The Response of Colorimetric Sensor Arrays to Chemical Warfare Agents

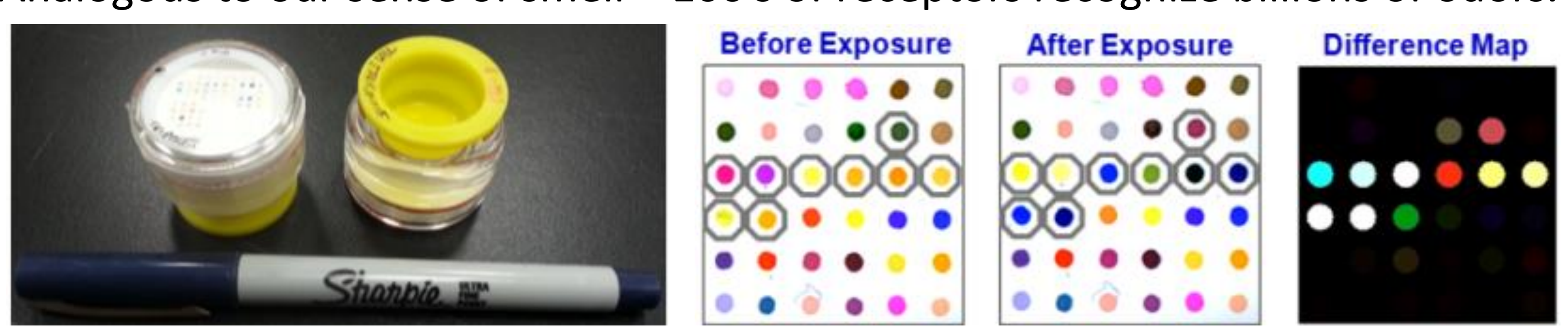
Aleksandr Miklos[1], Charles Davidson[2], Ronald Miles[3], Melissa Hulet[4], Barry Williams[4], Melissa Dixon[3], Avi Ben-David[3], Sung Lim[5], Paul Rhodes[5], Alan Samuels[3], Peter Emanuel[3], Calvin Chue[3]
[1]Excet, [2]STC, [3]ECBC, [4]Leidos, [5]iSense

Abstract

Colorimetric sensor arrays (CSAs) are cheap and disposable means to identify unknown samples. We have been testing CSAs and have found them to be capable of distinguishing between closely-related chemical warfare agents (CWAs) and robust in 'red-light / green-light' detection. We are engaged with iSense, the developer, to produce 'CWA-optimized' arrays. This effort is informed by multiple laboratory testing efforts and analytical projects investigating both image analysis and pattern interpretation. Closely coupled to this research is the design and testing of prototype hardware intended to bring the capabilities of CSAs into the field. Integrating all of these efforts will provide a powerful on-target ID capability to the Warfighter and assist in meeting the requirements for NGCD 4.

What is a Colorimetric Sensor Array?

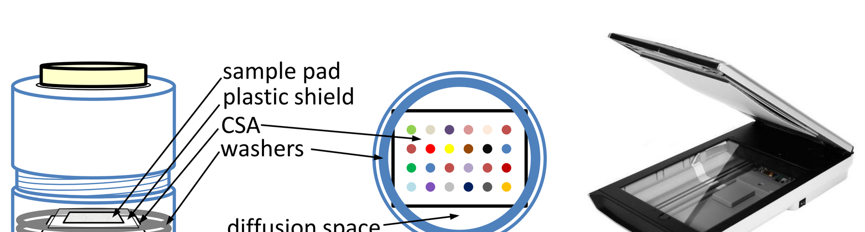
- CSAs are multiplexed chemical assays printed on a small (≈1 in^2) piece of paper
- Each dot on the array is unique and responsive to a different moiety or property.
- This is NOT specific "1-for-1" chemistry – Read the Pattern!
- Analogous to our sense of smell – 100's of receptors recognize billions of odors.



