Visually indicative paint for detecting radioactive surfaces

Phase 1: Identification & development of indicators

2010. 07. 15.

KITCO R&D Center

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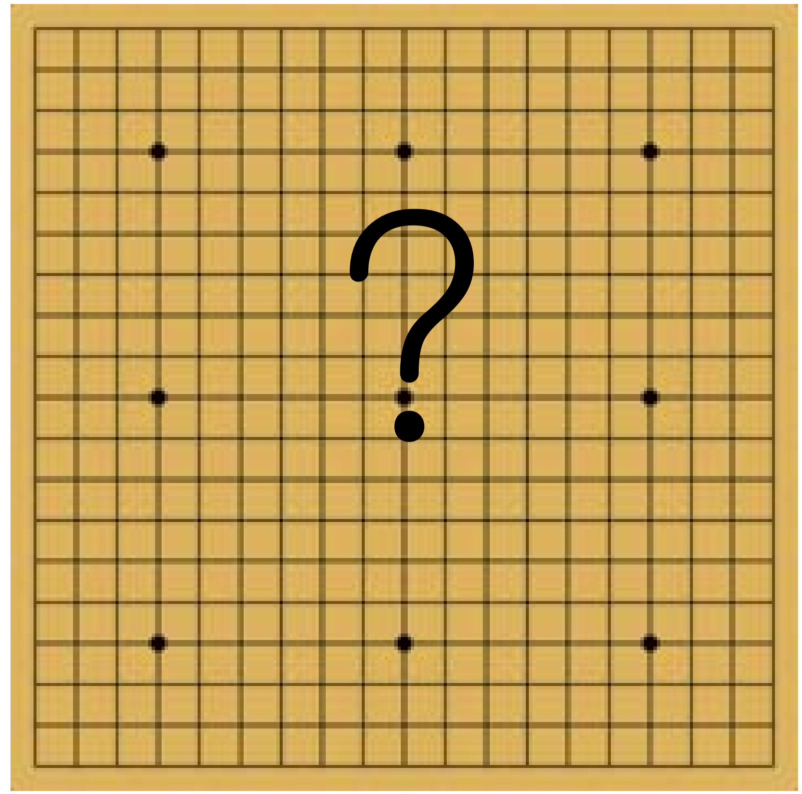
Radiological Contamination

	Alpha	beta	gamma
Common source	Uranium / Plutonium contamination	Strontium90 / Phosphorus32	Iridium192 / Cobalt60
Penetration	Weak (paper)	Weak (Al foil)	Strong (thick lead)
Contamination Risk	Low	Medium	High
Usual site of contamination	Nuclear fuel Inspection Site	Laboratories	Nuclear plant, Hospitals

- Where contamination risk is high by using beta and gamma radiation sources.
- Contamination indicator is useful tool for the detection of beta & gamma radiation

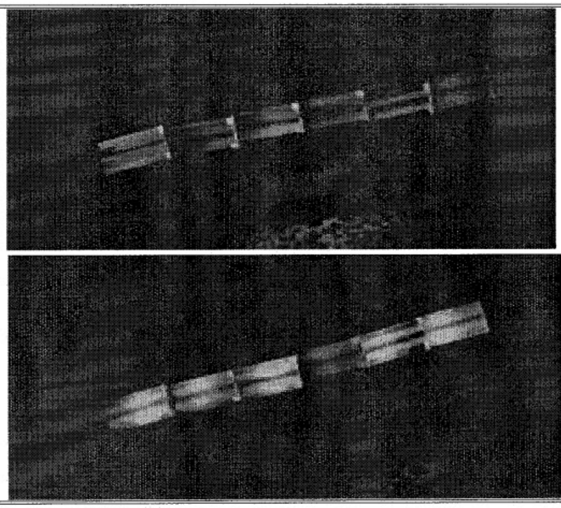
Where on Earth is the contamination source???



SMEAR???

