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Method for Detection of Chemical Attribution Signatures From Surfaces After Release of a Chemical Threat Agent

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Presentation Overview

- Definitions
- Objectives
- Technical approach
- Results
- Conclusions
- Acknowledgments

Definitions

- Chemical Attribution Signature (CAS)

  A set of features or observables that uniquely identify a chemical of interest.

- Chemical Threat Agent (CTA)

  A toxic chemical that could be used in a terrorist attack against civilians, or chemicals that could be released at toxic levels by accident or natural disaster.

- Chemical Forensics

  A means of measuring and applying the detection of CAS to enable source attribution and sample matching.

Objectives

1) Develop a method for sampling CAS from surfaces and that is applicable across a broad range of CTAs.

2) Demonstrate the efficacy and performance of the sampling method on material substrates that would likely be present at a chemical release site.

3) Contribute to the DHS Chemical Forensics Program (ChemFP) knowledgebase on counterterrorism and enhance capabilities for field investigations.

Technical Approach

- Identify CAS targets through review of open literature
- Evaluate potential collection media
- Demonstrate CAS recovery, detection, and stability on selected media
- Determine chemical uptake from sampled substrates
- Test sampling method under simulated field conditions

CTA/CAS Selection Process

- ✓ Potential CTA/CAS identified from review of open literature
- ✓ SME review to evaluate:
  - o Signature value
  - o Likelihood of environmental persistence
- ✓ Availability of standard reference materials to conduct study
- ✓ Determine if CAS are amenable to GC/MS or LC/MS analytical finishes

Result:

- o Target CTAs: 4 chemical categories ➔ 9 CTAs
- o Target CAS: 29 identified ➔ 24 included in study

CTA / CAS Targets Evaluated

CTA class	CTA	Chemical attribution signature	Abbrev.	Significance
Nerve agent	VX	Ethyl methylphosphonic acid	EMPA	Degradation product
		N,N-diisopropylaminoethanol	DIPAE	Synthetic pathway
	GA	Diethyl ethylphosphonate	DEEP	Synthesis impurity
		Diethyl phosphonate	DEP	Degradation product
		Diethyl *N,N*-dimethylphosphoramidate	DMAPA	Synthesis impurity
		O-Ethyl *N,N*-tetramethylphosphordiamidate	ETMPA	Synthesis impurity
	GB	Diisopropyl methylphosphonate	DIMP	Synthetic pathway
		Dimethyl methylphosphonate	DMMP	Synthetic pathway
		Methylphosphonic acid	MPA	Synthesis byproduct
		Isopropyl methyl methylphosphonate	IMMP	Synthetic pathway
		Isopropyl methylphosphonic acid	IMPA	Degradation product
		Malathion	MAL	Analytical surrogate

Summary:

- Three nerve agents
- Ten CAS
- One simulant (Malathion) for quality control (QC) use

CTA / CAS Targets Evaluated

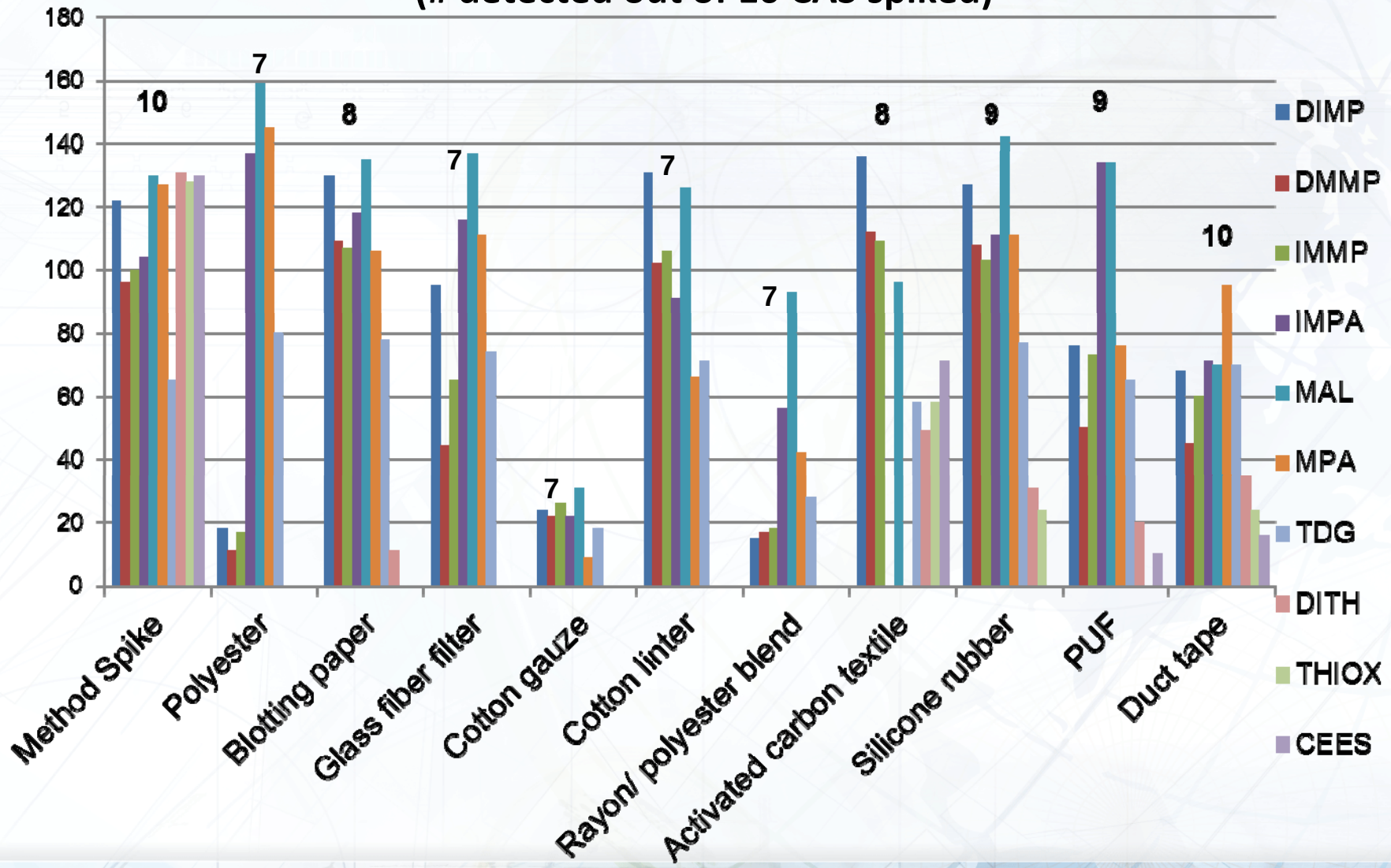
CTA class	CTA	Chemical attribution signature	Abbrev.	Significance
Blister agent	HD	1,4-Dithiane	DITH	Synthetic pathway
		1,4-Thioxane	THIOX	Synthetic pathway
		Thiodiglycol	TDG	Synthesis pathway
		2-Chloroethyl ethyl sulfide	CEES	Analytical surrogate
	HN-3	Triethanolamine	TEA	Degradation product
Biotoxin	Ricin	Ricinine	RIC	Alkaloid component
TIC	Dichlorvos	Dichlorvos	DDVP	Parent compound
		Dimethyl phosphate	DMPOA	Degradation product
	Dichrotophos	Dichrotophos	DCP	Parent compound
		Trimethyl phosphonoacetate	TMPA	Synthesis pathway
		O,O,O-Trimethyl thiophosphate	TMTP	Synthesis impurity
		N,N-Dimethylacetoacetamide	DMAA	Degradation product

Summary:

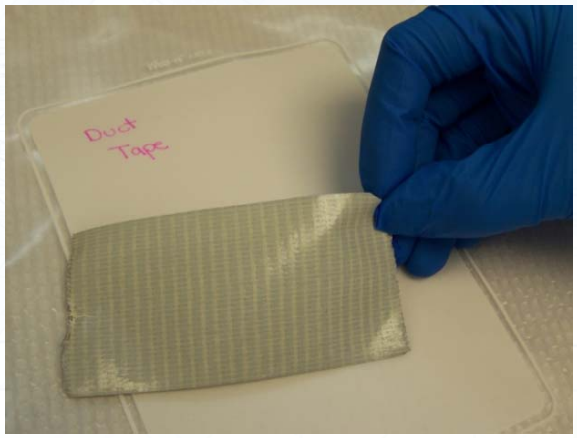
- Two blister agents
- One simulant for HD (CEES or “half mustard”)
- One biotoxin (Ricin)
- Two toxic industrial chemicals (TICs)
- Two TIC parent compounds (pesticides)

