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The Chemistry of Odor: How understanding odor can foster a better detector

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Overview

- 1. Odor basics
 - Definitions
 - Factors that affect odor profiles
 - Training aid storage and contamination
 - Odor availability
- 2. "Canine research research"
 - Reported operational knowledge/information gaps
 - Literature review
 - Recommendations for research areas



Odor Basics

- Canines do not necessarily alert to the parent molecule
 - Examples:
 - TNT \rightarrow 2,4-DNT
 - Cocaine \rightarrow methyl benzoate
- **Odorant =** Molecule that gives off odor
 - Analyte to be detected
- Odor profile = collection of odorants that make up the *unique* odor of a target object



K9 smells DNT but thinks TNT

Human smells acetylpyridine but thinks popcorn





Environmental factors

- Example: Ammonium nitrate
- Increasing temperature / humidity
 - Temperature and humidity can work in competing ways
 - Environmental conditions did not effect all forms in the same way
 - Increasing temperature may increase odor from impurities \rightarrow complicates odor profile





Environmental factors

- Example: Heat with aluminum powder
 - Al powder is commonly mixed with AN in HMEs
 - Headspace of fresh Al powder contains alkanes and organic acids comes from stearic acid coating (smells like crayons)
 - Heat does not always increase volatiles \rightarrow *Exposure to heat drives off volatiles*





Aging and storage

- Example: HMTD
 - Known to decompose into highly volatiles compounds at room temperature





Hexamethylene triperoxide diamine



Aging and storage

- Example: HMTD
 - Odor profile changes with time, storage conditions, temp and humidity exposure, and formulation



DeGreeff, L.E. et al. "Variation in the headspace of bulk HMTD with time, environment, and formulation." Forensic Chemistry, 4 (2017) 41-50.



Differences between brands and manufacturing processes

Example: Ammonium nitrate variants

AN variant / HS component	Lab	Indust, ground	Indust, prill	Fert, ground	Fert, prill	CAN	lce pack
acetic acid	Х	Х	Х			Х	
propanoic acid	Х						
methylphenyloxime	Х	Х	Х	Х	Х		Х
1-butanol				Х	Х		Х
acetamide						Х	
2-ethyl-1-hexanol						Х	
acetone							Х
pentanal							Х
hexanal	Othe	rode	rouc	comp	onon	te in	Х
pyridine	Other odorous components in					Х	
2-methyl pyridine		vario	us tv	nos o	Γ ΔΝ		Х
4-methyl pyridine		vanc	us ty	pes o			Х
2,6-dimethyl pyridine							Х
2,4-dimethyl pyridine							Х
2,3-dimethyl pyridine							Х

Main odorant is ammonia BUT amount of ammonia can vary





Example: HMTD

Factors that Affect Odor Profiles

Differences between brands and manufacturing processes

HTMD changes with <u>time</u> and synthesis <u>method</u>:

(Supplier A = unexperienced; Supplier B = experienced chemist)



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Training Aid Contamination

- Faulty handling
- Faulty storage
- Improper cleaning
- Residual odor in training facilities
- Odor imparted by storage container or manufacturer
- Another consideration: weathering and aging



Related target odors

- Training materials stored together in one case or bunker will absorb odors of the training materials around them
 - Example: In one study, dogs could only find 3 of the most volatile odors instead of the 9 parent explosives used in training
- Degradation of compounds in aged training aids means odor profile changes during maintenance training





Odor Availability

Mass of bulk material ≠ amount of odor available! Odor concentration is dependent on:

- Vapor pressure of material (how much vapor is in the gaseous phase at a given time)
- Surface area
- Rate of evaporation (usually related to vapor pressure)
- Interactions with container / wrapping material (i.e. absorption to plastic etc.)
- Temperature and humidity (environmental conditions)



Odor Availability

Mass of bulk material *≠* amount of odor available!

- Odor concentration is dependent on:
 - Surface area: more surface area = more odor!

Note: when you pack a powder tightly into a block or into a container, surface area \downarrow and odor availability \downarrow



Ammonium Nitrate: Crystals

Ammonium Nitrate: Beads

Of the same brand of AN, ground has more surface area than prill \rightarrow will give off more odor



Flake has more surface area than cast \rightarrow will give off more odor

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Canine Research – Past, Present, Future: Analysis of Gaps and User Needs

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"CANINE RESEARCH RESEARCH"



Surveys Results





What does it mean?

Knowledge gaps: 2 possible reasons

- Most commonly reported knowledge gaps have the least amount of research in the literature
 More research is needed
- 2. There is a considerable amount of research in an area of a frequently reported knowledge gap
 - Disconnect:
 - Researching the wrong thing?
 - Poor quality of research
 - Information not being disseminated to the user

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Analysis of Gaps

and devices / storage and	delivery / concealment		
	concediment		Number of
	<u>Total survey</u>	Related literature	<u>database</u>
Knowledge gap category	<u>responses</u>	search terms	<u>returns</u>
Odor chemistry / delivery /			
concealment			
Buried/concealed odor	35	Buried odor detection	15
	30	Odor diffusion or	0
Odan diffusion / dispension / profiles		dispersion	
Outraijjusion / dispersion / profiles		Odor / scent profile	31
		Odor / scent plume	5
Odor quailability / delivery	26	Odor availability	4
Out availability/ aerivery	20	Odor delivery	14
Training aids			
		Training aids	31
		Narcotics training aids	6
Training aids		Cadaver / human remains	10
(explosive/narcotics/human remains)	14	training aids	
(exprosive/narcones/naman remains)		Explosives training aids	19
		Simulant / pseudo /	20
		mimic	
		Training aid shelf-life	0
Training aid shelf life/storage	15	Training aid storage	5
		Storage	10
Training devices (boxes etc.)	9	Training device / box	22

- "Odor chemistry"
 - Most commonly reported user need
 - "Reasonable" amount of literature (room for more)
 - User topics could better-match user needs
- "Training aids"
 - Second most reported gap
 - Also greatest amount of literature
 - Disconnect!
 - More information needed?
 - Better training aids needed?
 - Little research on shelf life/storage

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Analysis of Gaps



	<u>Total survey</u>	Related literature search	Number of
Knowledge gap category	<u>responses</u>	terms	database returns
	30	Explosives detection	102
Contrology I data stren		Landmine detection	13
Contraband detection		Homemade explosives	12
		Narcotics detection	31

- "Contraband detection"
 - 102 sources for "explosive detection" but only 12 related to HMEs

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Recommendations for Research

- 1. Odor delivery, diffusion, dispersion and availability
- 2. Training aids:
 - i. What is lacking for operational community?
 - ii. Storage protocols (degradation and contamination)?
 - iii. Shelf-life?
- 3. Homemade explosives

Connect researchers and research results with operational users

Build better partnerships between government agencies



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