Prior Arts

Emitting scene*



* Measurement samples: FSA00

Table 3.2.7 Visibility measurement according to source activities

Source activity [Ci]	Illuminance [lux]	Luminance [mCd/m²]*	Visibility	Remarks
6.6	3.9	53	poor	
27.9	3.9	231	good	

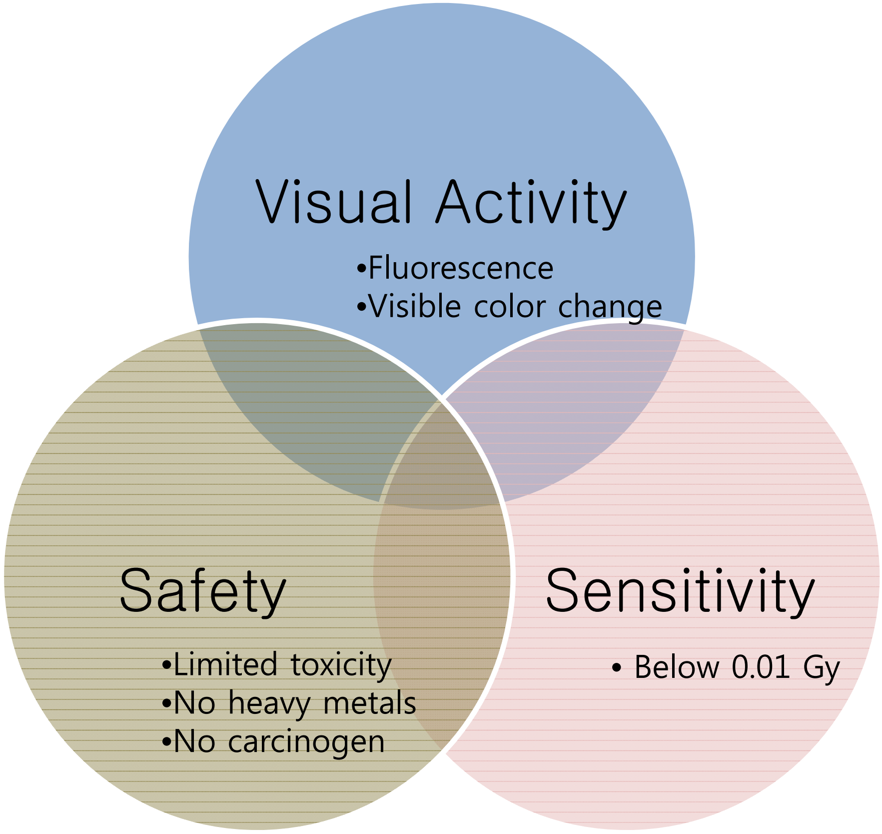
- Author: Future and Challenge
- Title: Development of Scintillating film for Detection of Radioactive Source Position
- Organic and inorganic crystal scintillators were fabricated into plastic strips for fluorescent visualization of gamma-radioactive surface.
- While it showed good visibility at high source activity (~28 Ci), visualization at lower activity (<6.5 Ci) produced poor results.

Project Goal

Phase	Symptom			Exposure (Gray)		
		1–2Gy	2–6Gy	6-8Gy	8-30Gy	>30Gy
Immediate	**Nausea and vomiting**	5-50%	50-100%	75-100%	90-100%	100%
	Time of onset	2-6h	1-2h	10-60m	<10m	immediate
	Duration	<24h	24-48h	>48h	>48h	48h - death
	Diarrhea	None	Slight (10%)	Heavy (10%)	Heavy (90%)	Heavy (100%)
	Time of onset	--	3-8h	1-2h	<1h	<30m
	Headache	Slight	Mild (50%)	Moderate (80%)	Severe (80–90%)	Severe (100%)
	Time of onset	--	4-24h	3-4h	1-2h	<1h
	Fever	Slight-None	Moderate (50%)	High (100%)	Severe (100%)	Severe (100%)
	Time of onset	--	1-3h	<1h	<1h	<30m
	CNS function	No impairment	Cognitive impairment 6–20 h	Cognitive impairment >20 h	Rapid incapacitation	Seizures, Tremor, Ataxia
Latent Period		28–31 days	7–28 days	<7 days	none	none
Overt illness		Mild Leukopenia; Fatigue; Weakness;	Leukopenia; Purpura; Hemorrhage; Infections; Epilation;	Severe leukopenia; High fever; Diarrhea; Vomiting; Dizziness and disorientation; Hypotension; Electrolyte disturbance;	Nausea; Vomiting; Severe diarrhea; High fever; Electrolyte disturbance; Shock	Death
	Mortality w/o medical care	0-5%	5-100%	95–100%	100%	100%
	Mortality w/ medical care	0-5%	5–50%	50-100%	100%	100%

- Biological damage occurs even at relatively low level radiological exposure (0.5~6 Gy).
- Hence, visual indicators of low level radio activity would greatly help clean-up of radio-contaminated surfaces and improve the work environment safety.

