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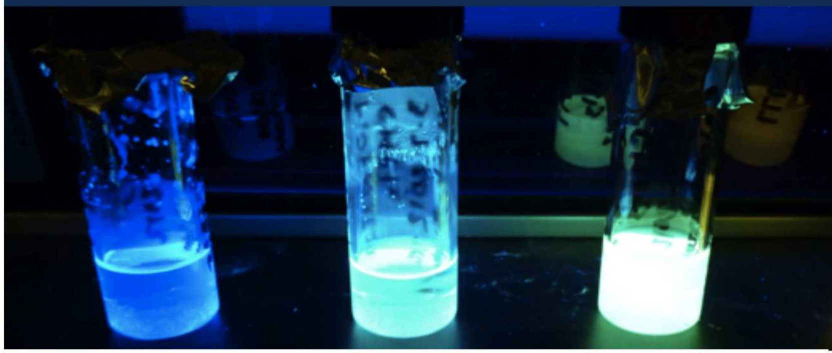

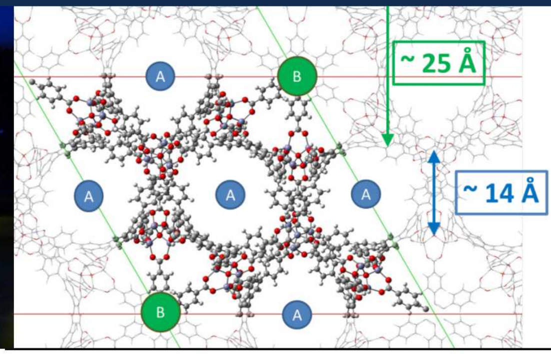

Exploiting the Tailorable Nanoporosity of Metal-Organic Frameworks for In-Situ Identification of Radioisotopes

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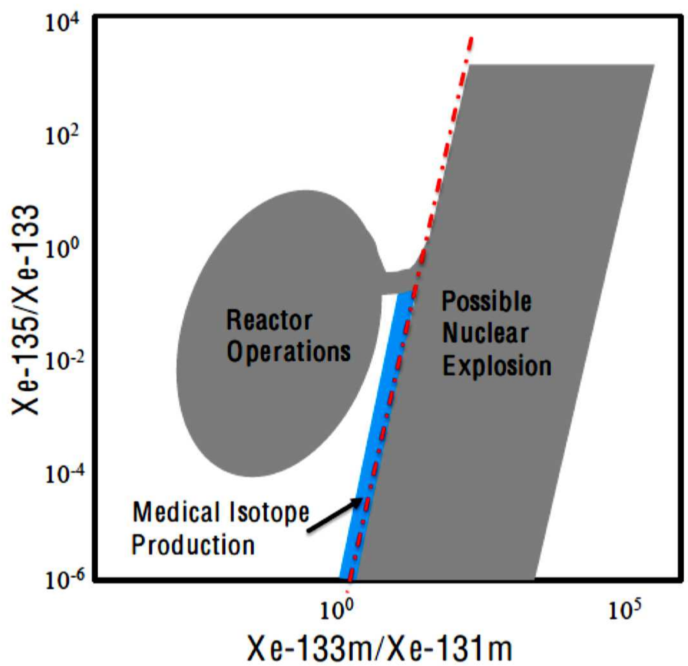
Xenon isotopes used for nuclear detonation detection

Nuclide	^{131m}Xe	^{133m}Xe	^{133}Xe	^{135}Xe
Fission Yield per kT Pu (Bq)	5×10^{9}	2×10^{13}	2×10^{14}	2×10^{16}
Half-life (days)	11.93	2.19	5.25	0.38
γ Ray (keV)	163.9	233.2	81	249.8
X-rays (keV)	29.5–34.6	29.5–34.6	30.6–36.0	30.6–36.0
β Endpoint (keV)	-	-	346	905
Conversion electron (keV)	129	199	45	214



Isotopic ratios can distinguish nuclear detonations from medical isotope production and reactor operations

Airborne radionuclide detection by the IMS

Source terms and events:

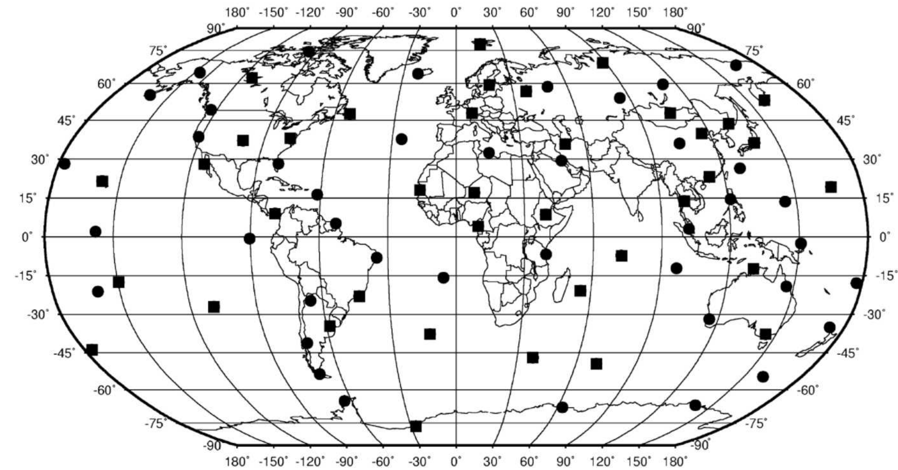
- Nuclear reactors
- Fukushima accident
- Medical isotope production facilities
- Nuclear testing in North Korea

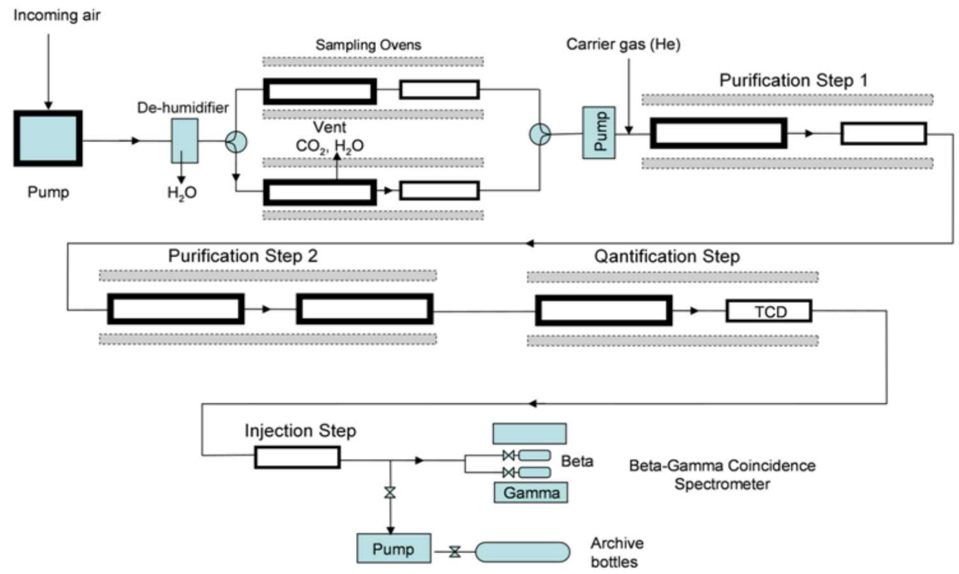
Detection of noble gas radioisotopes by IMS monitoring systems