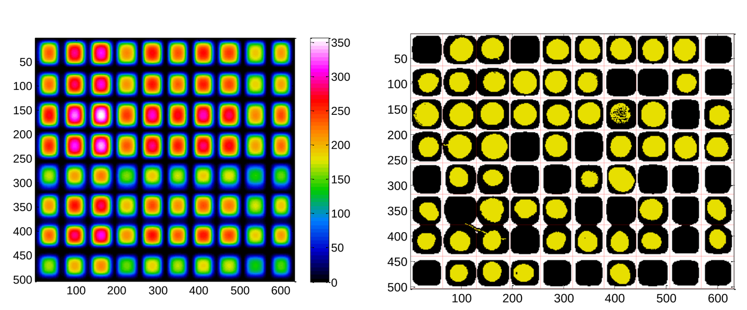
Left, CSAs installed in jars for confined headspace analysis. **Right**, a series of three ticket images. Left to right, a ticket before exposure, after exposure to ammonia for 30 minutes, and a difference image generated by subtracting "after" from "before" yielding a representation of the color change.

Headspace Vapor Analysis

We evaluated the responses of CSAs to chemical agents, their precursors and degradation products, fuels, lubricants, cleaning products, solvents, agricultural chemicals, and hygiene products. Our strategy was to co-confine each analyte and a CSA in a test fixture, capturing time lapse images using a flatbed scanner.



For more information on data collection, see Alan Samuels's Poster!



For more information on image analysis, see Charlie Davidson's Poster!

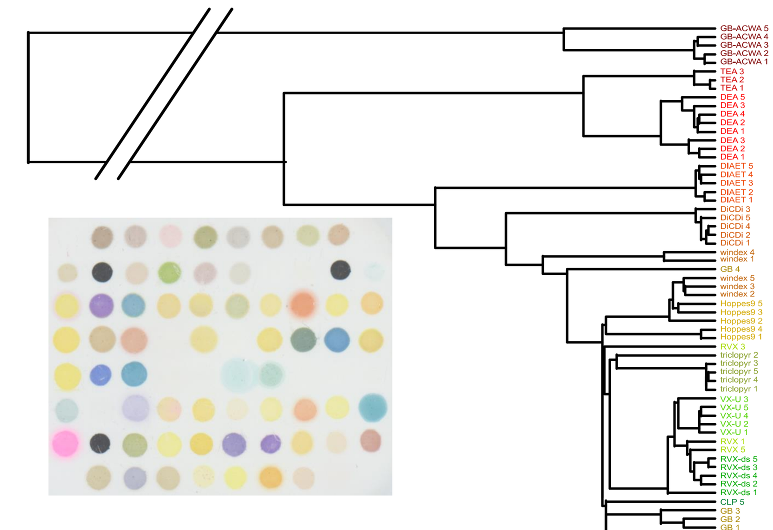
Approved for Public Release

Confined Vapor Exposures

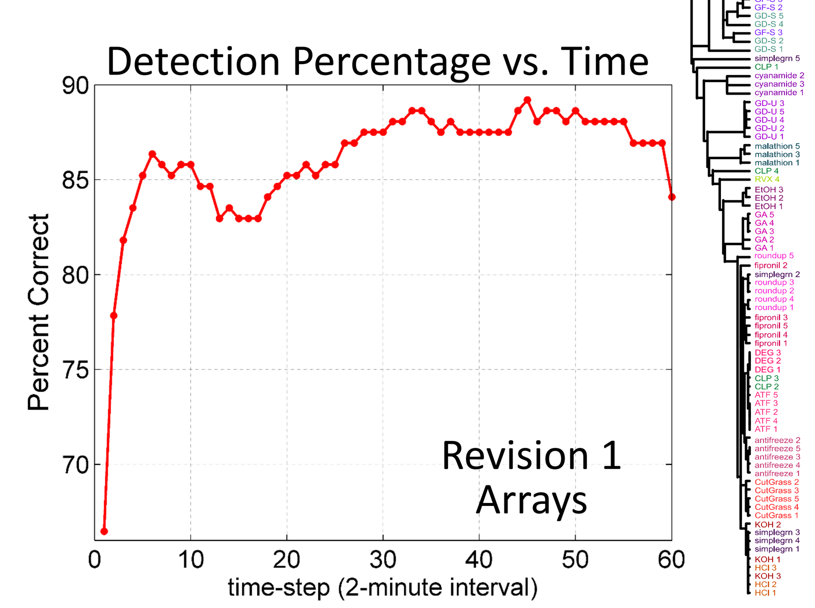
Vapor array performance is being assessed by exposing the arrays to the headspace above a sample and quantifying the color changes. Array performance can be visualized by performing hierarchical clustering analysis (HCA) and detection/identification performance can be assessed using a 1st-nearest-neighbor algorithm operating on the Euclidean distance matrix generated in the HCA analysis.

