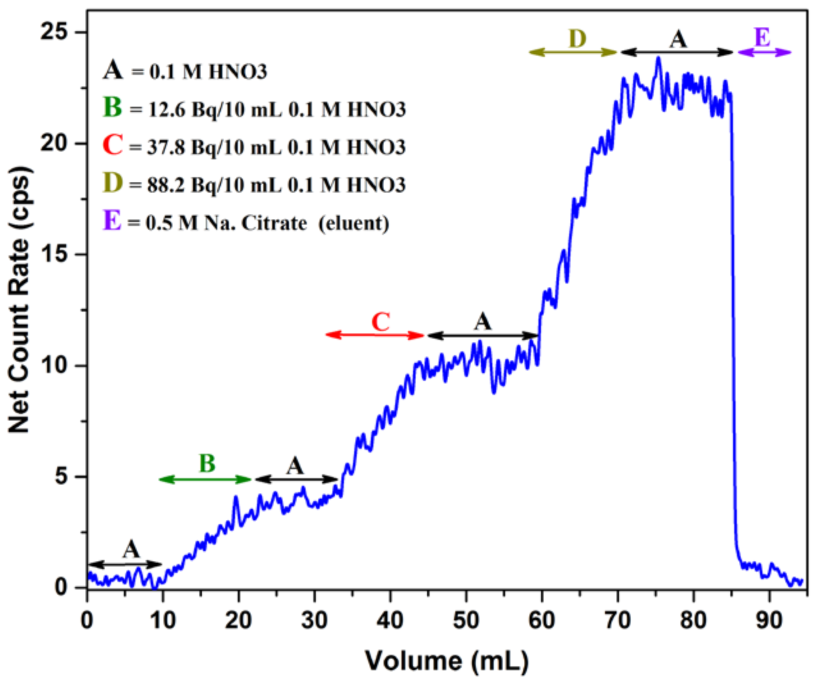


Balance between uptake and luminosity

Approach 3a: Online detection of ^{90}Sr



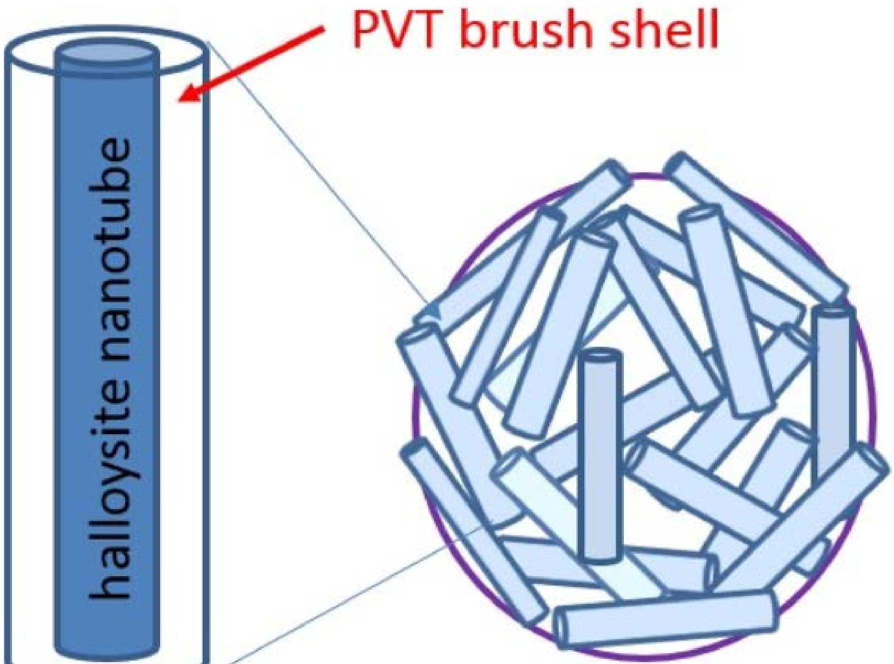
Online successive analysis of ^{90}Sr using SurfW1 extractive scintillating sensor



