Awareness and Localization of Explosives-Related Threats (ALERT)

A Department of Homeland Security Center of Excellence

UNIVERSITY OF Rhode Island

Addressing Issues with Sample Collection

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ALERT
AWARENESS AND LOCALIZATION OF EXPLOSIVES-RELATED THREATS

This material is based upon work was partially supported by the U.S. Department of Homeland Security, Science &Technology Directorate, Office of University Programs. Views and conclusions contained in this document are those of the authors and should not be interpreted as necessarily representing the official policies, either expressed or implied, of any other agency.

To Optimize Detection We Must Optimize Collection

Questions:

How much explosive is available for collection or detection?

Where can it be found?

Approaches:

to collecting sample

to presenting sample to detectors

to laboratory analysis of our progress.

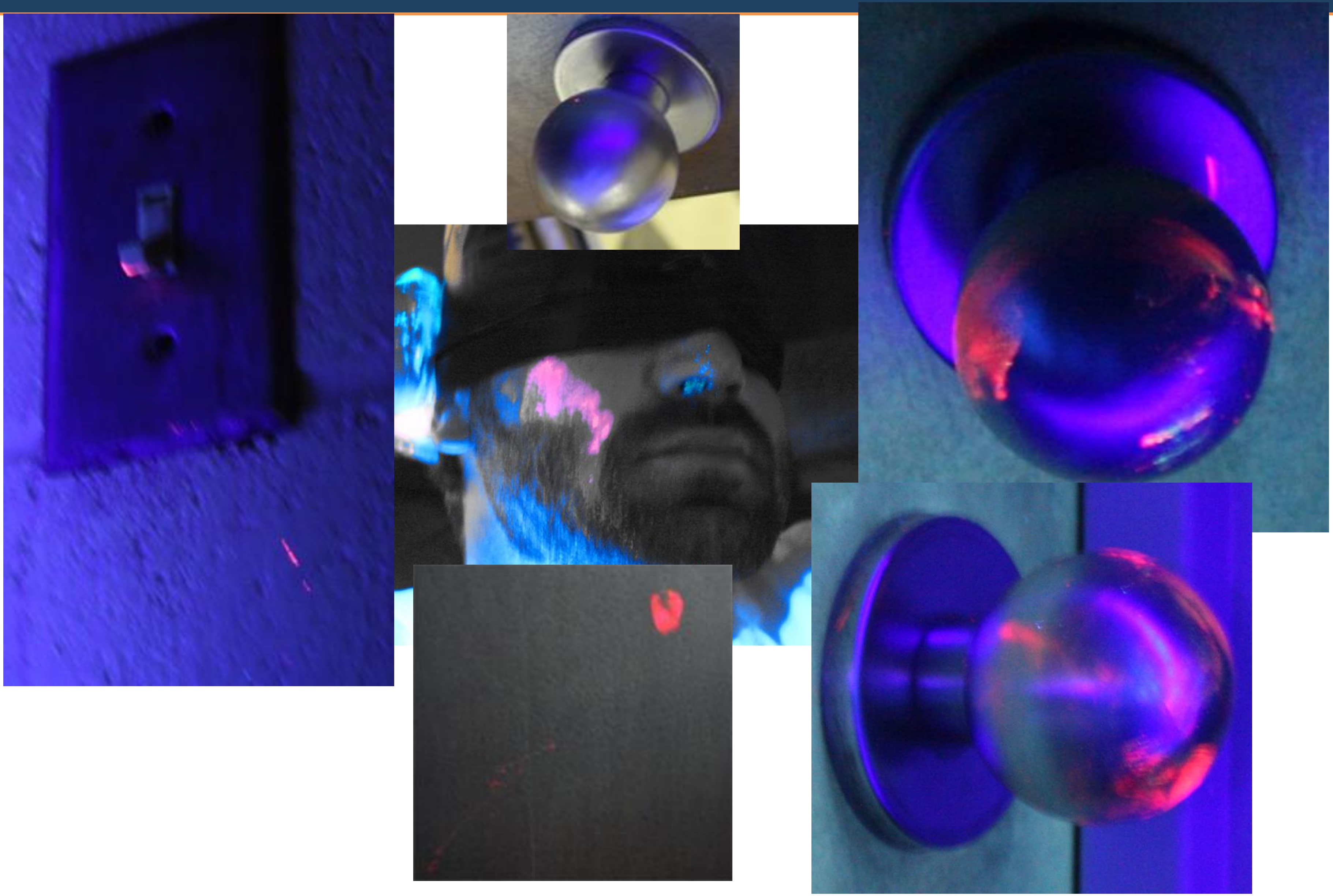
Volunteers put together "pipe bombs" with fluorescent dye filler