- **^{131m}Xe, ^{133}Xe, ^{133m}Xe, ^{135}Xe**
- Completely automatic commercial systems
- 12-hr collection, followed by 12-hr count

"Real-time" detection (≤ 30 min) advantages:

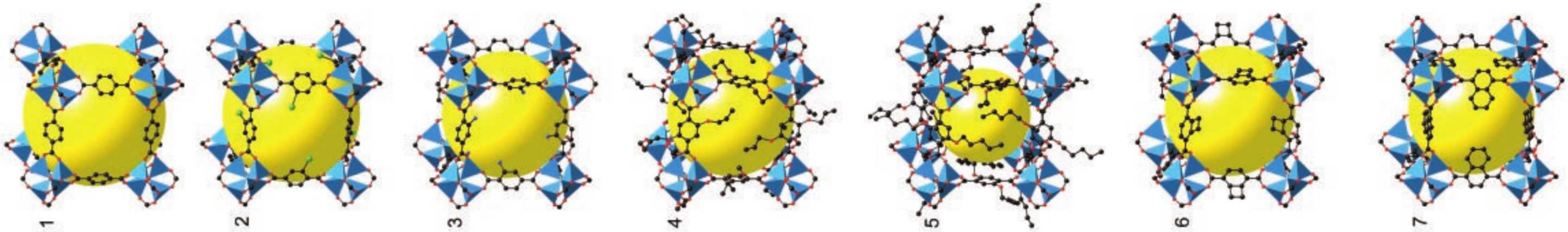
- Time—resolved isotope concentrations
- Trigger system for other detectors
- Lower-yield detection threshold



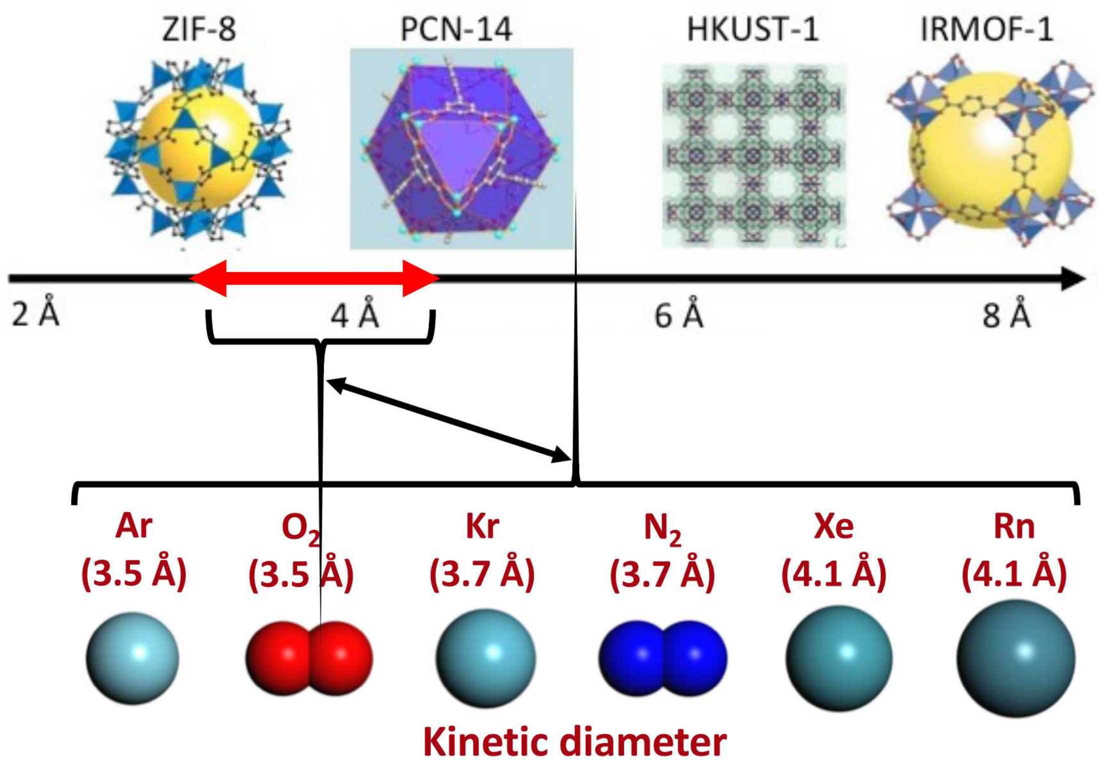


Courtesy, Dr. Ted Bowyer, Pacific Northwest National Lab.

Metal-Organic Frameworks (MOFs) have well-known ability to adsorb noble gases

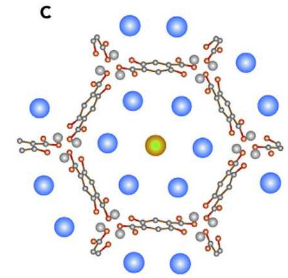


- **Thousands of MOFs are known**
- **Ultrahigh surface areas (record is 7000 m^2/g) enable preconcentration of noble gases**
- **Selective gas uptake due to tailorable pore size/chemical environment**
  - **Uptake of Kr, Xe, and Rn is a factor of ≥ 6X higher than N_2**
- **Stable in air to ≥ 200 °C; allows fast sorbent regeneration**



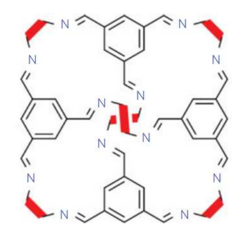
Although many MOFs have high uptake and selectivity for Xe, most are not luminescent

MOF	Xe Uptake (mmol g^{-1}[a] or mmol Kg^{-1}[b])	Xe Q_{st} (kJ mol^{-1})	Xe/Kr Selectivity
CaSDB (SBMOF-1)	1.4[a] (13.2)[b]	35	16[a]
SBMOF-2	2.06[a]	26.4	10[c]
Ni-MOF-74	4.19[a] (4.8)[b]	22	7.3[c]
$Co_3(HCOO)_6$	2[a]	28	12[d]
HKUST-1	3.3[a]	26.9	8.4[e] (3)[b]
MOF-5	1.98[a]	15	–
FMOF-Cu	0.8[a]	15	2[f]
MFU-4l	1.8[a]	20	4.7[e]
MOF-505	2.2[a]	–	8[g]
SIFSIX-3-Ni	2.51[a]	18.9	–
SIFSIX-3-Fe	2.45[a]	27.4	–
CROFOUR-1-Ni	1.8[a]	37.4	22[c]
CROFOUR-2-Ni	1.6[a]	30.5	15.5[c]
UIO-66	1.58[a]	–	3.8[g]
PCN-14	7.1[a]	17.9	6.5[d]
NOTT-100	6.1[a]	18.6	6.7[d]
NOTT-103	4.1[a]	19.7	5.5[d]
ZIF-8	–	–	1.9
$[Zn(tmz)_2]$	3[a]	23	15.5[f]
MOF-74 Mg	5.58[a]	–	5.92
MOF-74-Co	6.1[a]	–	10.37
MOF-74-Zn	3.88[a]	–	5.76
Porous Organic Cages, Carbons, and Covalent-Organic-Framework-like Materials			
Noria	1.55[a]	24.5–26.9	9.4[a,b]
CC3	2.2[a] (11)[b]	31.3	20.4[a] (16)[b]
COP-4	1.7[a]	–	1.5
Activated Carbon	4.2[a]	–	8
Carbon-Zx	4.42[a]	–	–
Carbon-Z	3.17[a]	–	–



