The chemistry of odor and odor detection

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Canine as a Detector

Canine = *field detector*

- **Sampling** = *sniff*
- **Pre-concentration** = *nasal cavity*
- **Detection** = *olfactory nerves*
- **Discrimination** = *olfactory bulb*
Strengths and limitations of the canine detector

• **Strengths**
  - Sensitivity
    - Generally unmeasured, but considered to be below the detection limits of most instruments*
  - Selectivity
    - Ability to “see” unique odor signature and ignore background
  - Ability to follow scent to source

• **Limitations**
  - Lack of standardization and calibration
  - Odor targets to many analytes unknown

*Estimated LOD for nitromethane in ppt range – Kurry et. al., 2003
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➢ Research should be carried out to improve canine efficiency, training, and acceptance in the scientific community
Odor Detection: Defined

• **Odor detection** = vapor sampling/analysis
  • Volatile organic compounds (VOCs) from scent object are released into the environment → detected

• **Odorant** = analyte to be detected
  • VOC that gives off an odor

• **Odor profile** = Unique group of odorants associated with object of interest
Odor Detection Challenges

• Target compound may have low volatility
  • Low concentration of target available in headspace
  • Ex. TATP >> TNT > PETN / RDX > HMTD (?)

• Odor profiles may change with time / environment
  • Changes due to temp / humidity (i.e. increased /decreased volatility)
  • Changes due to degradation

• Odor profiles may be complicated
  • May contain many components ➔ which ones are unique/important?
  • Ex. Human remains, some drugs / explosives
Odor Detection Challenges

• All of these challenges are complicated by field conditions
  • Sensitivity issues due to dilution in air
    • Also burial, wrapping, etc.
  • Selectivity issues due to background odors
  • Inability to control environmental conditions
    • High/low temp or humidity
    • Rain
    • Sunlight (photochemical changes)
Odor Profiles

• Low volatility explosives
  • Challenges:
    • Minimal availability of parent compound
    • Real-world sampling conditions compound difficulties
  • Utilize whole odor profile:
    • Canines utilize the whole odor profile instead of parent compound alone
    • Detect the most unique and abundant volatiles associated with parent compound
  • Maximizes sensitivity and selectivity
• Researchers should understand odor profile of target compounds
  • Improve training / training aids
  • Enhance scientific understanding of canine abilities
Odor Profiles

• Odor profile = collection of odorants that make up the *unique* odor a target object

• Canines do not necessarily alert to the parent
  • Examples:
    • TNT $\rightarrow$ 2,4-DNT
    • Cocaine $\rightarrow$ methyl benzoate

![Headspace of TNT](image1.png)

![Headspace of cocaine](image2.png)

Courtesy of Dr. Kenneth Furton and Dr. Michael Macias
Odor Profiles

- Odor profiles of some profiles are simple (single component)
  - Example: TNT → 2,4-DNT
- Others are more complicated with many components composing the odor profile
  - Example: marijuana

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Odor profiles: Living vs. deceased human odor humans

Volatile compounds collected from living and deceased humans:

- Geranyl acetone
- Heptadecane
- Octanoic acid
- Phenol
- Pentadecane
- Decanal
- Benzoic acid, methyl ester
- Tetradecane
- 1-Octanol
- 2-2-Methoxyethoxy ethanol
- Nonanal
- Benzaldehyde
- 2-Ethyl-1-hexanol
- Tridecane
- 6-Methyl-5-hepten-2-one
- 1,2,3-Trimethyl benzene
- Undecane
- Styrene
- o-Xylene
- Toluene

Changes in odor

- Changes in odor profile
  - With time or storage condition
    - Examples:
      - Explosives: HMTD
      - Human odor: decomposition / blood
  - With formulation or brand
    - Examples:
      - Explosives
      - Narcotics
- Need to be aware and train appropriately
  - Consider how the canine generalizes / discriminates like odors
  - May need multiple training aids
Changes in odor

- Changes in odor profile - HMTD
- With time, storage condition, and formulation

Changes in odor

- Changes in odor profile - HMTD
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Changes in odor

- Changes in odor profile – Blood (human decomp)

Field conditions

- Available odor concentration may be reduced / increased by:
  - Temperature, humidity
  - Absorption - wrapping, packaging, etc.
  - Odor transport – through soil, through container, etc.
Field conditions

- Available odor concentration may be reduced / increased by:
  - **Temperature, humidity**

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Ammonium nitrate vapor composition changes!

- \( \text{NH}_3 : \text{HNO}_3 \) in vapor is highly humidity dependent
  - **Dry air**: \( \text{NH}_3 \approx \text{HNO}_3 \)
  - **Humidified air**
    - Initially \( \text{NH}_3 > \text{HNO}_3 \)
    - \( \text{NH}_3 \) decays slowly while \( \text{HNO}_3 \) remains steady
    - **New exposure to humidified air renews cycle**
    - **AN deliquesces (>62% RH at 25°C)**
Field conditions

- Odor transport
  - Burial of target may not only reduce odor, but also change scent picture
  - Transport properties of odorants may differ
  - Example: TNT buried in sand
    - 0.1 g TNT buried in 39 g sand, in vial
    - Both TNT and 2,4-DNT were detected
    - Ratio of TNT to 2,4-DNT changed with time

![Graph showing transport of explosives](https://example.com/graph.png)

Figure 3. TNT and 2,4-DNT vapor concentration in headspace from TNT buried in sand at different times after the mixture was. TNT values have been multiplied by a factor of 50 for visualization purposes.
Field conditions

- Absorption to surfaces
  - Wrapping / surfaces may absorb odor
  - Example: TNT with materials commonly associated with landmines
    - TNT bonds to some surfaces more strongly than to others

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Surface adsorption and retention of TNT vapors

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![Graph showing desorption of TNT deposited on surfaces from the vapor state](image-url)

FIG. 4. IMS analysis of TNT adsorbed on various surfaces from the vapor state using 250 ng TNT in the vapor generator/collector system.
Improving detection through science

- Understand odor profile
- Understand how odor profile changes
- Encourage generalization across variants of a single target
  - Canines trained only a single variation of a target, might not detect other variations in target
  - May need multiple training aids
- Consider field conditions

**When given the chance to train with new conditions or variants...take it!**
Knowledge gaps???

• Project: “Canine Research – Past, Present, Future; An Analysis of Gaps and User Needs”
  • Where are the knowledge gaps in canine detection?
    • To include detection of explosives, narcotics, human remains, and human tracking
    • Related research in veterinary and behavioral sciences
  • Research gaps?
  • Operational needs?
  • Average cost of research?

• To contribute:

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