Fingerprints were on the device

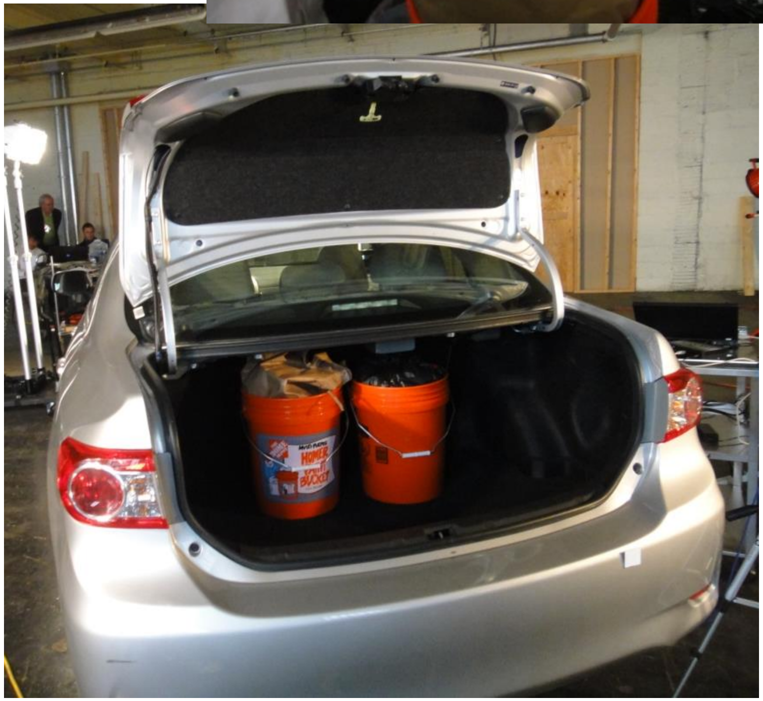
Residue was on bench & floor

Attempts to clean up mess generally scattered more residue

Residue was found wherever hands touch



Chemical A (50 lb) was ground, loaded in a vehicle, & driven a short distance. This was repeated on two consecutive days.