MOF-74

MOF-505

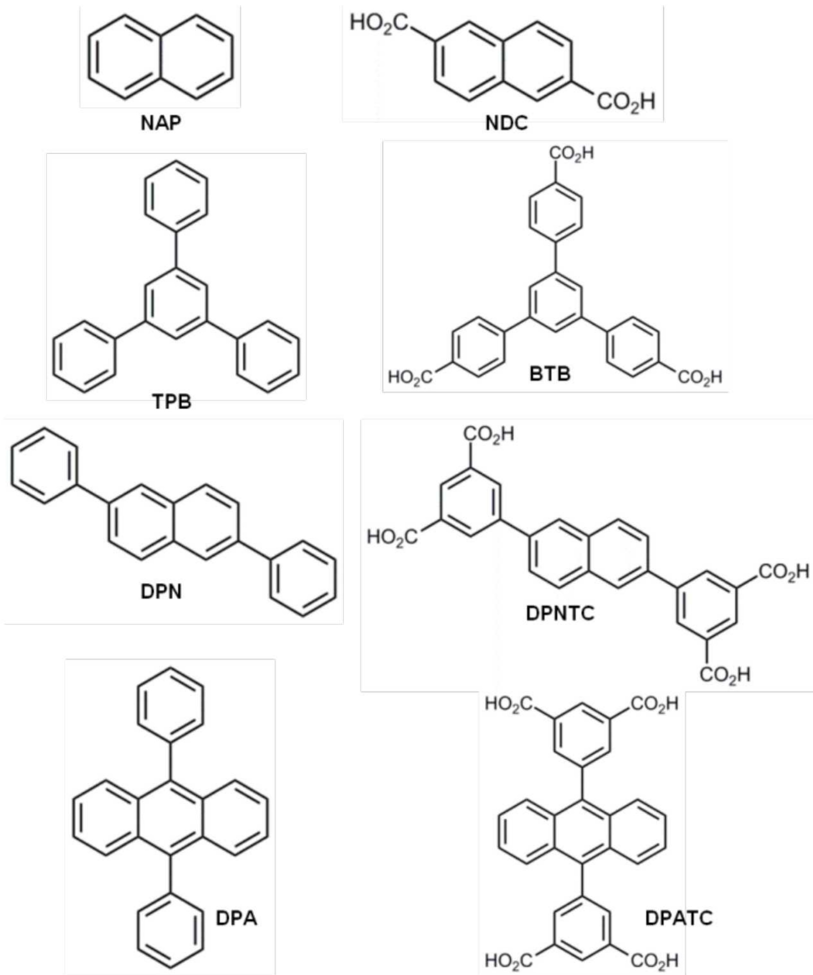


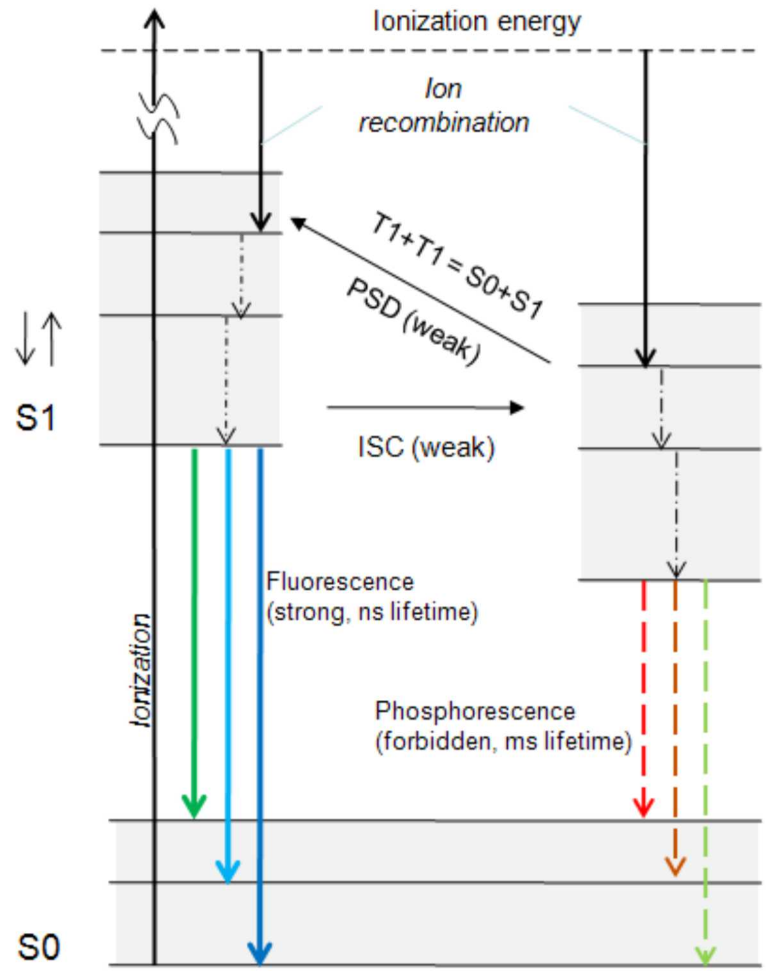
CC3

D. Banerjee et al. *Chem.* 4 (2018), 466–494

Basics of radiation detection using organic scintillators

Typical luminescent MOF linkers have fused aromatic rings, similar to conventional organic scintillators



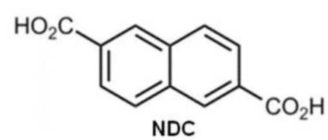


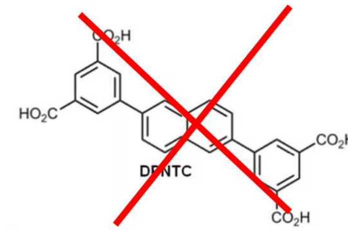
We developed design principles for MOF-based Scintillators

- **Use closed-shell metal cations**
  - **E.g., Zn or Cd**
  - **No MOFs with open metal sites**