Development Considerations



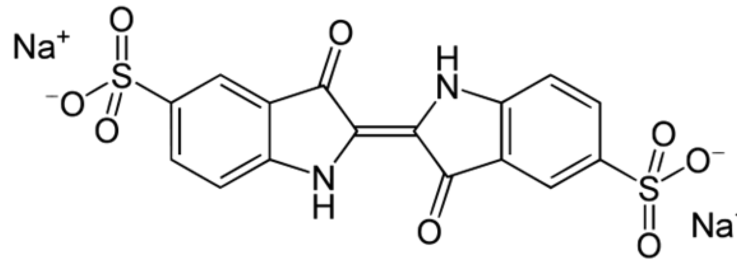
Candidate indicators

a. Au-NP/dye conjugate system
b. Organic scintillators
c. Aqueous coumarin system

Au-NP/dye Conjugate System*

Colloidal Gold

Au-NP/dye conjugate



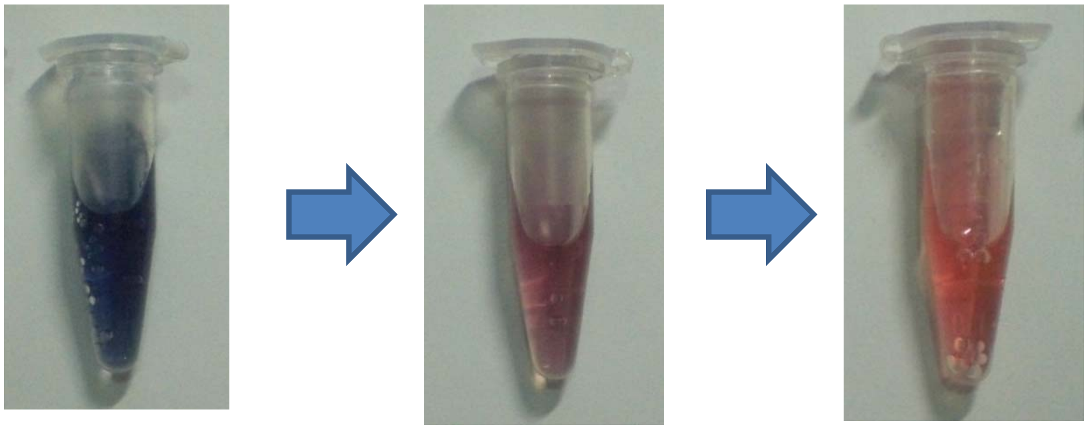
Indigo Carmine
(Radical-sensitive blue dye)

- Both Au-NP and indigo carmine are nearly non-toxic & water soluble.
- *Au-NP is an excellent converter of radiation energy into radical ions, given the efficiency of 9.491 rad/R. (Strong primary and secondary photoelectric effect)
- *Primarily sensitive toward X and gamma rays of 10 keV ~ 1 MeV energy.
- Indigo carmine, a blue dye, readily loses color when it is exposed to hydroxyl radical.
- Further sensitization of the system toward ionizing radiation may be possible.

*Irradiation stability and cytotoxicity of gold nanoparticles for radiotherapy: Zhang et al.

Result & Discusstion

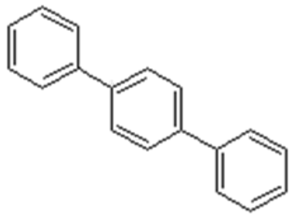
Au-NP/Indigo Carmine color transition per ~2 Gy radiation



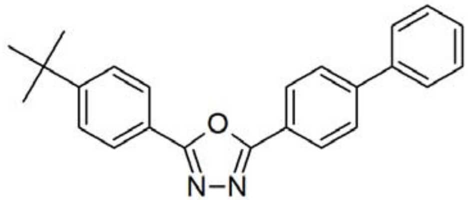
0 hr 3 hr 6 hr

- Strength: Obvious color shift from blue to red may allow for clear indication.
- Weakness: Slow reaction time & low sensitivity (No reaction observed below 1 Gy).
- Points of Improvement.
  - Adjust catalytic conditions for radical generation & organic degradation upon irradiation.
  - Additionally identify other aqueous organic dyes that may be more sensitive to oxidation