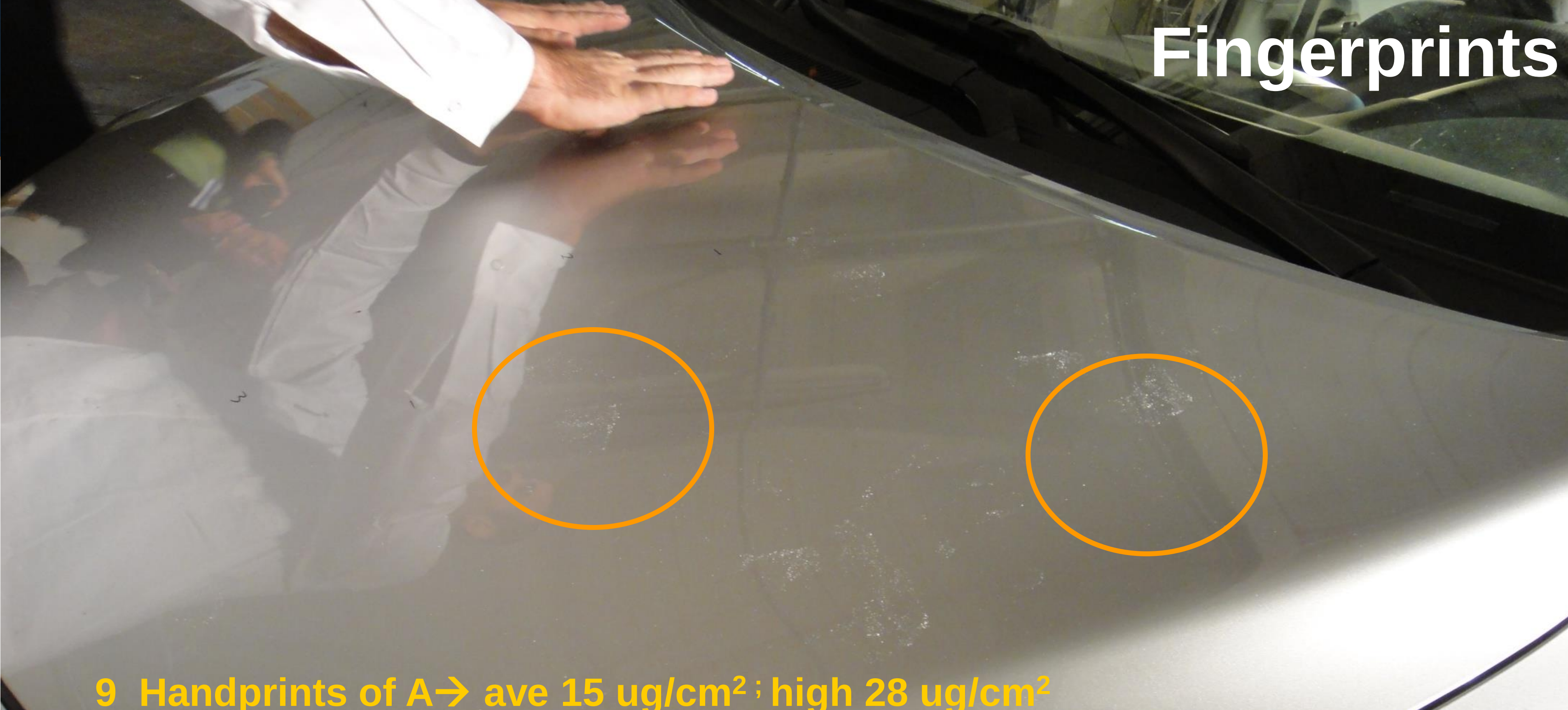


Residue was where hands touched

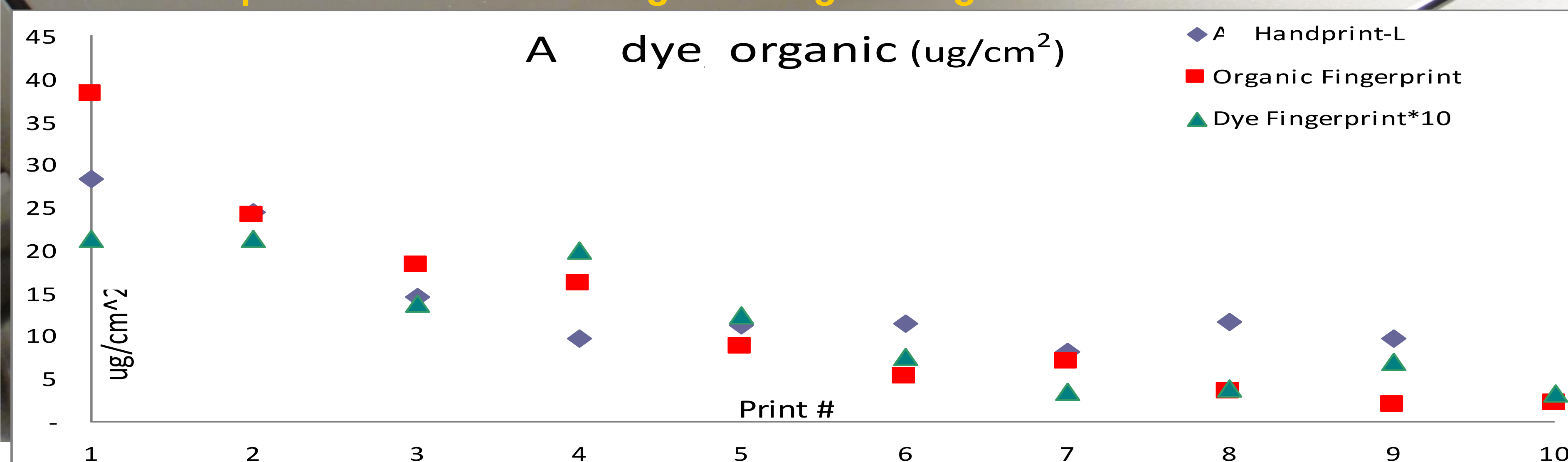
	Day 1		Day 2	
	area cm^2	**A ug/cm^2**	area cm^2	**A ug/cm^2**
INTERIOR				
gear shift	9	**355**	9	**4848**
steering wheel	1218	**5.5**	1218	**80**
door frame driver	6	**0.87**	2	**358**
door handle driver	45	**11**	45	**112**
door handle passenger	45	**49**	45	**162**
EXTERIOR				
door handle driver	10	**15**	23	**90**
door handle passenger	8	**0.13**	2	**458**
truck by plate, right	70	**0.48**	85	**78**
truck by plate, right	70	**7.9**	35	**35**
CAR BLANK	98	**0.024**	16	**0.064**

Typical amount chemical A
0.1 to 0.4 mg/cm^2 on interior
30-90 ug/cm^2 on exterior

Fingerprints



9 Handprints of A→ ave 15 ug/cm^2 ; high 28 ug/cm^2



Lessons Learned

- Plasticized "explosive" left cleaner assembly area but adhered to hands longer than powdered material.

- Contamination of handlers' clothes was minor; < 20% of time was contamination found.

- Dye on clothing was usually on right, front side where hands touch, e.g. pocket

- Amount dye ranged from 10^{-1} to 10^{2} ug/cm,^{2}
  mode: 2 to 4 ug/cm^{2} & median: 4.7 ug/cm.^{2}
  68% of samples < 16 µg/cm^{2}.

- Size residue spot: 0.15 to 268 cm^{2} 70% samples < 3 cm^{2}

Explosive Residue on Hair

Explosives easily adhere to hair within minutes of exposure.

Even those just observing others handling explosives were contaminated.

Particle of explosive on hair observed under magnification

Generally, explosives contaminate hair by particle transfer, not by their vapor (which is minor).

Explosives in cut hair persist for days despite washing.

Persistence: % explosive remaining on hair after standing 5 days or 2 washing

	TATP	EGDN	TNT	PETN
hair standing	20%	20%	100%	not done
hair washed	70%	30%	50%	3%

Sampling Hair on Heads of Explosive Handlers & Suspects

Hair of those working with explosive was combed. Even Monday AM, explosive residue was found in hair of some. At end of week, despite evening showers, all were contaminated. Example is shown for tests at AP Hill (2003)