$Zn_4O(O_2CR)_6$

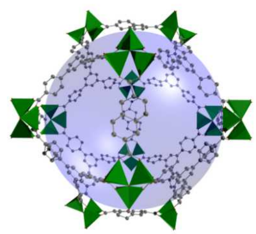
- **Avoid non-rigid linkers with non-radiative pathways**



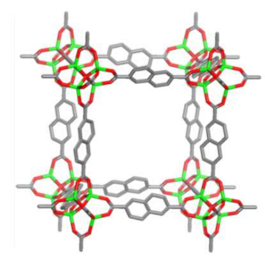


- **Adopt rigid framework topologies**

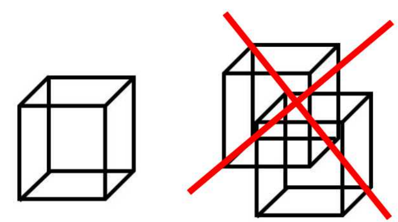
- **Electronically isolate linkers**



DUT-6



IRMOF-8

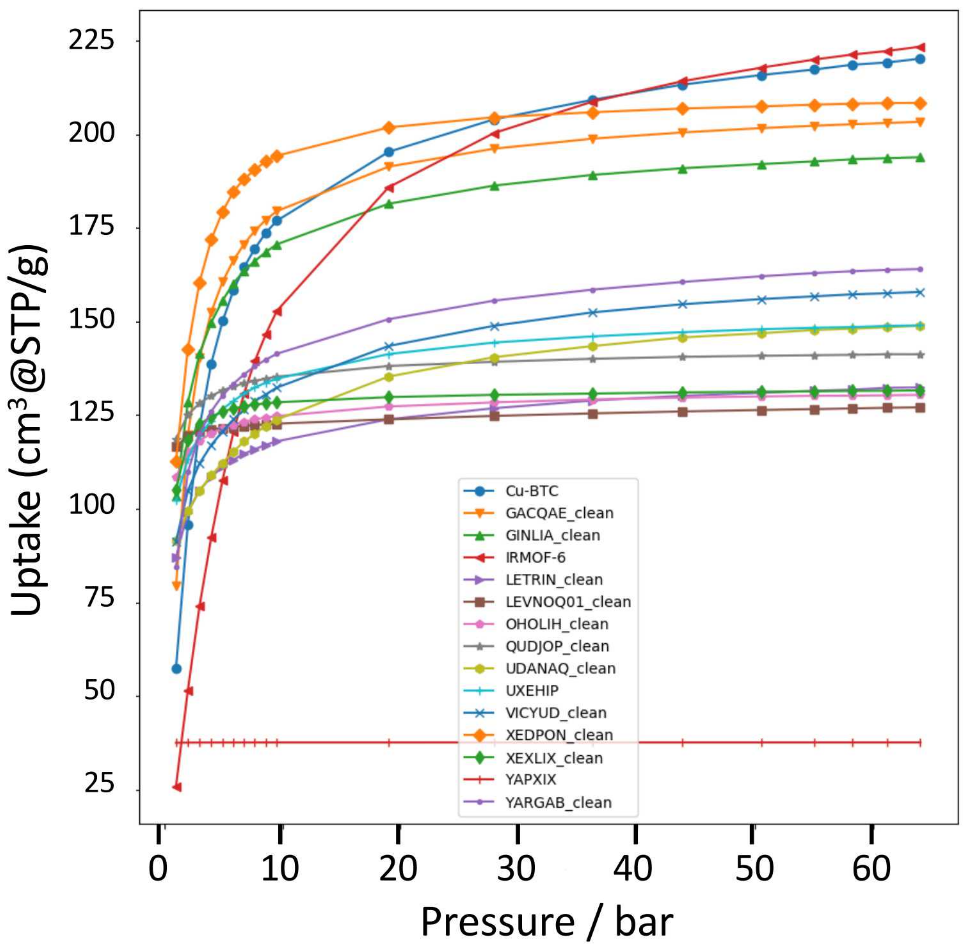


J. J. Perry et al. *J. Mater. Chem.* 2012, **22**, 10235

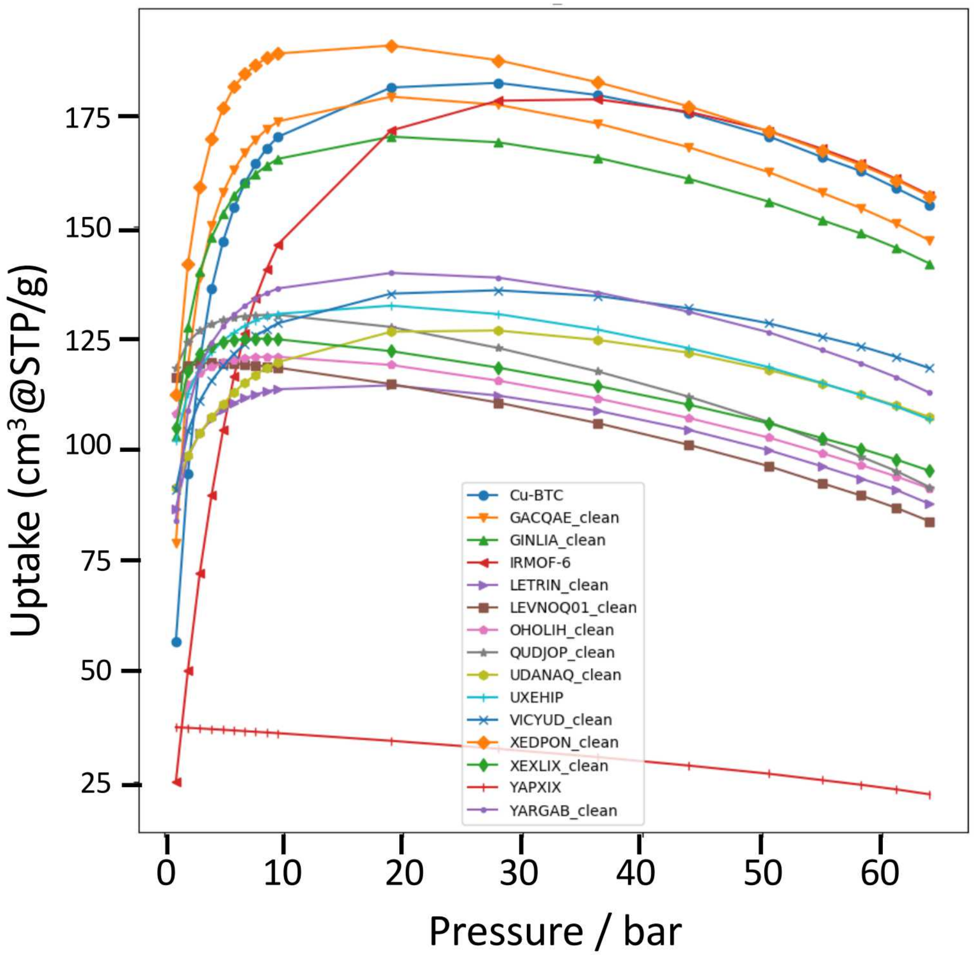
The high surface areas of MOFs and other nanoporous sorbents enable them to uptake more gas than an empty volume