Initial Evaluation of Potential Sample Collection Media

(# detected out of 10 CAS spiked)



Collection Media Selected for Testing



Adhesive "lift" tape

- ✓ 10 of 10 targets recovered
- ✓ No pre-treatment needed
- ✓ Commercial off-the-shelf (COTS) product

Silicone rubber

- ✓ 9 of 10 targets recovered
- ✓ Used for CWA contact hazard studies
- ✓ Available in different thicknesses (COTS product)
- ✓ Pre-treatment needed (water-rinse and thermal desorption)

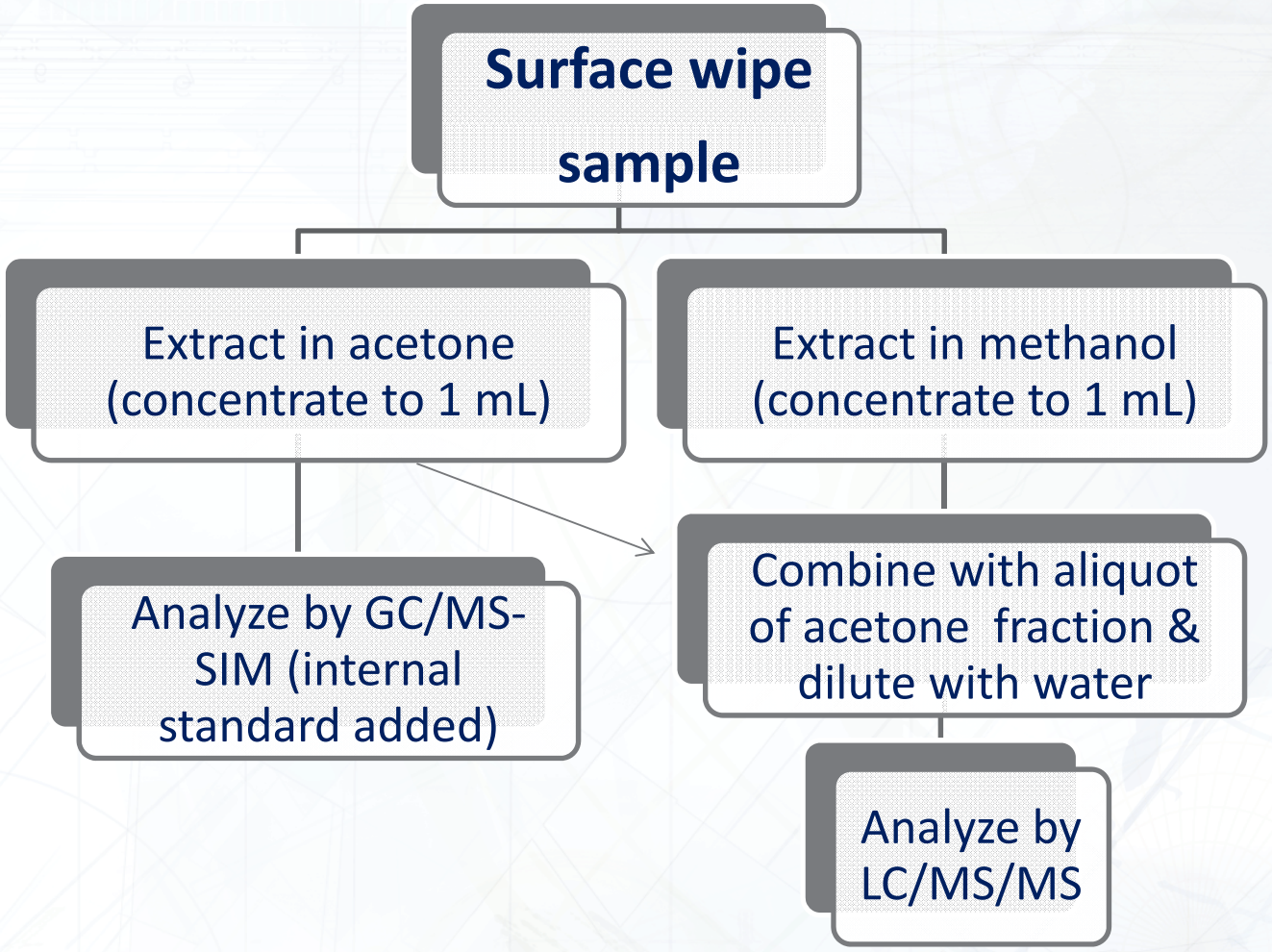
Cellulose blotting paper

- ✓ 8 of 10 targets recovered
- ✓ High quality COTS product (Whatman 3MM Chr) used for electrophoresis & protein blotting
- ✓ No pre-treatment needed
- ✓ Can be "pre-wetted" with solvent to enhance chemical uptake

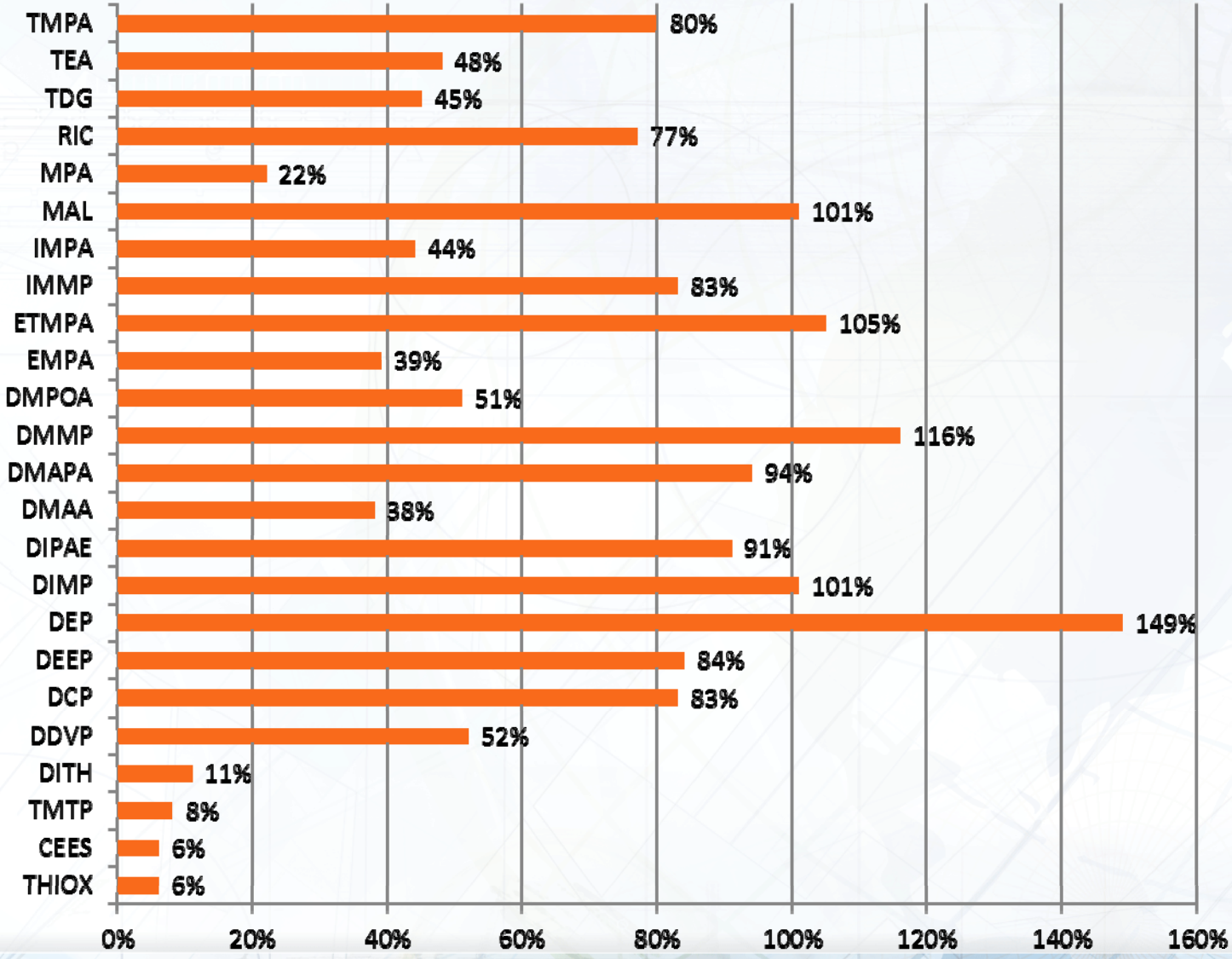
Collection Technique

- Identify target surface area
  - Include dust and residue in sample collection
  - Use template for spatial distribution (i.e., mass / area)
- Collect sample
  - Blotting paper: wipe surface with pre-wetted swatch
  - Silicone and tape: 15 min contact with surface
- Place sample in glass container & store at 6^{o}C
- Extract & analyze