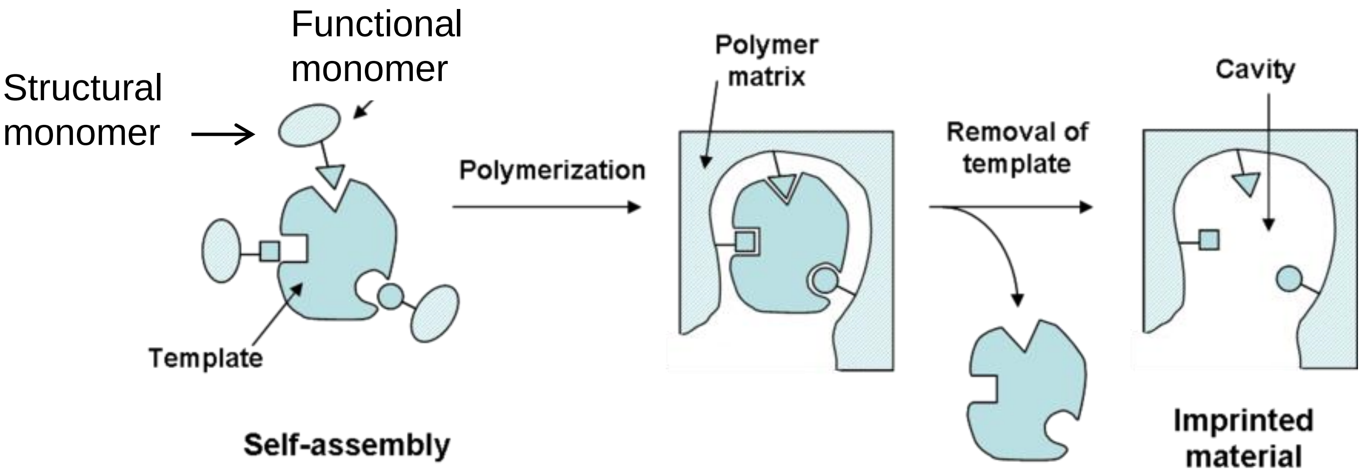
% of people (30) with detectable amounts of indicated explosive combed from hair

	Monday		Tuesday		Wednesday		Thursday	
	Start day	End day	Start day	End day	Start day	End day	Start day	End day
PETN	3%	67%	26%	75%	0%	90%	60%	100%
RDX	3%	17%	4%	40%	6%	20%	0%	54%

In 2009 ~600 combs were sent to theater & used on suspects. About 1/3 showed TNT, RDX, or PETN residue, but no immediate feedback was available to the warfighter.

Future studies will seek for in-field analysis to provide immediate results.

Molecularly Imprinted Polymers (MIP)-Selective for Explosives



http://en.wikipedia.org/wiki/Molecularly_imprinted_polymer

Can this "selectivity" be exploited to collect explosives?

The variables

a backbone -- the structural monomer

a binding site – the functional monomer

a template

a polymerizing agent & method

the ratio of structural and functional monomers & their ratio to the template

MIP Results

MIP mg TNT	Control Polymer mg TNT	TNT uptake over control	Functional Monomer	Structural Monomer	Ratio TNT: F:S
2.3	1.8	128%	PTMS	TriEOS	1:4:20
7.1	6.0	118%	PTMS	TEOS	1:8:36
7.7	8	96%	PTMS	TEOS	1:8:18
4.9	3.7	132%	PTMS	TEOS	1:4:27
4.9	3.7	134%	PTMS	TEOS	1:10:50
6.7	2.9	231%	PTMS	TEOS	1:8:40
2	2	100%	TMOTFS	TEOS	1:4:20
5.7	4.8	119%	TEOTES	TEOS	1:4:20

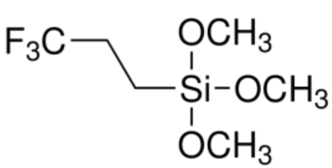
Functional PTMS= phenyltrimethoxysilane

TEOS= tetraethoxysilane

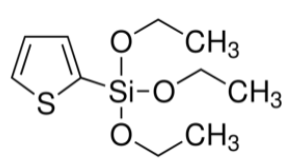
TMOTFS= trimethoxytrifluoropropyl silane