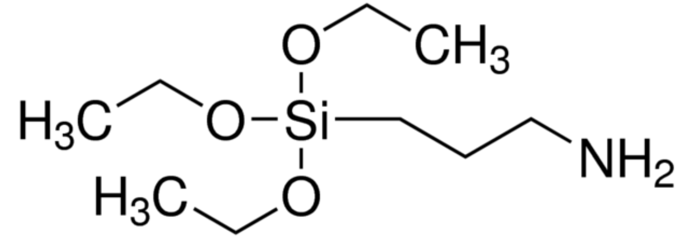
Sample	Loading Efficiency (%)	Detection Efficiency (%)
SL 620	100	2.0±0.7
SurfD1	100	32.5±1.4
SurfW1	100	32.5±1.4

Loaded Activity (Bq)	Loading Efficiency (%)	Detection Efficiency (%)
12.6	100	30.8±6.7
25.2	100	26.5±4.7
50.4	100	25.5±3.4
Average	100	27.6±4.9

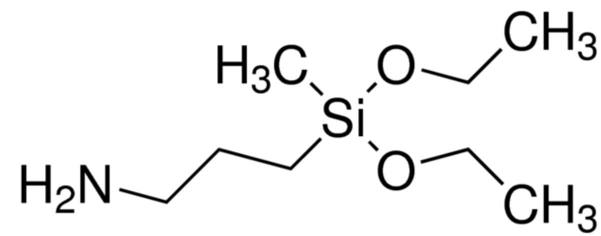
Approach 4: Nanocomposites



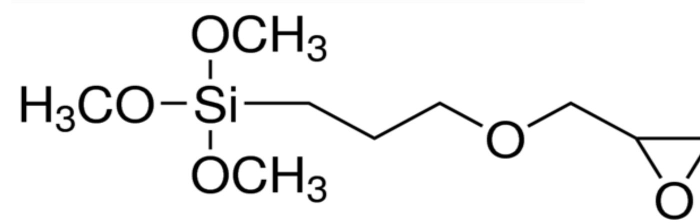
SL particle coated with PVT brush modified halloysite nanotubes



(3-Aminopropyl) triethoxysilane (APTES)