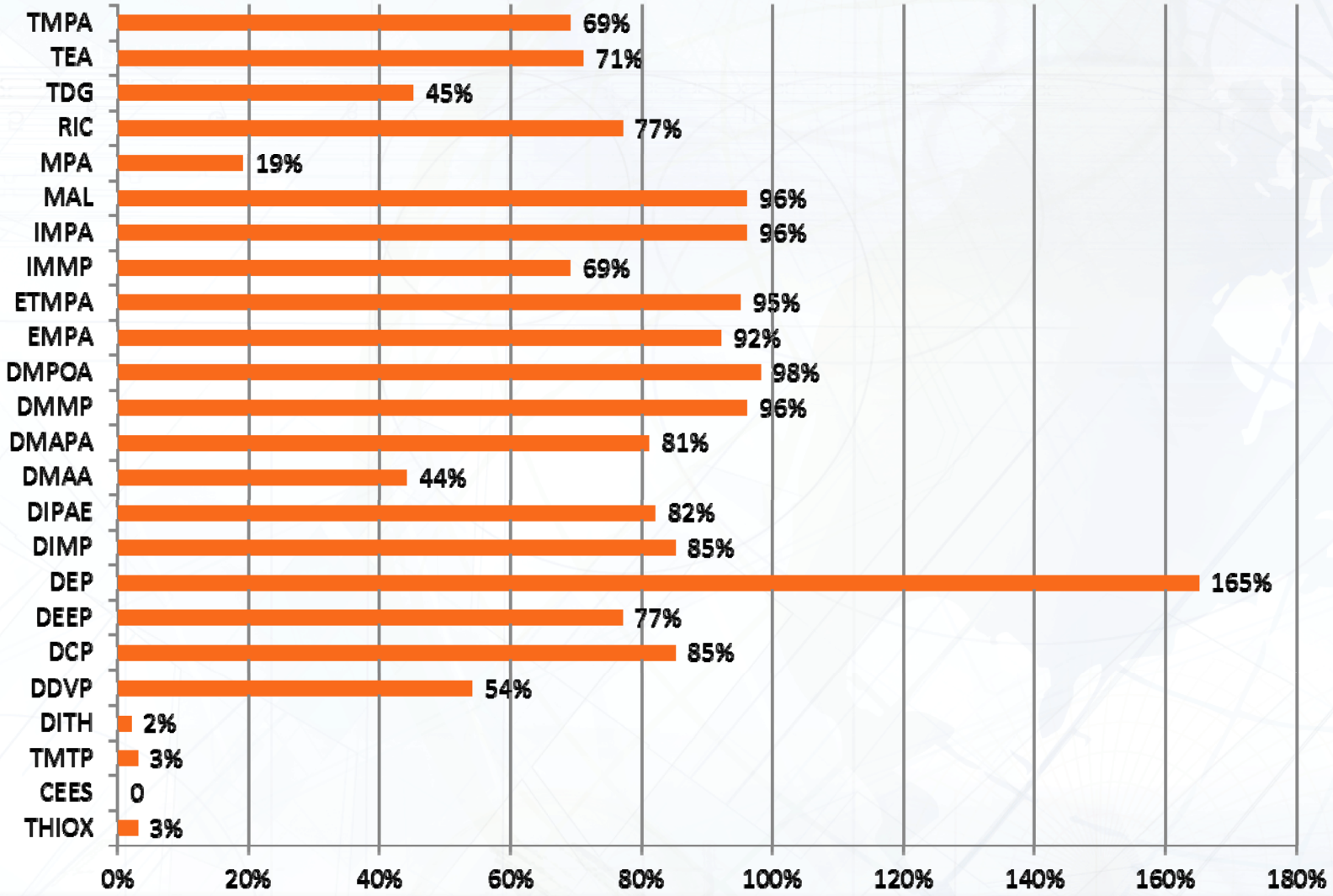
SAMPLE PREPARATION & ANALYSIS



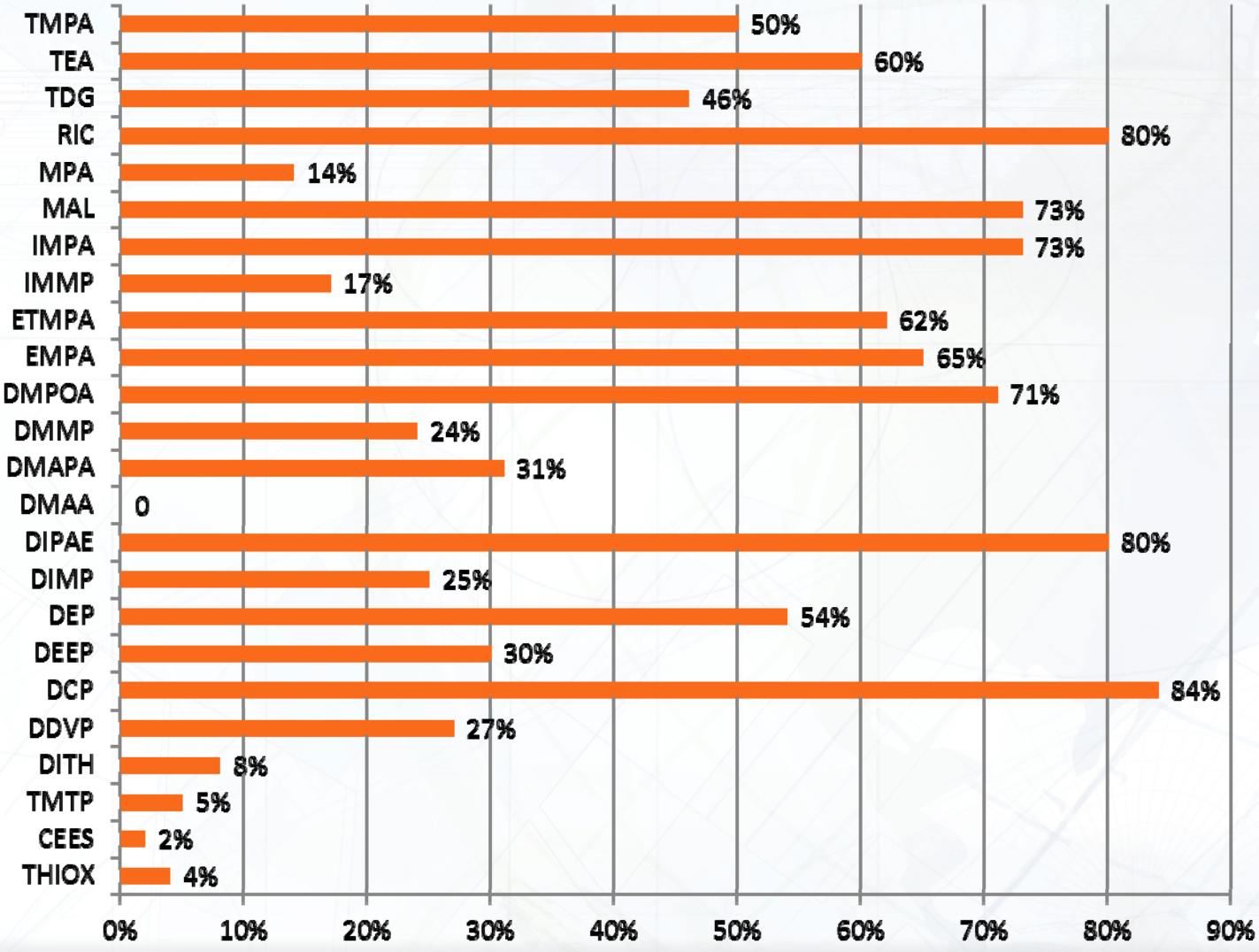
CAS Recovery from Silicone (direct spike)