TriEOS =methyltriethoxysilane

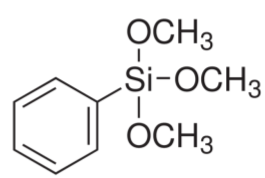
TEOTES= Triethoxy-2-thenylsilane



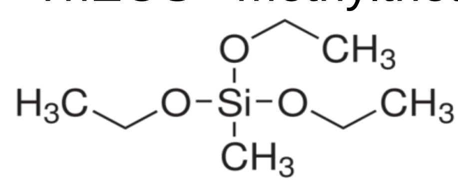
TMOTFS



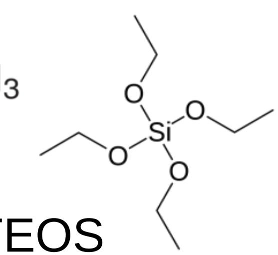
TEOTES



PTMS

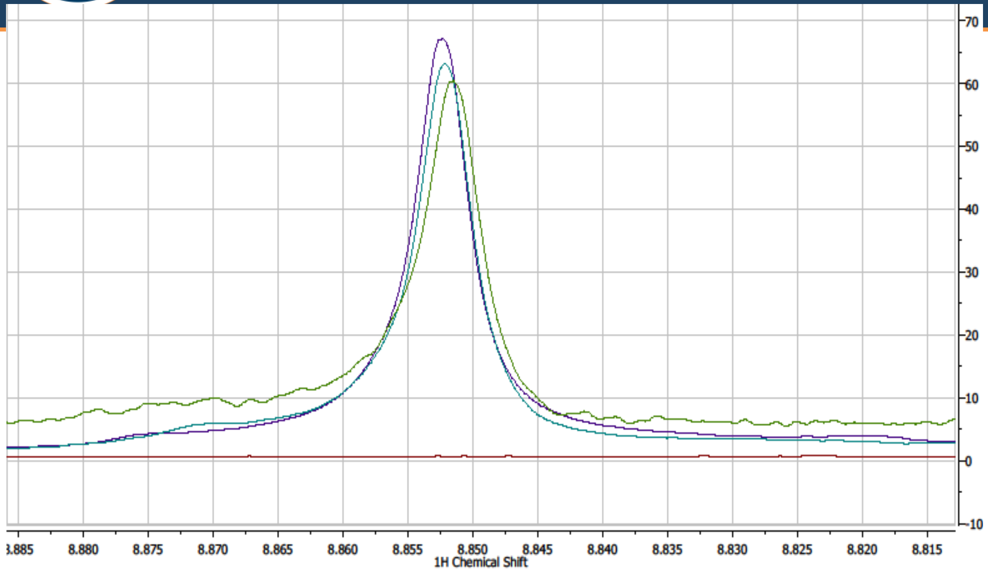


TriEOS

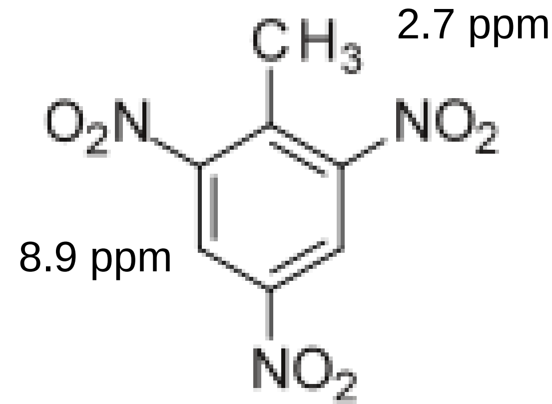


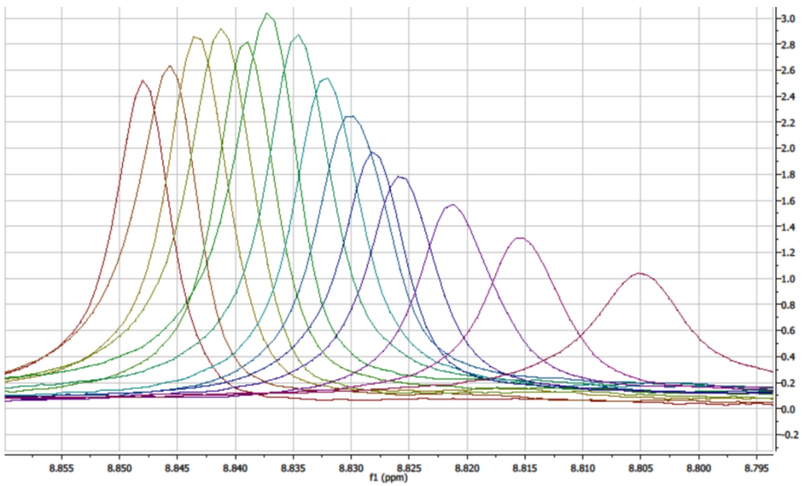
TEOS

Analysis Metric-NMR Titration TNT & Methacrylic Acid

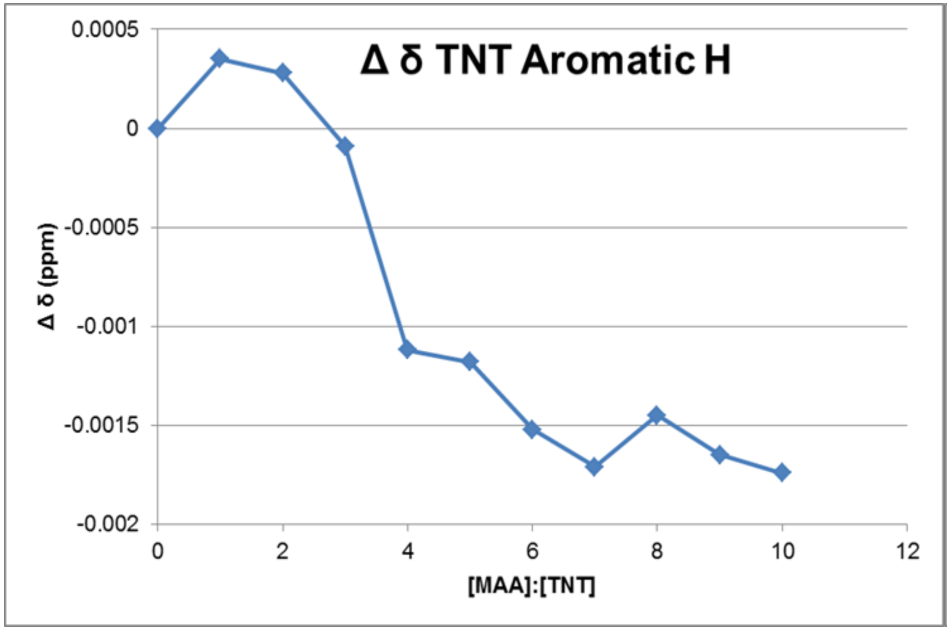


Chemical Shift of Aromatic Protons on TNT. **Red – no TNT**, **Green – 1:10 TNT:MAA**, **Blue – 7:10 TNT:MAA**, **Purple – 1:1 TNT:MAA**