Grand Canonical Monte Carlo simulations

Predicted "absolute" (i.e., total) Xe absorption



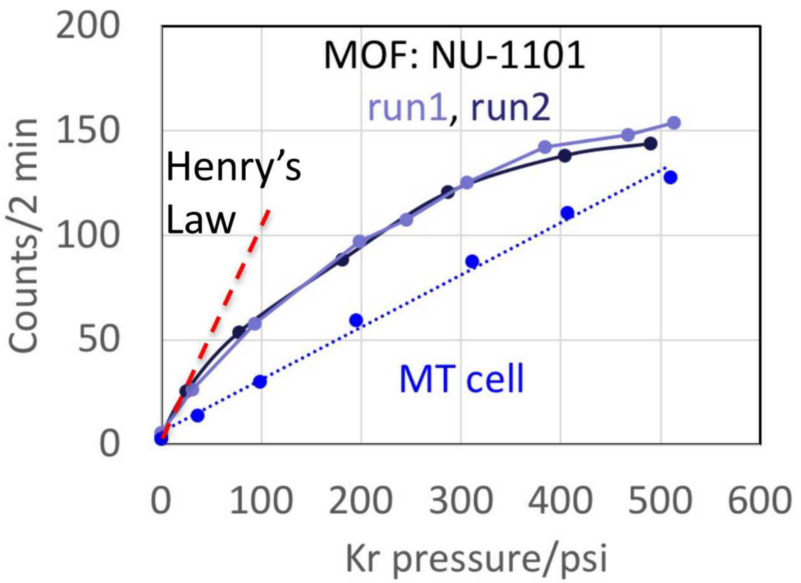
Predicted "excess" Xe absorption



MOF "excess capacity" due to ultrahigh surface areas produces dramatic concentration enhancements

Experiments: Pure component

- **40.8 mg of NU-1101**
- **High surface area: 4400 $m^2 g^{-1}$**
- **Packing density: < 30%**
- **Use Kr as a surrogate for Xe radioisotopes**
- **^{85}Kr (1 Bq/m^3 in air) as surrogate for short-lived Xe isotopes**

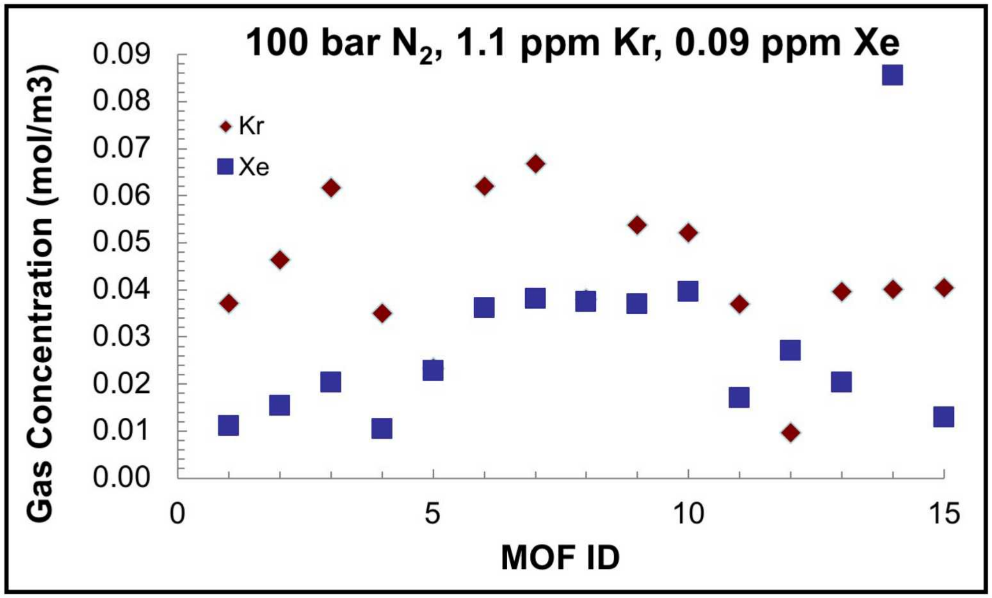


Modeling: Gas mixtures

- **Simulated air Kr/Xe/N_2 mixtures at 298 K**
- **$176x10^6$ steps due to the low gas concentrations → required weeks due to poor statistics at such low pressures**

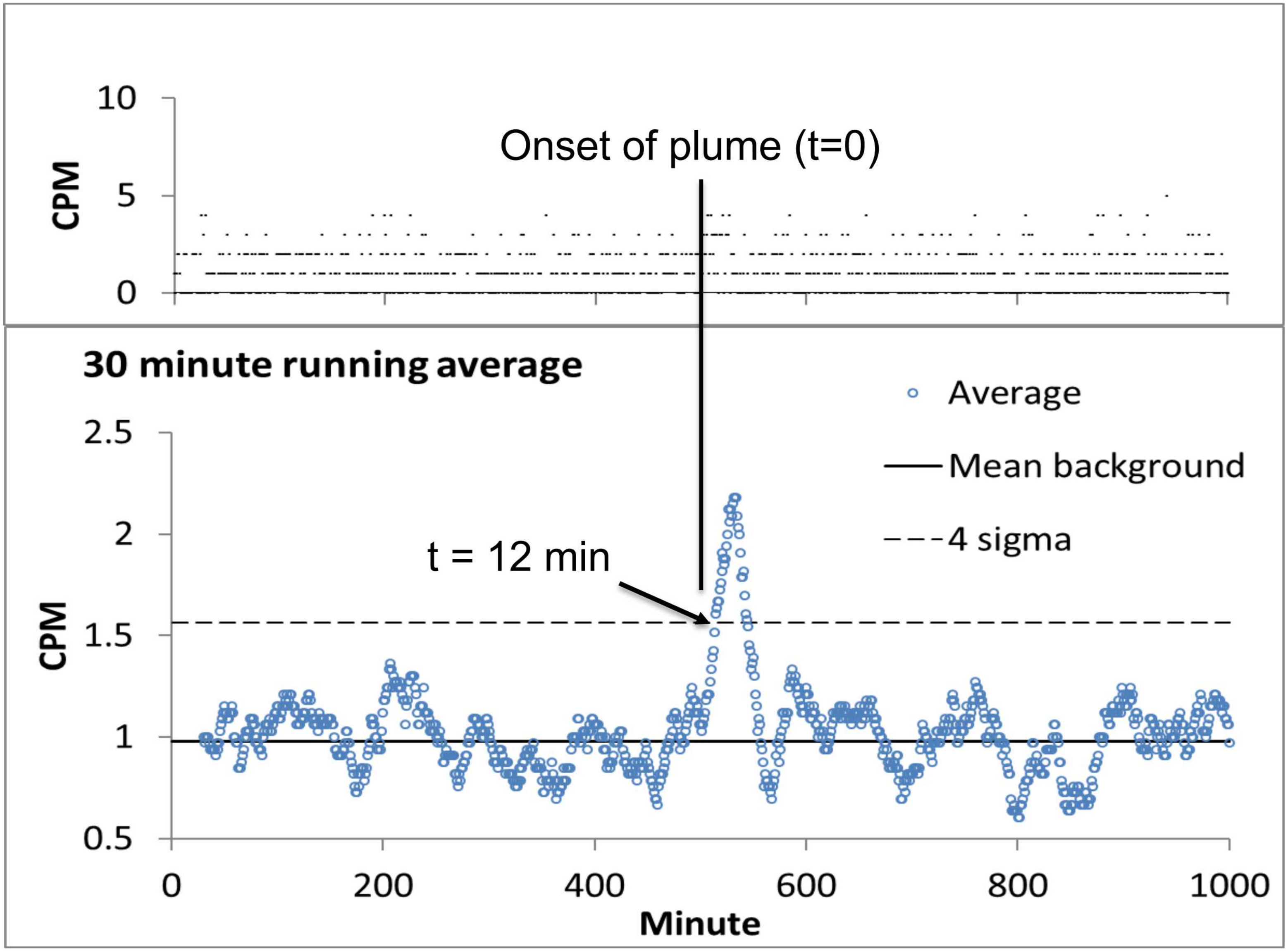
→ Predicted concentration increase factors relative to mixture at STP:

Kr: ~200X – 1500X
Xe: 3,500X – 23,000X

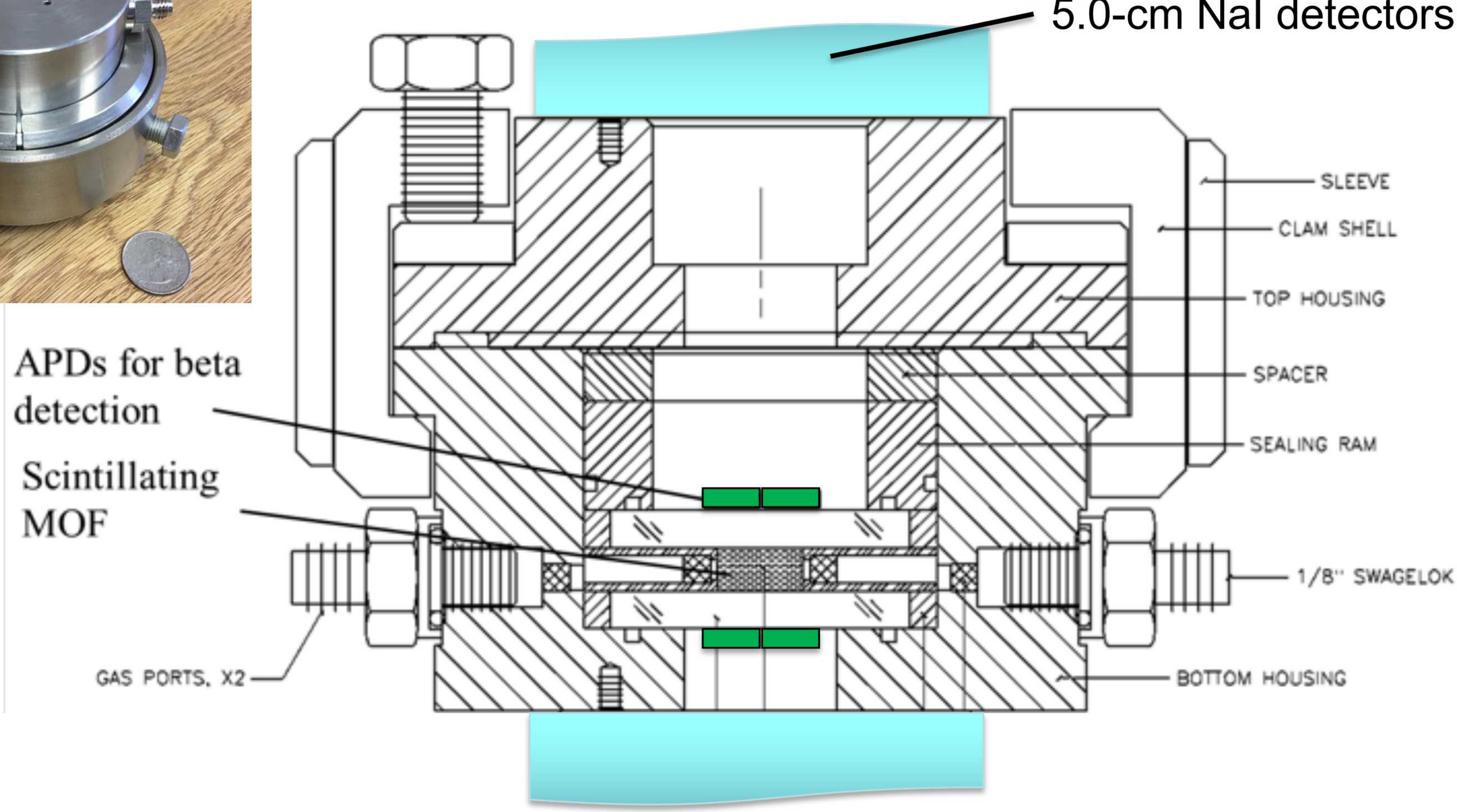


Real-time plume detection

Simulated plume of 1 Bq/m^3 above background, 30 Min duration

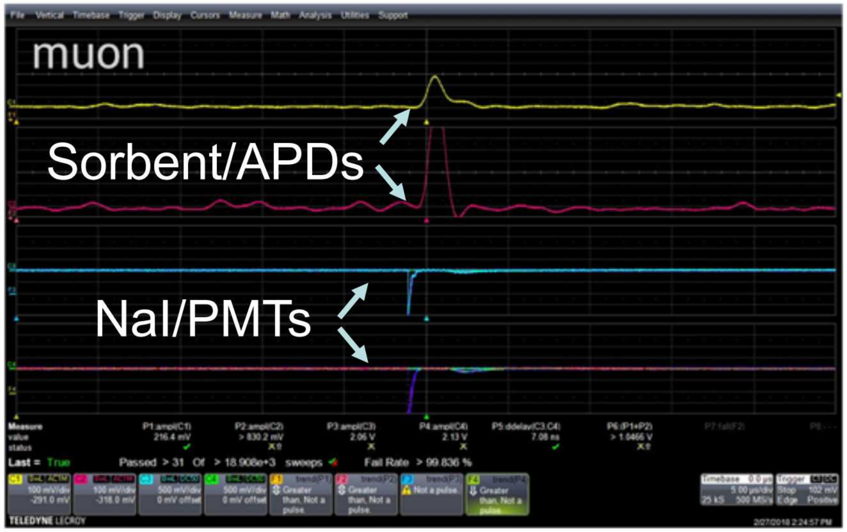


High-pressure gas cell for testing detection concept



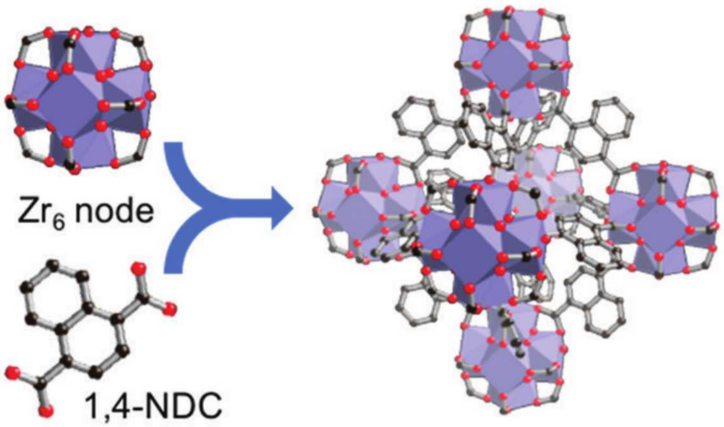
Scale drawing of the thin-window cell, showing location of the detectors and the scintillating MOF. The volume is scalable using a series of internal bushings.

Coincidence detection reduces threshold and discriminates background events – eliminates need for extensive shielding