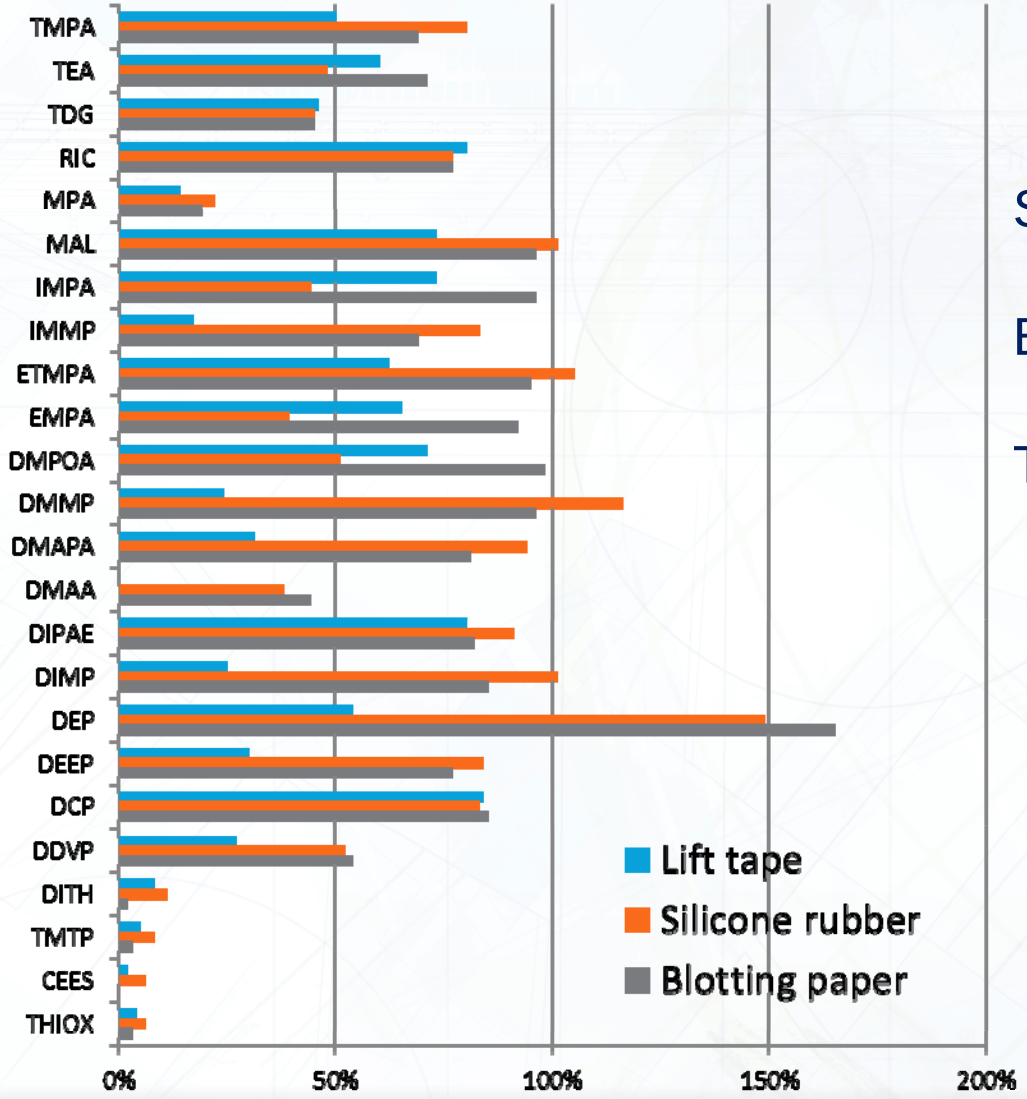
CAS Recovery from Blotting Paper (direct spike)



CAS Recovery from Tape (direct spike)



CAS Recovery Comparisons (direct spike)



Silicone: 24/24 detected

Blotting paper: 23/24 detected

Tape: 23/24 detected

Method Detection Limits (MDL)

(average MDLs across three collection media)

Determined using:

- Seven (7) spiked media at ~ 10 times the instrument detection limit (IDL)
- Samples prepared over several days
- MDL calculated using student's t value (99% confidence level) and std. dev. estimate with n-1 degrees of freedom (per EPA guidelines)

Significance:

- Minimum concentration that the chemical can be measured and reported with 99% confidence that concentration is greater than zero
- Results reported as mass/sample or mass/area
- Some MDLs adjusted higher due to low recovery or qualified as slightly outside EPA's criteria

CAS	Estimated Detection Limits (ng/sample or area)
EMPA	220
DIPAE	80
DEEP	890
DEP	7,800
DMAPA	13
ETMPA	27
DIMP	43
DMMP	29
MAP	1,600
IMMP	46
IMPA	190
MAL	5
DITH	10
THIOX	230
TDG	8,700
CEES	56
TEA	360
RIC	12
DDVP	1,500
DMPOA	990
DCP	11
TMPA	14
TMTP	5,200
DMAA	190

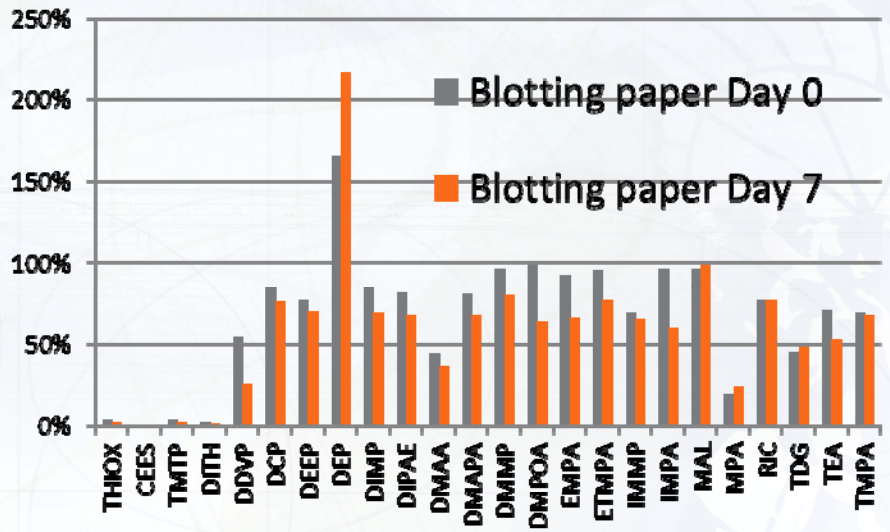
Sample Stability

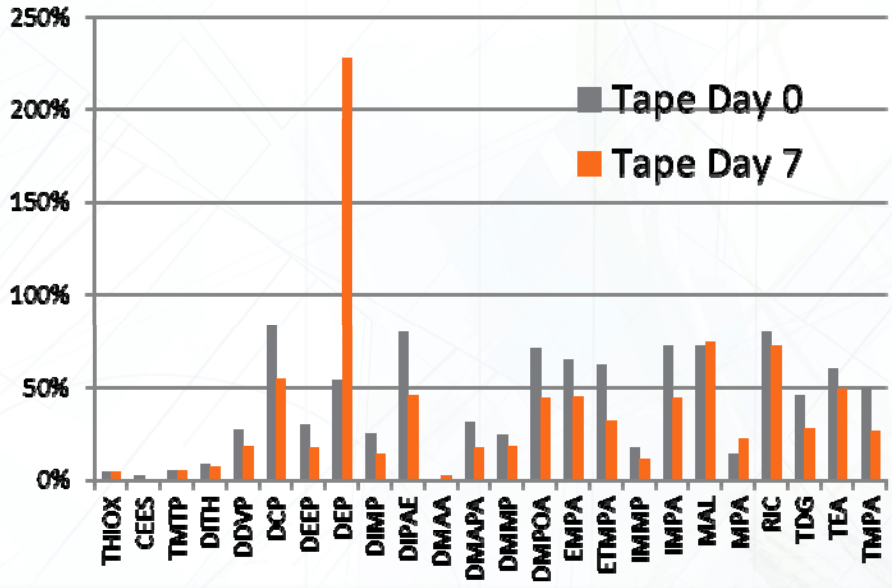
Determined from:

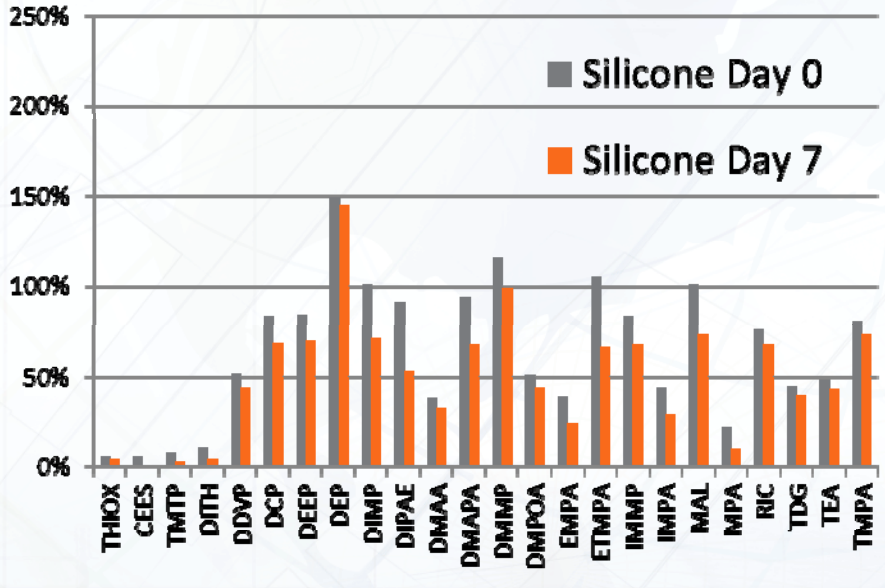
- Triplicate (3) spiked media (~ 10 times IDL)
- Storage at ambient and cold (~ 6°C) conditions
- Extracted after 1, 3, and 7 days
- Compared to “Day 0” recoveries

Results:

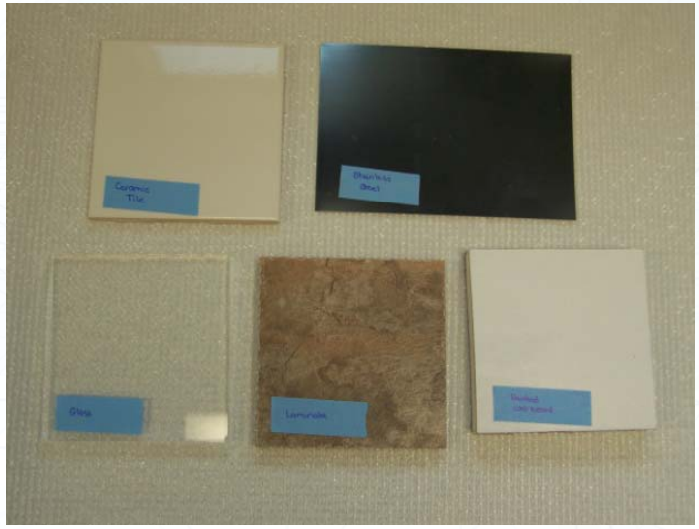
- All targets detected after 7 days for all samples
- Results for 7-day within 2 std. dev. of “Day 0” recoveries for blotting paper and silicone
- Some CAS less stable on tape samples







Chemical Uptake Experiments



Test Coupons
Ceramic tile, stainless steel,
glass, laminate, latex-painted wallboard

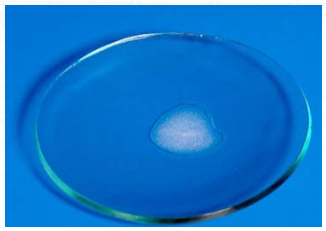
Teflon strips used to “dry transfer”
CAS onto porous substrates

Procedure:

- CAS solution deposited onto substrate surface using syringe
- Contact time of one hour (after delivery solvent evaporated)
- Triplicate wipe samples collected using each media (except for simulated field tests which were sampled once)

Materials Used for Simulated Field Sample Collection

Environmental contaminants

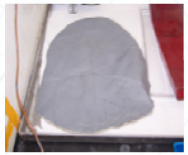


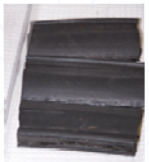
Water residue

Oil residue

Dust

Weathered materials





Leather, rubber gasket, molded plastic, painted metal, unpainted galvanized metal obtained from local auto salvage yard

Spiking procedures:

- Control coupons (glass) pre-contaminated with water residue, used motor oil, and dust
- CAS spiked onto contaminated surfaces as before – one hour dry contact time
- Dry transfer of targets using Teflon swatches for porous substrates (leather, paint, rubber gasket)
- Samples collected using three collection media

In situ surfaces

Indoor surfaces, such as: painted metal, painted wood, bench tops, painted walls

Average Recovery from Substrates (all collection media)

Chemical threat agent (CTA)		CAS	Spike level (ng)	Average recovery from substrate (%)										
				Laboratory study						Simulated field test				
				Laminate	Glass	Steel	Tile	Painted Wallboard	Teflon	Painted metal	Leather	Galvanized steel	Molded plastic	Rubber gasket
Nerve agent	VX	EMPA	190	14	30	25	24	4	13	9	19	29	30	8
		DIPAE	100	19	30	44	29	5	28	18	18	37	58	13
	GA	DEEP	2,100	1	3	6	—	2	12	3	1	2	2	2
		DEP	3,500	42	40	46	44	22	9	30	29	39	39	26
		DMAPA	30	1	2	3	1	1	7	3	—	1	1	1
		ETMPA	40	5	10	16	2	4	25	5	3	10	1	2
	GB	DIMP	100	—	2	3	1	1	20	4	1	1	1	1
		DMMP	60	4	2	4	7	2	27	4	—	—	1	1
		MAP	5,200	7	9	9	8	2	4	2	7	12	12	3
		IMMP	110	—	1	3	—	1	15	2	—	1	1	1
		IMPA	150	22	30	24	22	6	13	7	6	22	23	7
		MAL	10	32	52	40	27	10	28	9	10	38	33	8
Blister agent	HD	DITH	90	—	—	—	—	7	—	2	—	—	2	1
		THIOX	430	—	1	2	2	1	1	1	—	1	1	1
		TDG	25,000	3	8	12	3	3	13	4	4	19	16	5
		CEES	80	—	—	—	—	2	—	1	—	—	—	—
	HN-3	TEA	320	18	23	26	15	1	13	4	4	9	25	10
Biotoxin	Ricin	RIC	20	23	34	33	29	4	20	14	25	34	32	10
TIC	Dichlorvos	DDVP	1,300	22	—	17	17	9	1	1	—	—	2	1
		DMPOA	880	23	29	30	24	4	12	8	16	28	29	8
	Dichrotophos	DCP	14	25	38	39	40	5	17	10	6	29	25	7
		TMPA	40	22	31	43	13	14	38	12	10	36	26	6
		TMTP	9,600	1	—	—	1	—	—	2	—	—	2	—
		DMAA	320	1	3	3	1	—	17	1	1	1	1	—

Codes
> 10% Rec.
1-10% Rec.
— (not detected)

ChemFP Pre-Spiked Coupons

Specifications:

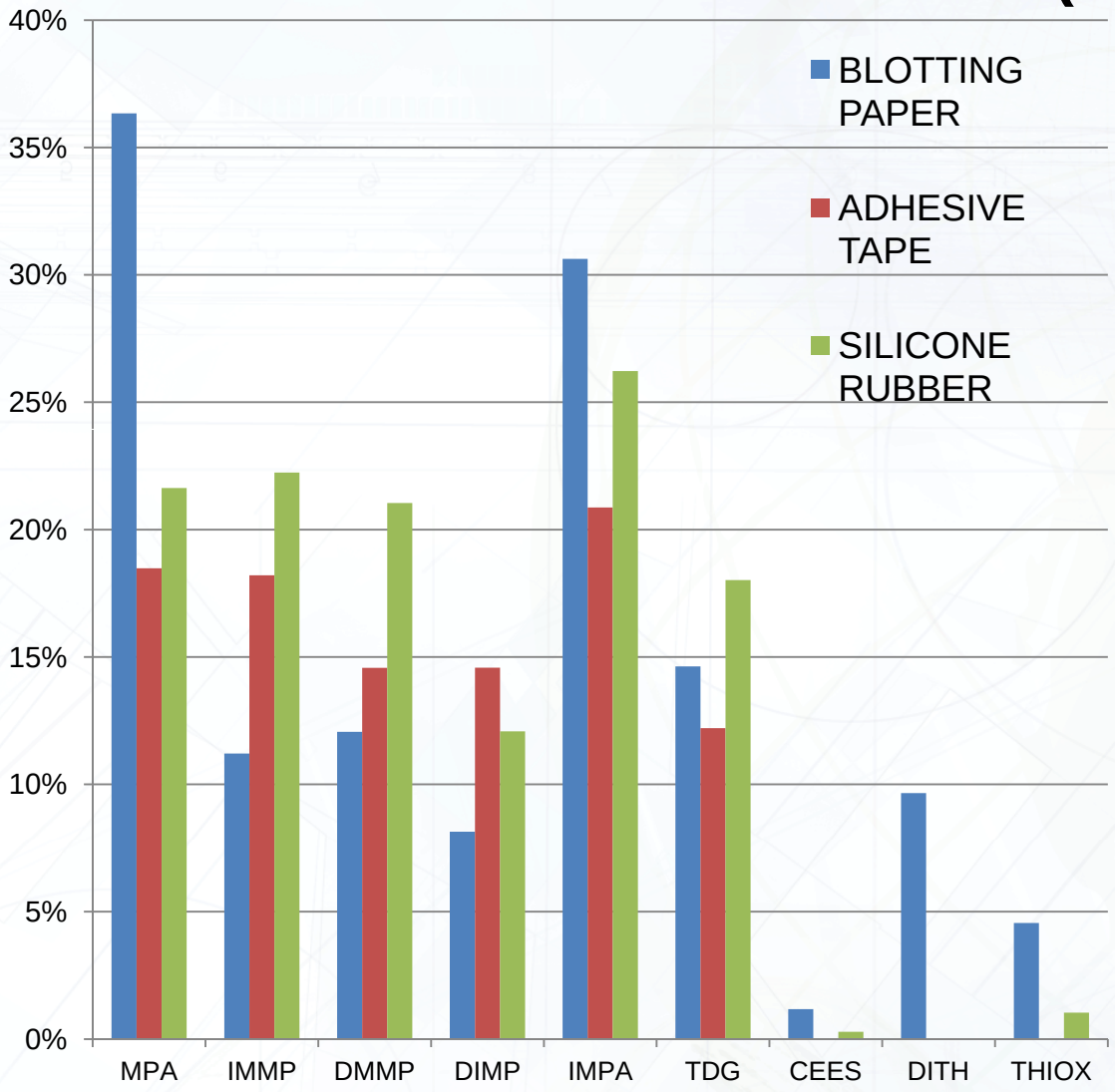
- Provided by independent ChemFP Performer
- Coupons pre-spiked with only subset of target CAS
- Four substrates tested
- Sampled with each collection media (averages listed)