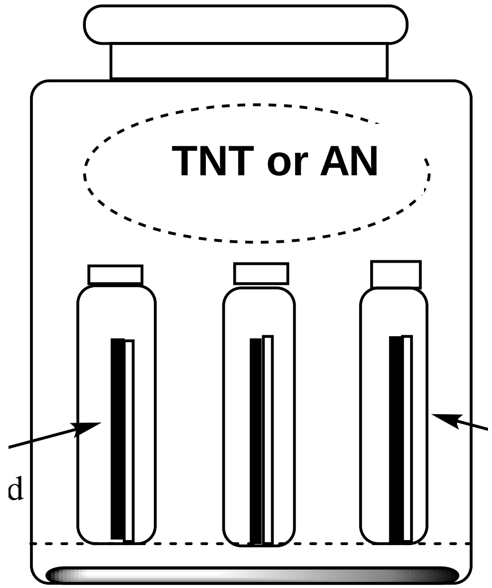




Aromatic TNT with addition of **PTMS**



Testing Method
Static Vapor Jars TNT or AN



5 uncoated & 7 coated samples Al foil or cardboard were stored with 500 mg TNT or AN at 60°C & then extracted-- TNT by 10 mL ACN & analyzed by GC/µECD or AN 5 mL DI water & analyzed by IC/ECD

Substance/Matrix	Target Explosive	Test Time	Average (µg/mL)
Polymer Powder in 1 L Container			
Empty 50mL Vial	TNT	3 days	0.139
PMAA (polymethacrylic acid)	TNT	3 days	0.179
Graphite	TNT	3 days	0.287
PS2DVB (polystyrene 2%Divinylbenzene)	TNT	3 days	0.328
Sand (SiO2)	TNT	3 days	0.343
Polypyrrole	TNT	3 days	0.389
PTMS (polyphenyl(trimethoxy)silane)	TNT	3 days	0.412
Tenax	TNT	3 days	0.477
Polyaniline (sulfate salt)	TNT	3 days	0.499
Polymer Coating on Cardboard in 1L/200 mL Container			
Polyaniline sulfate salt PVA (1g/1g)	TNT	1 hour	1.1
Uncoated Cardboard 1.5X1.5cm	TNT	1 hour	0.284
Polyaniline sulfate salt/Graphite (1g/2g)	AN	2 days	4.45
Uncoated Cardboard 3X3cm	AN	2 days	0.401

Polymer/Swab Evaluation by Pickup & Release

Sorption of TNT vapor
(60 min, 60C)(ng/mg matrix)

Substrate Type	**Average TNT/Polymer (ng/mg)**
Teflon	0.90
FLIR Nomex	0.90
1 PVA: 1 PANI Al Foil	0.97
1 PVA : 1 PANi	1.5
Uncoat SSW	2.7
2.5g PVA/2.5g PANi (CB)	3.9
2.5g PVA/ 2.5g graphite (CB)	4.5
2.5g graphite/ 0.5g PAA/ 2.0g PVA (CB)	4.8
Beta-Cyclodextrin	5.4
Cardboard (CB)	5.9
Polystyrene	5.9
Montmorillonite	6.6
Bentonite	7.1
Alpha-Cyclodextrin	7.3
Graphite	8.8
Tenax	10.3

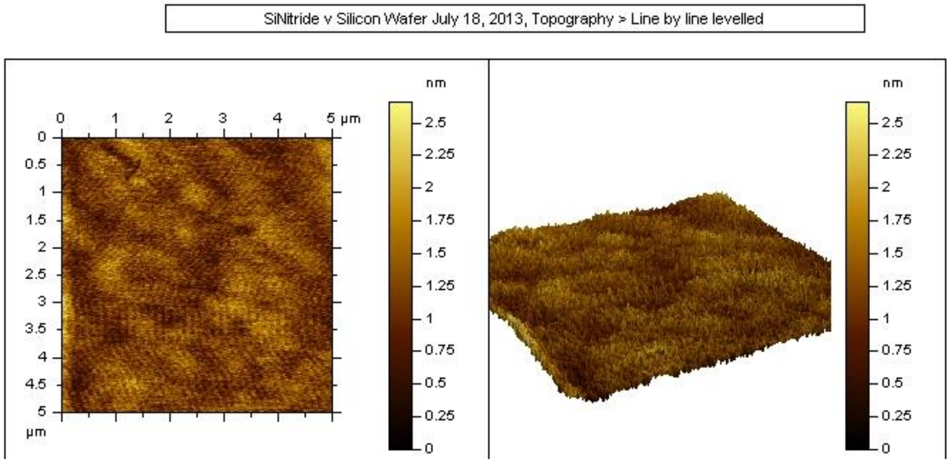
Sorption of vapor TNT is judged by exhaustive extraction by solvent.

Release is from a heated vial into GC.