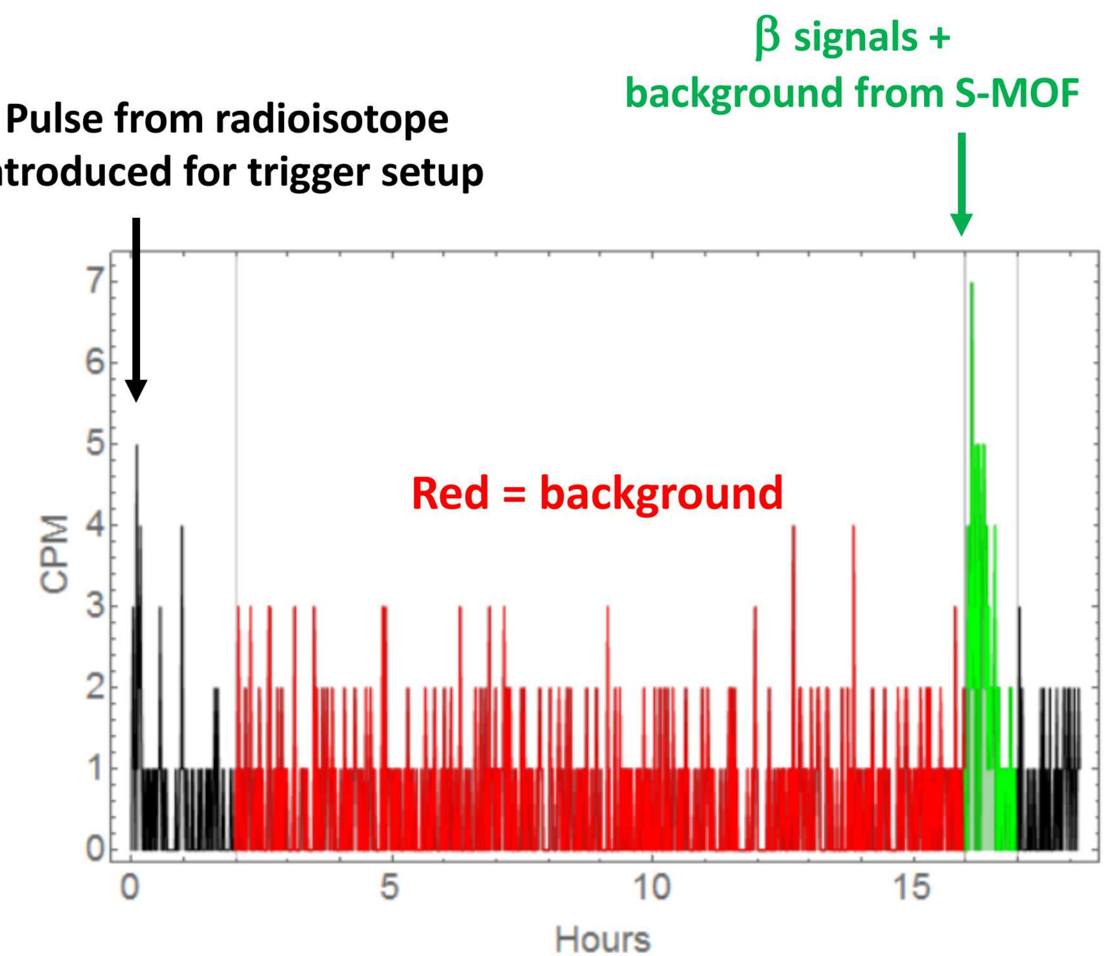
- **Muons are the main background detected in the laboratory**
- **Sorbent bed is insensitive to γ due to low mass (500 mg/cm²) and atomic number**
- **NaI attenuates γ and provides muon veto shield**

Detection of β particles from ^{85}Kr using Zr(NDC) as scintillating MOF



^{85}Kr as surrogate for short-lived Xe isotopes

- β emitter
- Half life 10.8 years
- ~ 1 Bq/m^3 in air

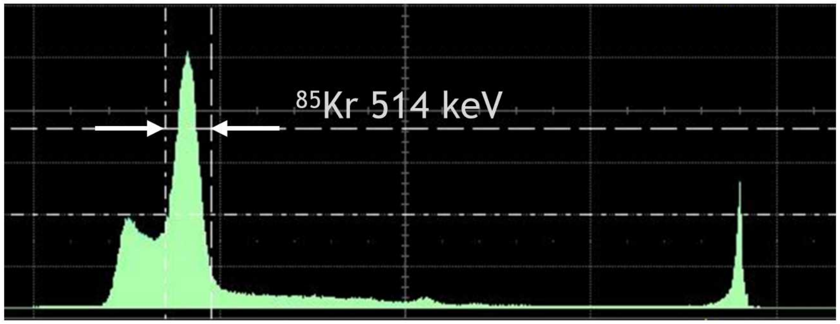


Signal:background ratio determined to be 8σ at 1 bar pressure, sufficient to detect the isotope