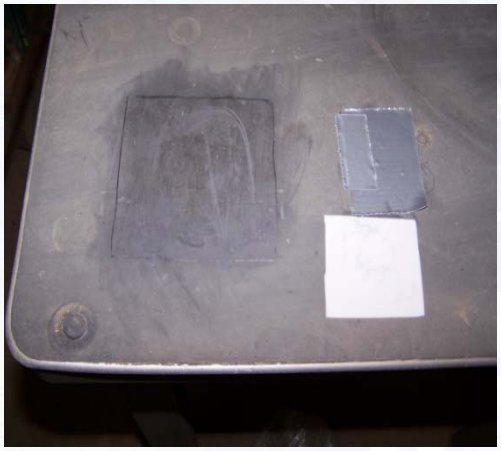
CAS	Average CAS detected (ng)				Minimum amount expected (ng) [2]			
	Concrete	Carpet	Glass	Painted drywall	Concrete	Carpet	Glass	Painted drywall
DIMP	1,800	600	35	1,600	86,000	35,000	—	30,000
DMMP	2,700	250	—	380	14,000	9,000	—	4,000
MPA	—	3,200	26,000	19,000	—	95,000	169,000	4,000
IMPA	8	75	290	160	—	61,000	67,500	15,000
TDG	—	42	4,600	2,000	4,000	35,000	—	30,000
Parathion [1]			Detected				333,000	
Nicotine [1]			Detected				285,000	

[1] Parathion and nicotine detected by full scan GC/MS on the glass sample (not quantitated-not part of target list)

[2] Minimum amount detected from extracted samples after expiration date (est. 2 weeks after preparation) as reported by provider

Earlier *In-situ* Field Tests (subset of targets)

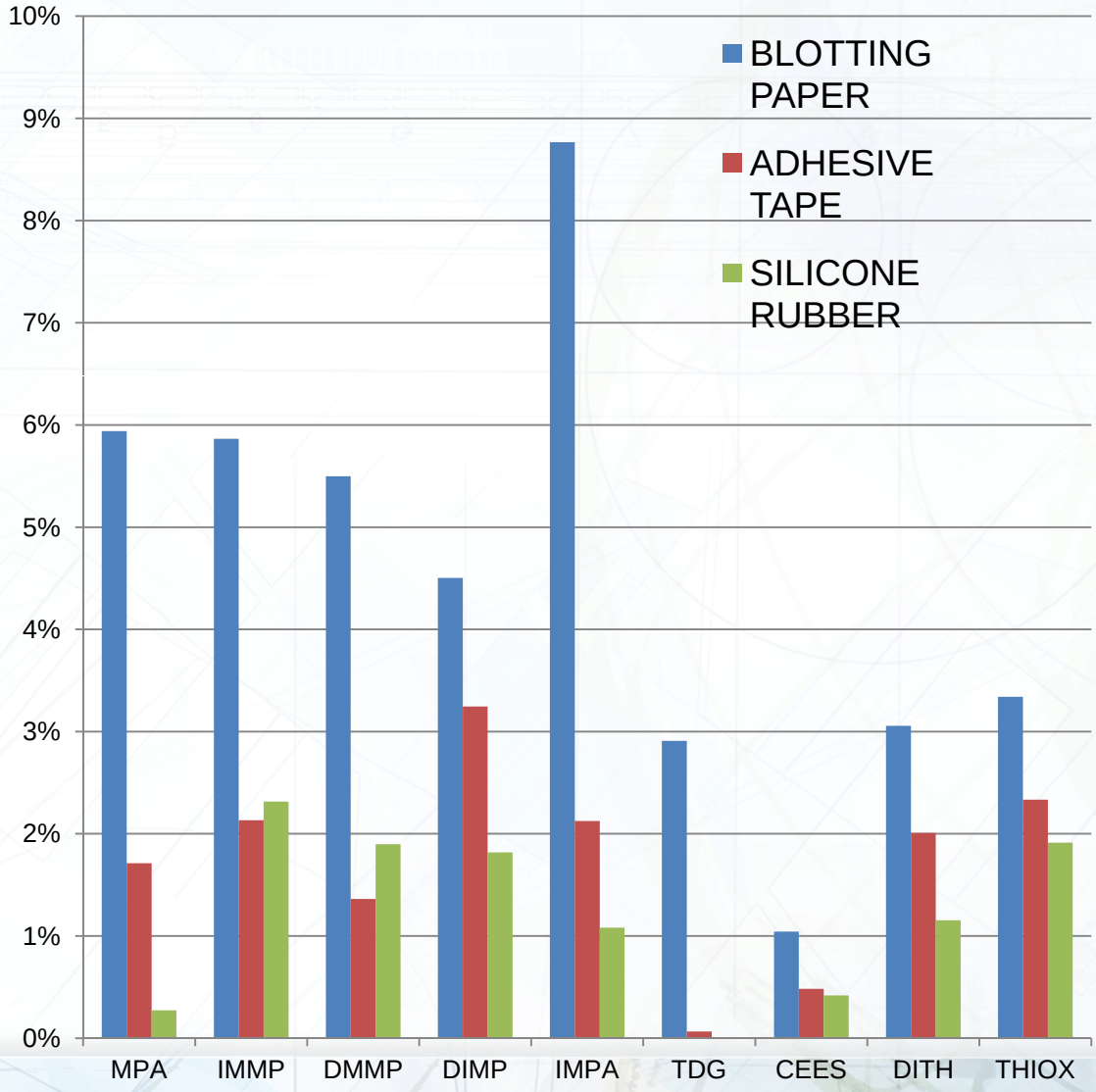


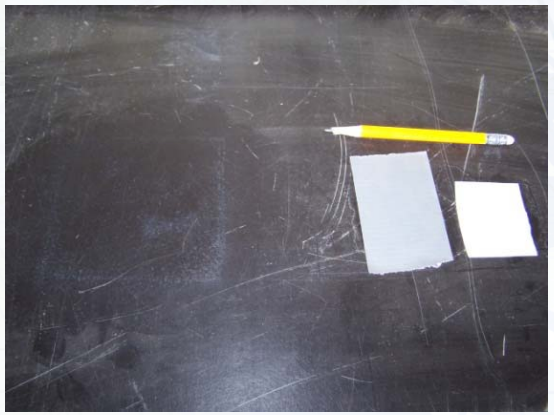


Laminate table top

Chemical	Spike level (ng)
MPA	114,000
IMMP	3,100
DMMP	180
DIMP	240
IMPA	2,100
TDG	50,000
CEES	1,400
DITH	800
THIOX	670

Earlier *In-situ* Field Tests (subset of targets)