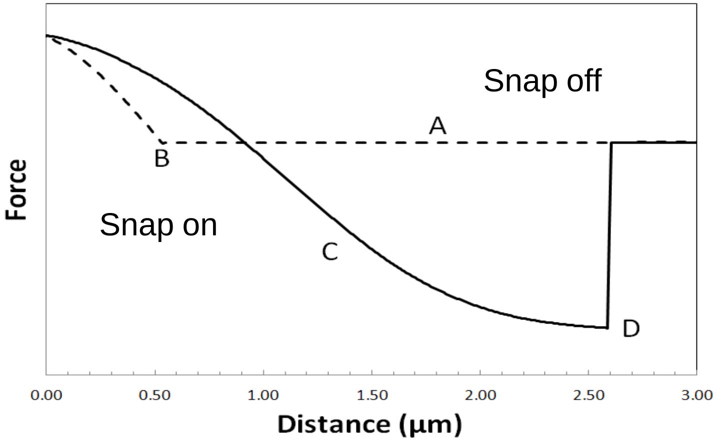
TNT vapor 60ºC, 60 min sorption & **release**

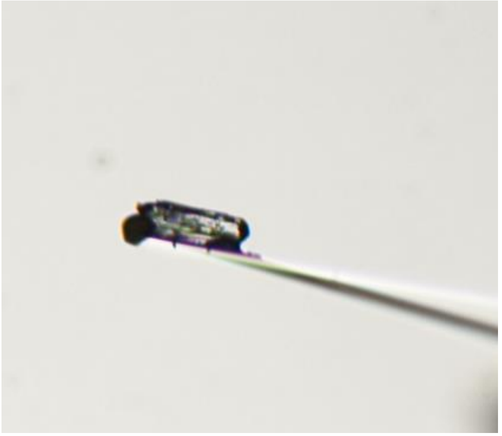
Polymer	Solution TNT/Polymer (ng/mg)	Headspace TNT/Polymer (ng/mg)	% TNT released
Tenax	16.4	0.16	1%
"	13.3	0.13	1%
"	14.9	0.20	1%
"	10.8	0.12	1%
"	10.9	0.08	1%
"	9.27	0.13	1%
"	8.76	0.11	1%
Poly(2,6-dimethyl-1,4-phenylene oxide)	4.50	0.21	5%
"	5.76	0.18	3%
"	5.59	0.17	3%
"	4.51	0.16	4%
"	5.62	0.16	3%
"	4.93	0.13	3%
"	4.92	0.19	4%
"	2.09	0.11	5%
Polystyrene	4.64	0.36	8%
"	4.05	0.31	8%
"	5.27	0.87	16%
"	6.33	0.49	8%
"	7.88	0.68	9%
"	9.78	1.58	16%
"	5.84	0.62	11%
Nomex	2.4	1.1	47%
"	2.5	2.3	92%
"	2.0	2.04	104%
"	2.6	2.37	91%

Metric of Adhesion of Explosive to Polymer: Atomic Force Microscopy (AFM)



AFM Micrograph of Si waver imaged with SiN_3 tip



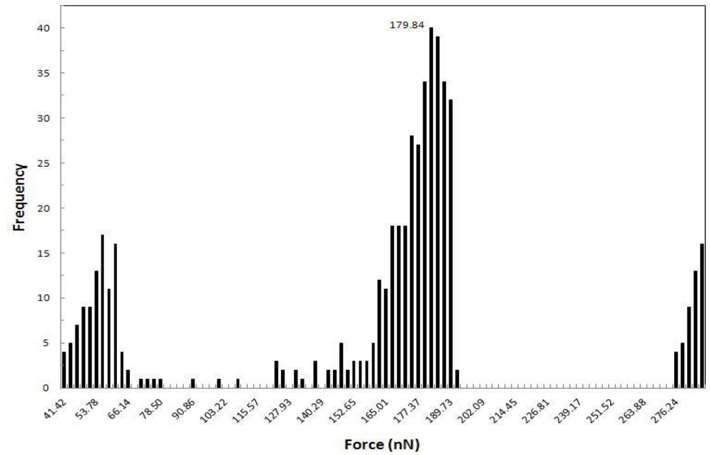


(1) 500 force curves are obtained in 3 separate static locations.

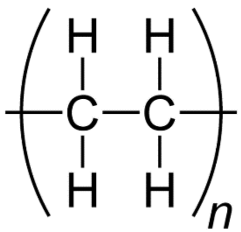
(2) 500 force curves are obtained in roaming area (25 μm^2 traveling at 1 µm/s).

Force curves deemed unusable are discarded from data set, leaving 1000 to 2000 curves.

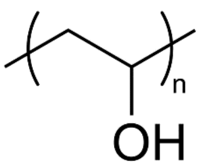
Metric for Matrix Pickup: AFM (snap-off)



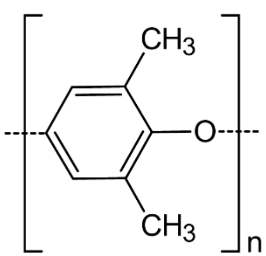
Force histogram of KClO3 v. Tenax.