Correlated β/γ events from ^{85}Kr using Zr(NDC) as scintillating MOF

Demonstrates detection of rare events in laboratory background

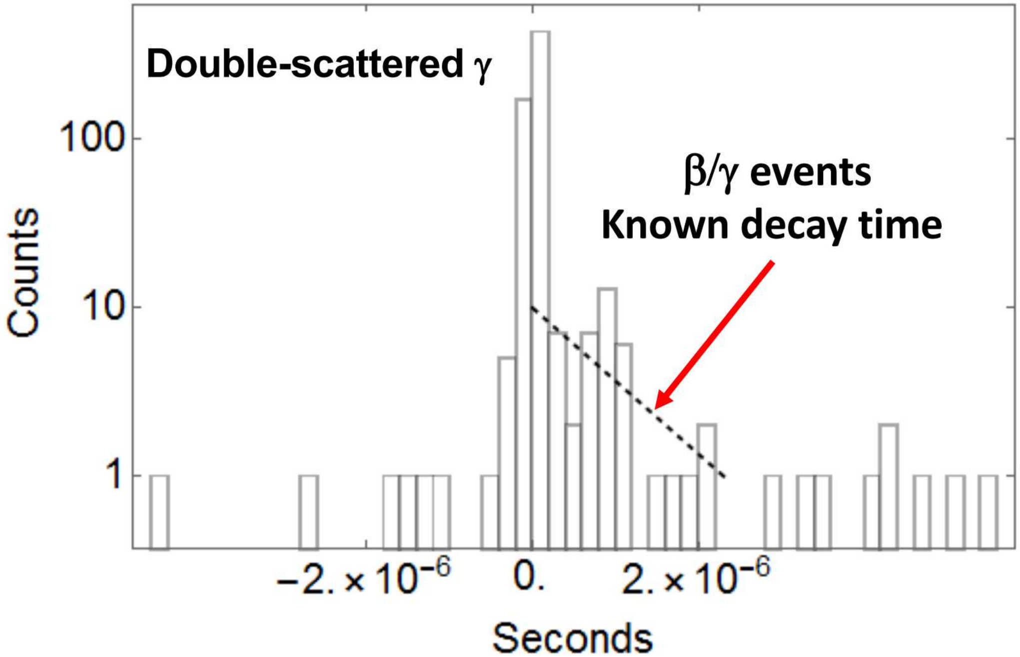
- **Low branching ratio and η**
- **48 hour acquisition time**
- **Isotope ID by energy and timing**



5.0 cm NaI gamma detector

Expected rate of gamma detection		
window transmission	0.88	
solid angle / 4π	0.165	
absorption efficiency	0.82	
PE/total	0.47	
photopeak efficiency	0.055722	
Branching ratio	0.004	
gammas detected per beta	0.000223	
beta activity	2	Bq
gamma rate	0.000446	/s
	1.604792	/hr
	38.51501	/day

Timing distribution for correlated events

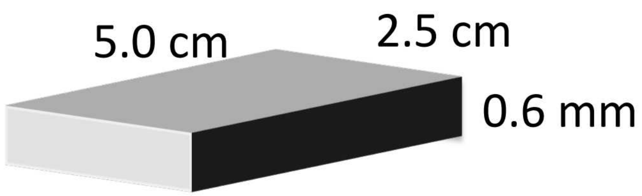


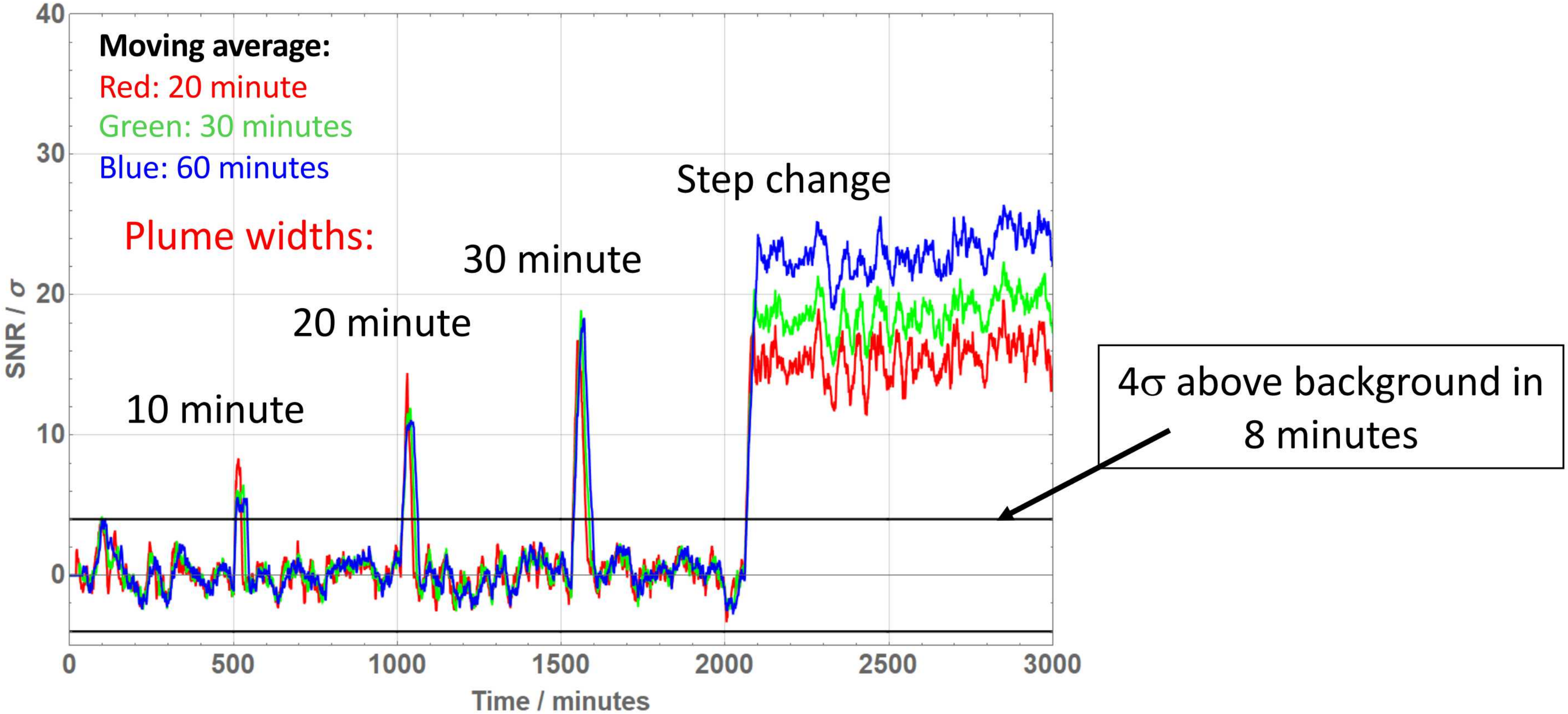
Simulated radioxenon counting

Simulation assumes:

- Activity enhancement of 20,000 (for Xe)
- Detector scaled for 10 cpm background
- 1 Bq m^{-3} background
- 1 Bq m^{-3} plumes of varying width

Enhancement (by MOF and high pressure) enables compact detector geometry





Conclusions

- **MOFs possess a unique combination of properties that make them useful for detecting noble gas isotopes**
  - **Scintillation**
  - **Selective uptake over majority atmospheric components**
- **Detection of β and γ particles was demonstrated using a surrogate for short-lived Xe isotopes**
- **Scintillating MOFs show potential to replace conventional porous carbons and allow rapid detection of trace gases resulting from nuclear detonations**

Acknowledgements

- GCMC simulations and MOF screening
  - Jeff Greathouse, Craig Tenney (Sandia-NM)
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