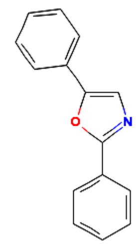
Organic Scintillators



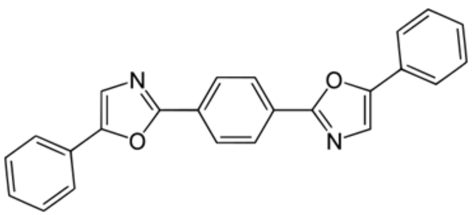
P-terphenyl
Ex/em=290/340



Butyl PBD
Ex/em=305/364
31 mg/L in mineral oil



DPO
Ex/em=300/350
4 g/L in toluene



POPOP
Ex/em=360/420

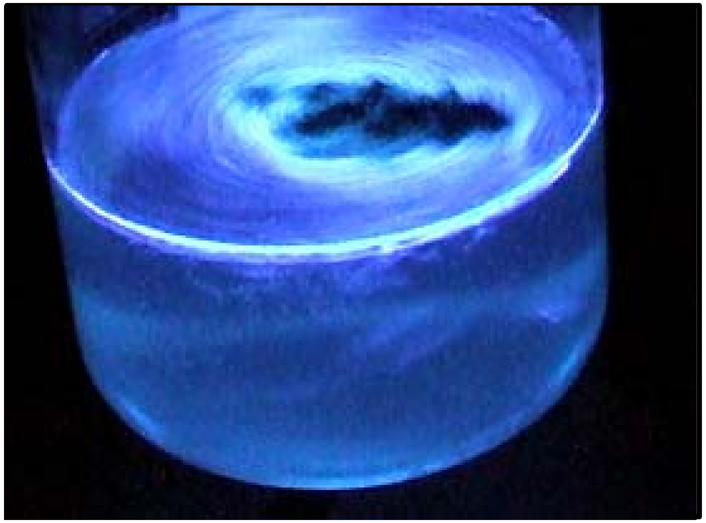
DPOPOP
Ex/em=330/380
1.25 g/L

- Organic solvent compatible (toluene, xylene, etc.)
- They can be embedded into plastics or exhibit flourescence when dried.
- It must consist of primary & secondary scintillators, as the primary scintillators give invisible photons near the wavelength of 350 nm.
- They have been successfully implemented in high level contamination.
- Sensitivity enhancement may be difficult.

*Radiation dosimetry: Instrumentation and methods, Gad Shani

Result & Discusstion

Luminol control experiment - Chemiluminescence



Base-activated 2 mM luminol with H2O2 (No irradiation)

- Strength
  - Bright blue glow is visibly noticable & the reaction takes place in water.
  - The reaction may be coupled with enzymatic catalysts for additional sensitization (i.e. HRP)
- Weakness:
  - Strong alkalinity required → It may present dangers of chemical burn.
  - Detecting glowing light may require dark ambience → Potential workplace hazard risks.
  - Actual chemiluminiscent light generated by gamma irradiation may be too weak for visual detection.
- Points of Improvement.
  - Try to employ various enzymatic & non-enzymatic catalysts for optimal generation of H2O2 upon gamma irradiation..
  - Try to find ways to ameliorate the alkalinity requirement associated with luminol chemiluminiscence.