Polyethylene (PE)

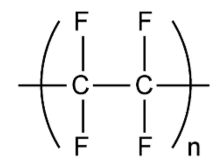


Polyvinyl alcohol (PVA)

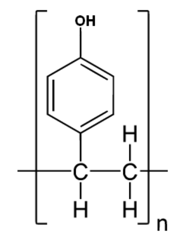


Polydimethylphenylene oxide
PMPO (PPO)

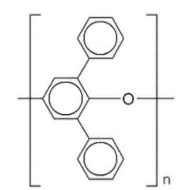
nN	TNT	PETN	RDX	HMX	KClO3
Teflon	17	N/A	N/A	61	19
PE	51	169	196	226	74
P4VP	54	133	203	188	109
PVA	256	132	270	335	179
PS	256	N/A	379	281	67
PMPO	329	160	332	256	105
Tenax	342	175	210	357	180



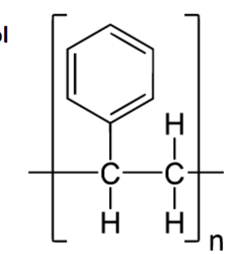
Teflon



P4VP
Poly 4-vinyl phenol



Tenax (PPPO)



Polystyrene (PS)

Better Pickup and Release

Conducting Polymers

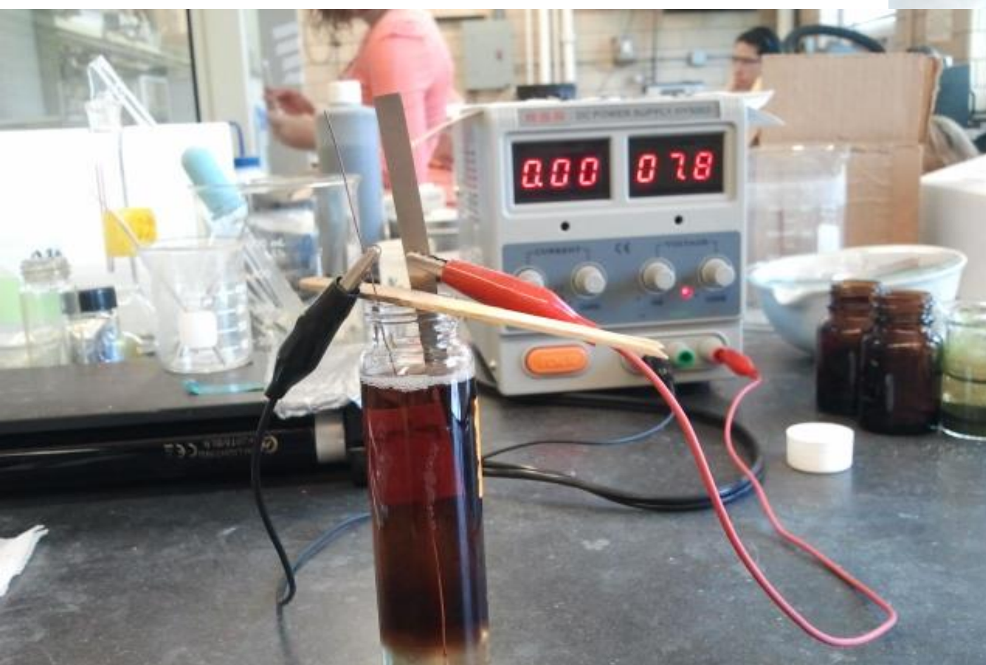
Attract (or repel) explosives with electrostatics

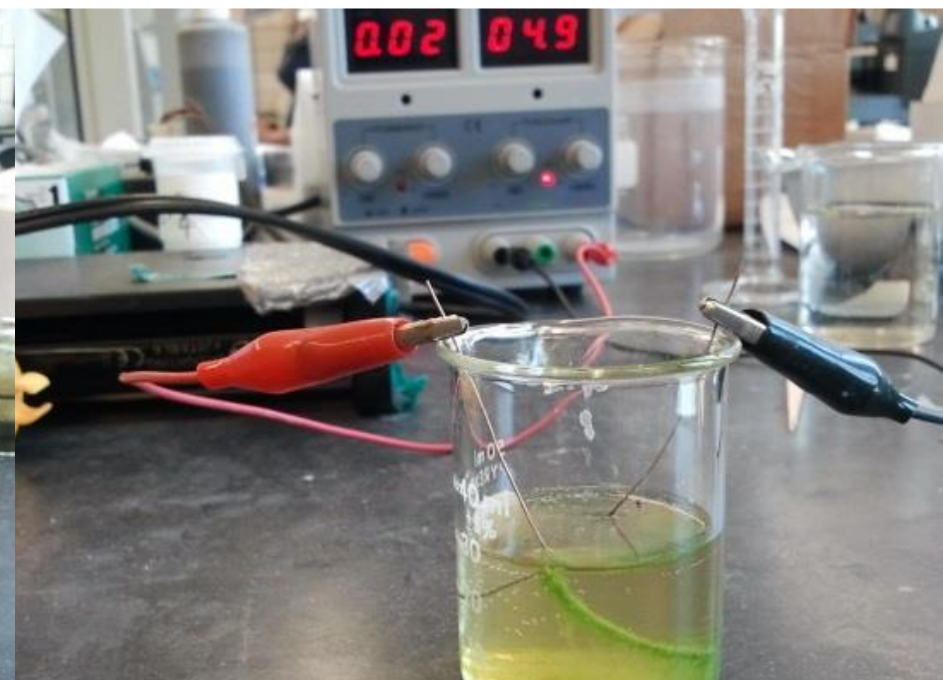
Switchable state (conducting/non-conducting) may allow easy release of explosive

NMR titration studies demonstrated aromatic compounds have affinity for TNT

Aromatics are common in conducting polymers

May allow for high sorption combined with high release efficiency





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