Lab bench

Chemical	Spike level (ng)
MPA	114,000
IMMP	3,100
DMMP	180
DIMP	240
IMPA	2,100
TDG	50,000
CEES	1,400
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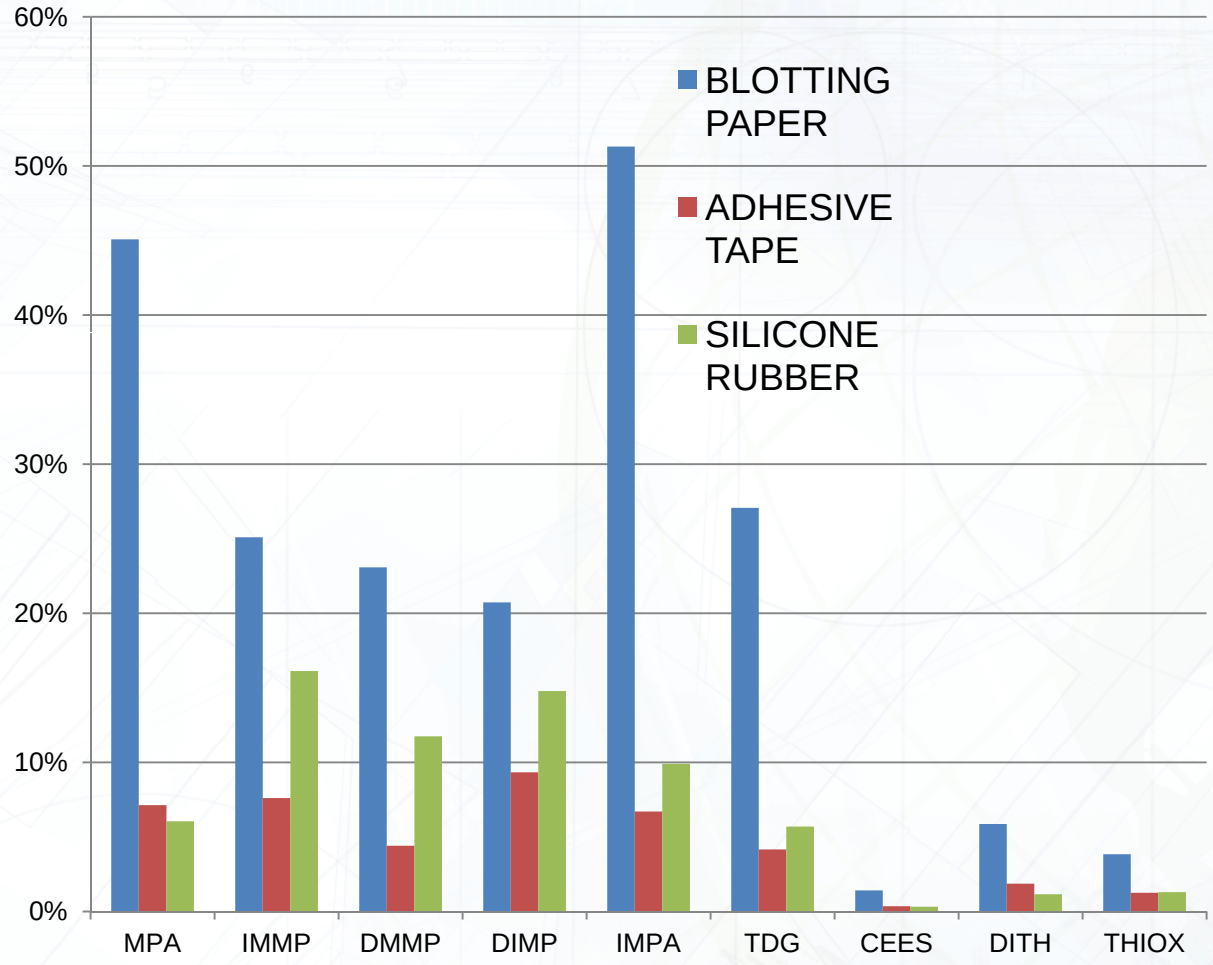

Painted metal chair

Chemical	Spike level (ng)
MPA	114,000
IMMP	3,100
DMMP	180
DIMP	240
IMPA	2,100
TDG	50,000
CEES	1,400
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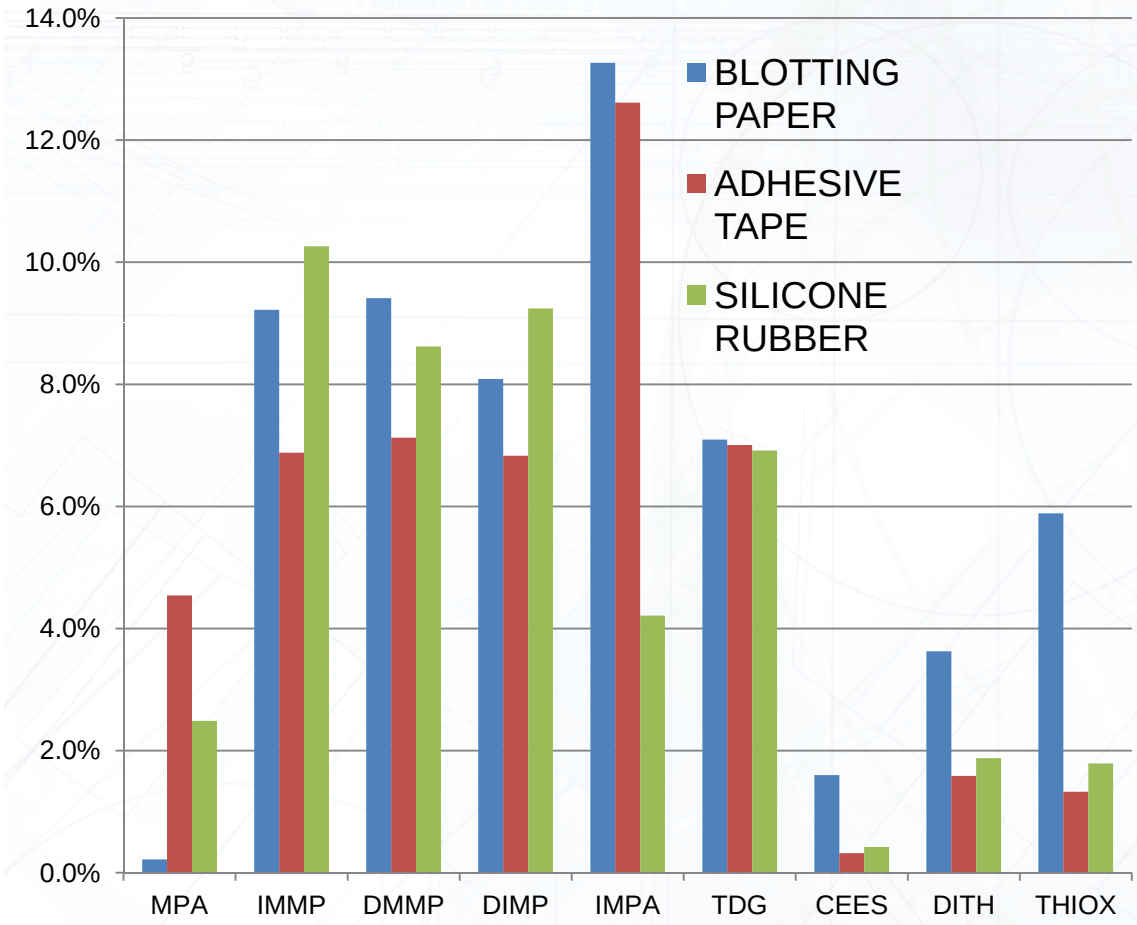
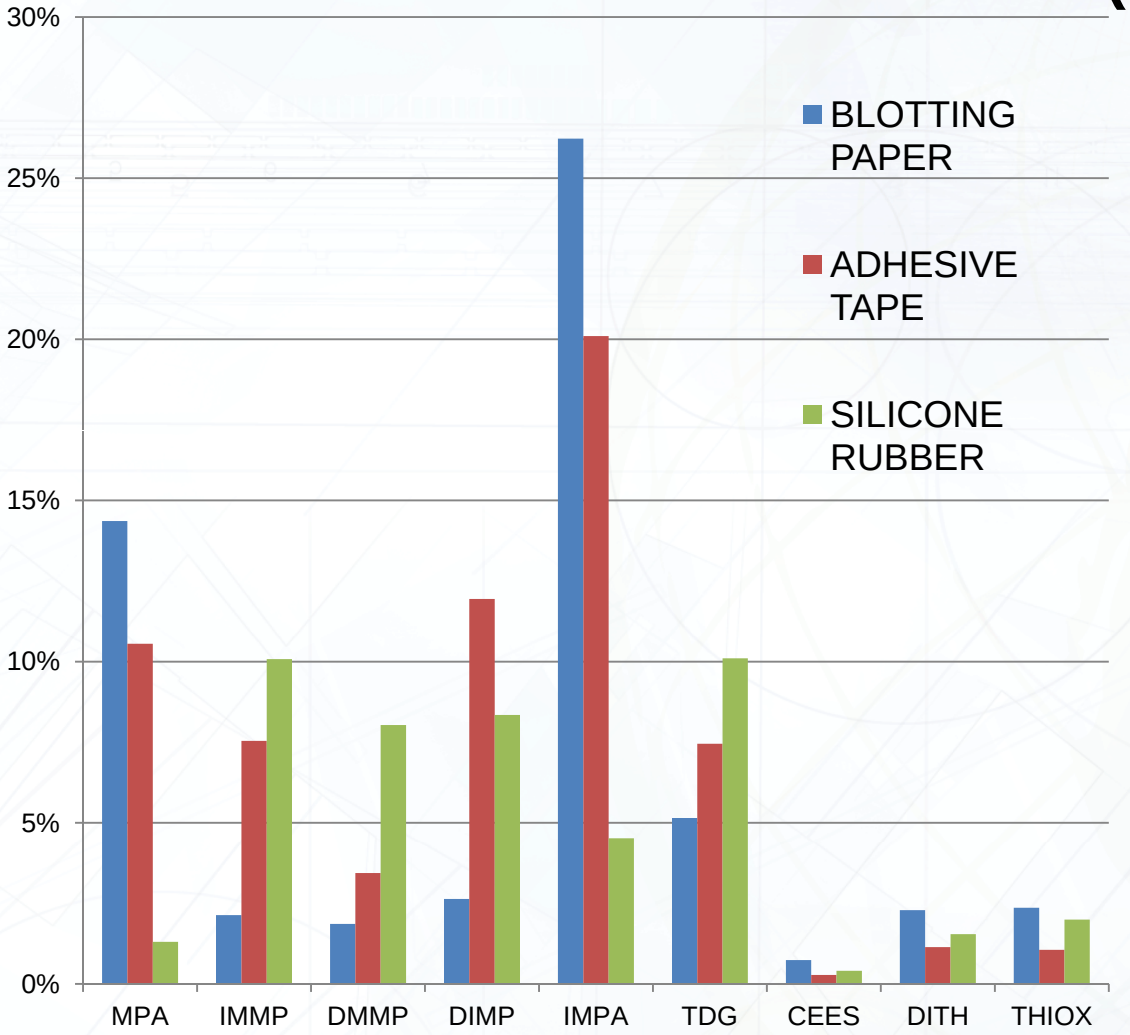