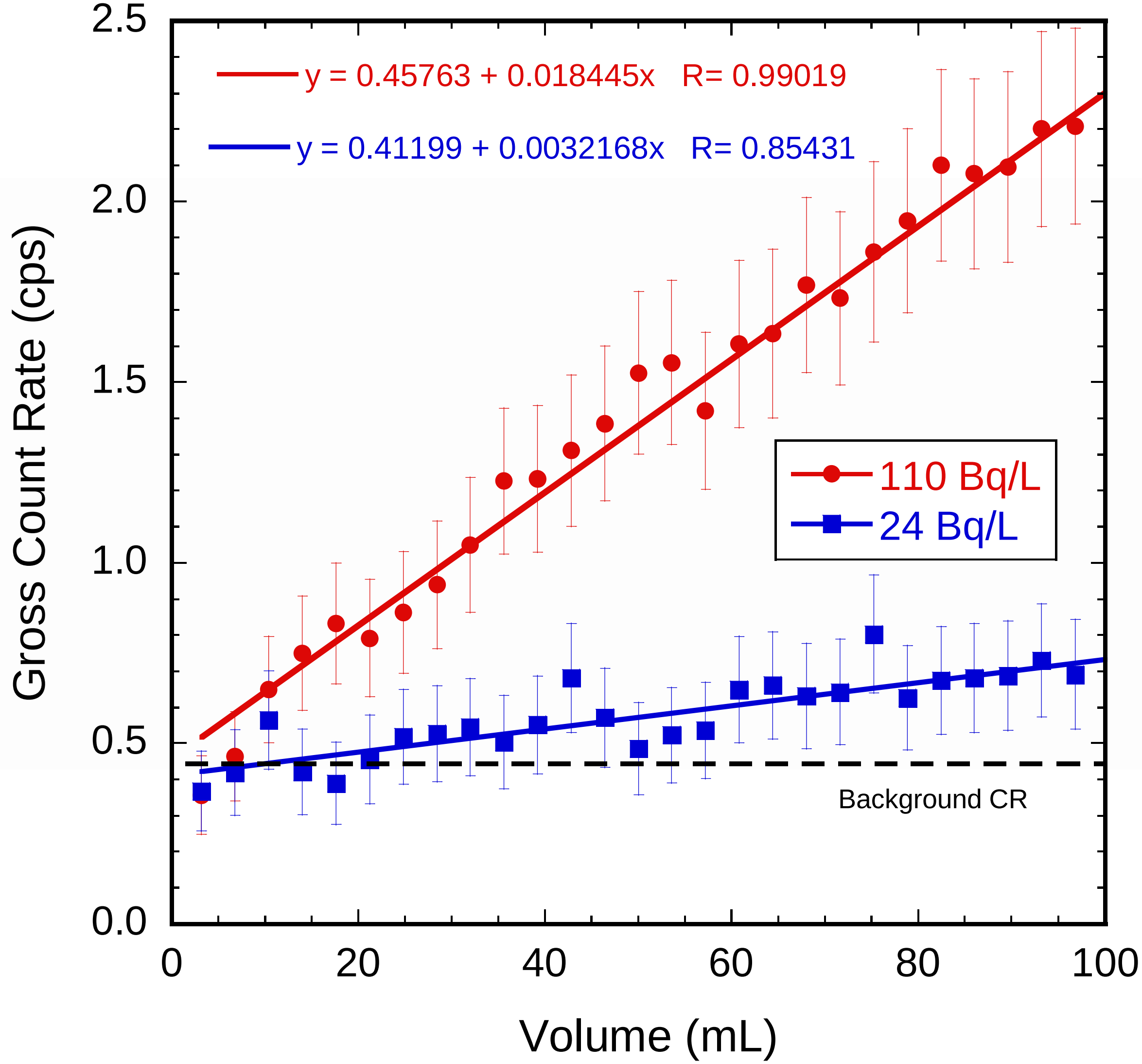


3-Aminopropyl(diethoxy) Methylsilane (APDEMS)



(3-Glycidyloxypropyl) trimethoxysilane

Nanocomposite Results



<u>Analysis of slope</u>
(assuming 100% uptake)
129 Bq/L (+17%)

22.5 Bq/L (-6.3%)

100 mL ~ 3000 DPV
(displaced pore volumes)

Conclusions

- Investigated several avenues for surface modification of commercially available Superlig®620 ligand material to introduce scintillating properties to it
- Direct grafting from process yields scintillating coating but creates impenetrable barrier for Sr ions, while grafting to attachment of fluor-modified dendritic macromolecules yields good permeability but low luminosity response
- Scintillating inorganic-polymer nanocomposite formulation based on halloysite nanotubes modified by ATRP grown PVT brushes: high uptake and potentially high detection efficiency

Approach	Flow-cell type	Sensor Code	Scintillator	Loading Efficiency (%)	Detection Efficiency (%)
1	Heterogeneous	SUPLiG-CaF_2:Eu	CaF_2:Eu	100	54.3±1.30
2	Homogeneous	Polymer	vNPO*	85.6±4.4	53.6±2.4
3	Homogeneous	Surf	vNPO*	100	32.5±1.40
4	Homogeneous	HS	vNPO*	100	14.3

*: 2-(1-naphthyl)-4-vinyl-5-phenyloxazole;

Acknowledgements

Prof. Yuri Lvov, Louisiana Tech University, Ruston, LA, USA
(halloysite nanotubes research)

Funding:
Defense Threat Reduction Agency (DTRA),
Basic Research Award # HDTRA1-12-1-0012