Aqueous Coumarin System*

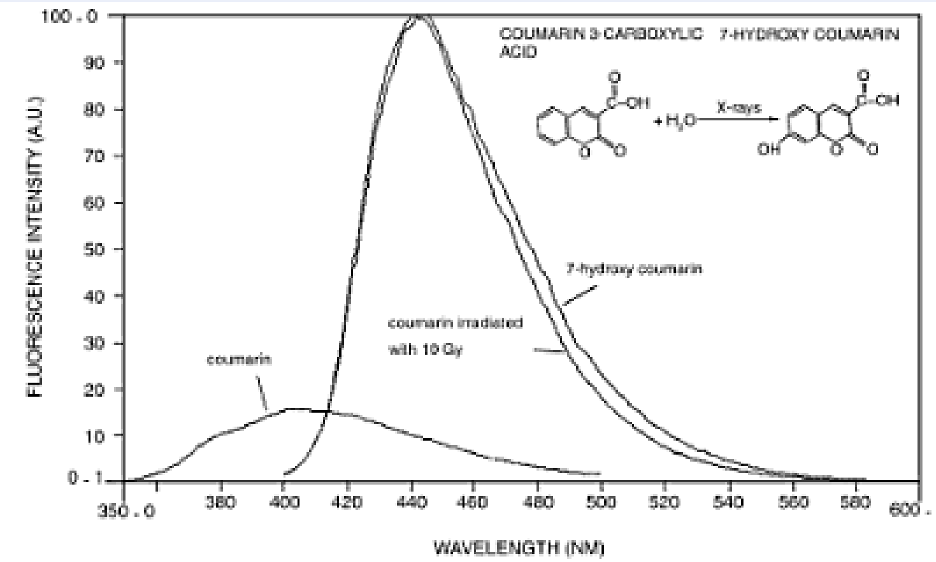


FIGURE 7.10 Room-temperature fluorescence of coumarin-3-carboxyl acid (10^{-7}M) and coumarin-3-carboxyl acid (10^{-4}M) irradiated with 10 Gy. (From Reference [7]. With permission.)

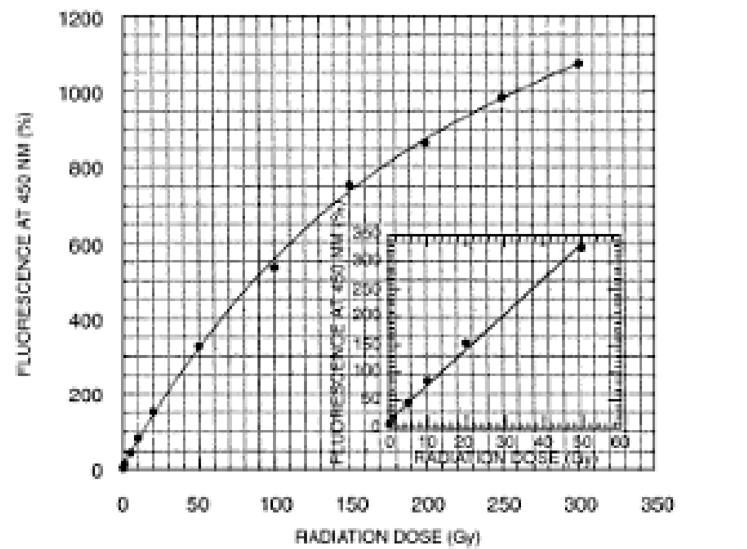


FIGURE 7.11 Fluorescence of irradiated 10^{-4} M aqueous coumarin-3-carboxylic acid vs. radiation-absorbed dose. The excitation was at 400 nm, the emission at 450 nm, and the resolution at 5 nm. (From Reference [7]. With permission.)

- A naturally occurring compound in plants.
- Widely used compound in medicine.
- It gains fluorescence property at 450 nm (400 nm em) in linearly proportional manner to the radiation dose between 0.1 ~ 250 Gy.
- The sensitivity is due to hydroxy-adduct formation at 7′ position upon irradiation, which is mediated by hydroxyl radical.
- Further sensitization of the system toward ionizing radiation may be possible.

*Radiation dosimetry: Instrumentation and methods, Gad Shani

Result & Discusstion

- Despite the previous work by Gad Shani and coworkers, we were unable to reproduce fluorescence of 3-carboxy-coumarin, at both acidic and basic conditions.
- Control oxidation experiment using hydrogen peroxide also failed to produce visible fluorescence.
- Possible explanations
  - Fluorescence being too weak to be detected visually on naked eyes.
  - Fluoresecence quenching effect by dissolved oxygen in water.

Assessment

	Visual Activity	Sensitivity	Safety
Aqueous Coumarin	Passive Flourescence (UV needed)	Linearly sensitive at low level (0.1 ~ 50 Gy)	Non-bioaccumulative & relatively little toxicity
Organic Scintillation	Active Flouresence (no UV needed)	Not-so-sensitive at low level radiation	Bioaccumulative & toxic in certain settings
Au-NP/dye	Visible color change (blue ->pink)	Not yet determined	Non-bioaccumulative & relatively little toxicity

Undesirable	Moderate	Highly desirable

Known sensitivity of each of the systems is still too high → Sensitizing agents are needed.

Future Directions

1. Additional assessment on visual identifiers.
2. Development of sensitizers
   – Lowering the sensitivity to below 0.01 Gy
3. Development of spray-paintable formulation.
   – Solvent, binder, aeration medium.