Painted metal furnace

Chemical	Spike level (ng)
MPA	114,000
IMMP	3,100
DMMP	180
DIMP	240
IMPA	2,100
TDG	50,000
CEES	1,400
DITH	800
THIOX	670

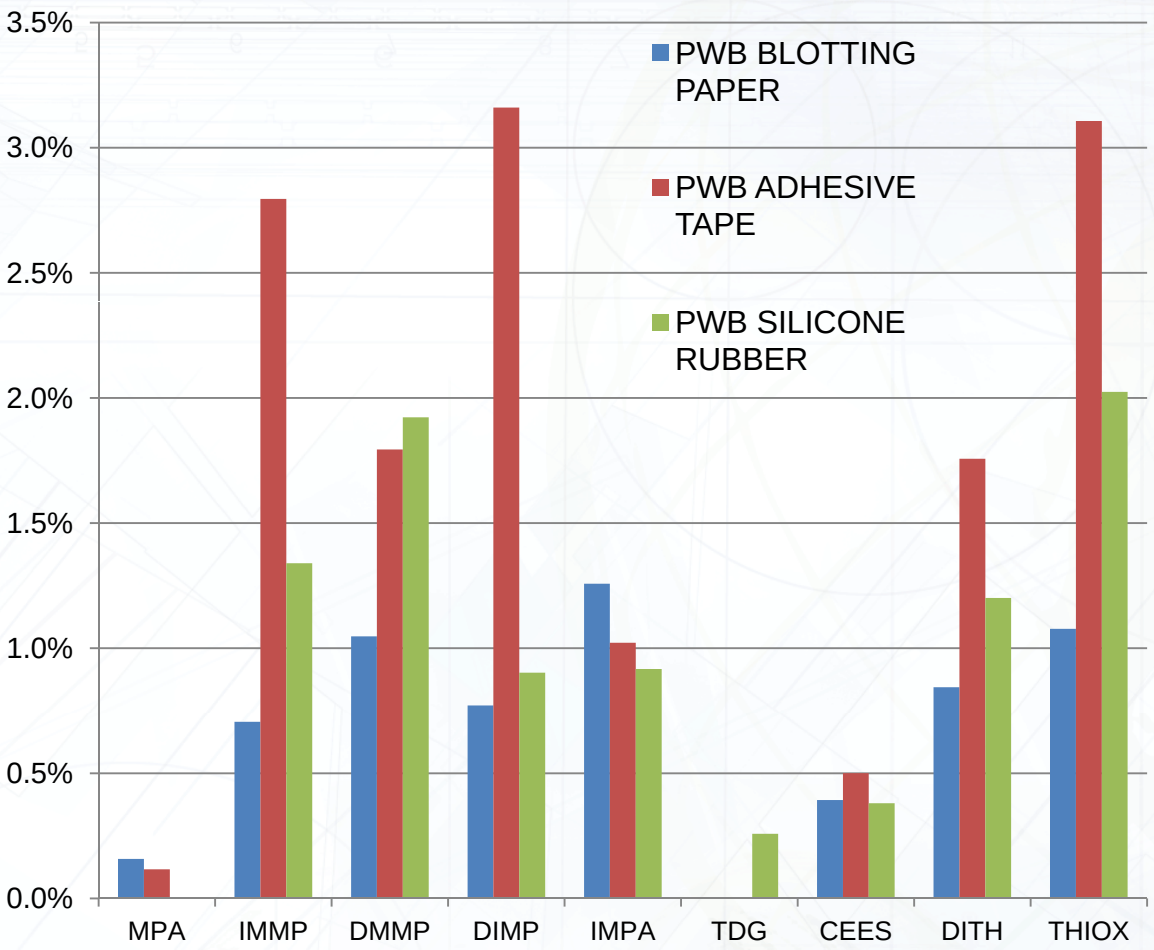
Earlier *In-situ* Field Tests (subset of targets)

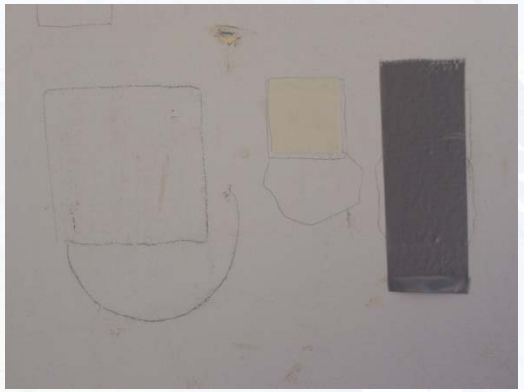


Painted wood shelving

Chemical	Spike level (ng)
MPA	114,000
IMMP	3,100
DMMP	180
DIMP	240
IMPA	2,100
TDG	50,000
CEES	1,400
DITH	800
THIOX	670

Earlier *In-situ* Field Tests (subset of targets)





Painted drywall
(multiple paint layers)

Chemical	Spike level (ng)
MPA	114,000
IMMP	3,100
DMMP	180
DIMP	240
IMPA	2,100
TDG	50,000
CEES	1,400
DITH	800
THIOX	670

Conclusions

- Sampling method can detect up to 24 target compounds associated with 9 chemical threat agents
- CAS uptake and recovery evaluated for 13 different substrates (including “difficult” matrices such as concrete, rubber, carpet, and paint)
- CAS recovery varies by chemical, collection media, loss or interaction on substrate prior to collection, and extraction efficiency
- CAS recoverable in the presence of environmental contaminants (water residue, motor oil, and dust) and for simulated field samples
- Detection at trace levels (ng) possible, and reportable as mass per sample or mass per area wiped
- Sampling method provides:
  - Simple, non-destructive collection method using COTS materials
  - Wipe samples that are stable for up to 7 days post-collection
  - Simple extraction (i.e., no-cleanup) and qualitative confirmation using mass spectrometric analysis

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