Our initial surveys were performed with 5-minute time steps for image acquisition and with multiple reagents tested per experiment, yielding a time resolution which was fairly low (±10 minutes). At the time our CONOP for the technology was focused on 'analyze in transit' type applications where time was not as significant. We discovered, however, that the responses were much faster than anticipated and have been recently testing multiple array types with much higher time resolution. The preliminary results are below.

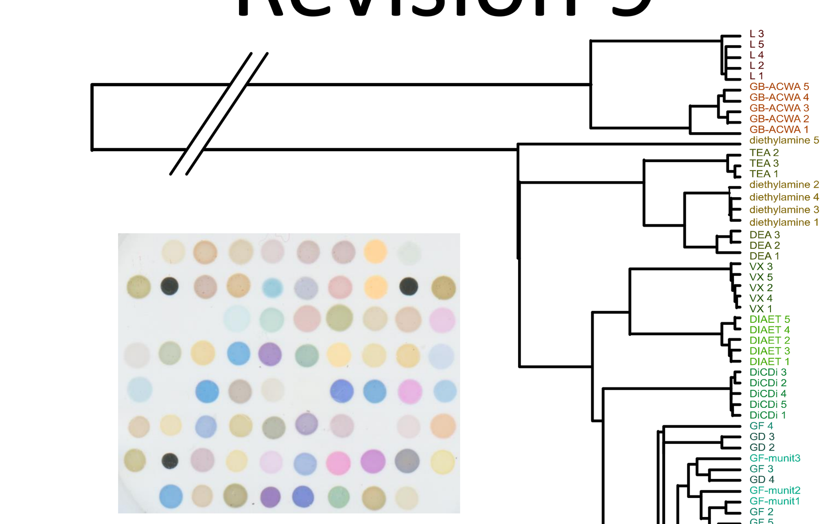
Revision 1



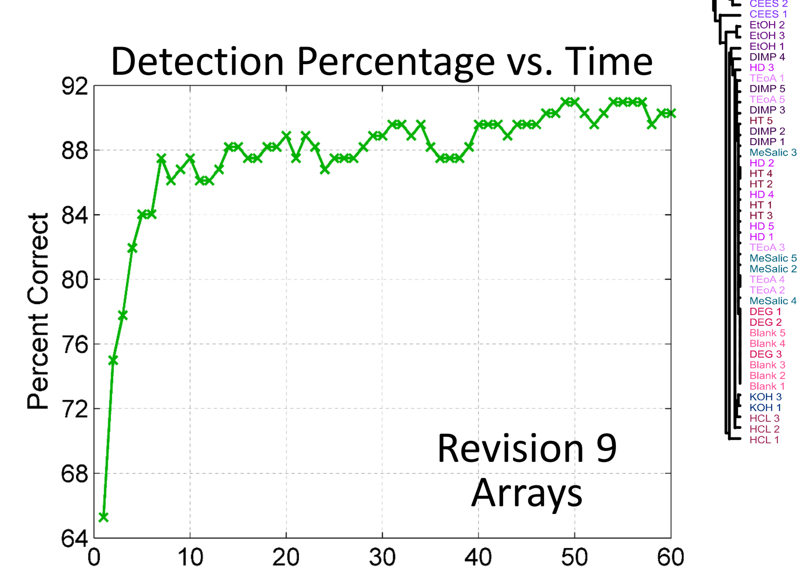
This is the first array type we worked with. While it performs well, the formulations lead to variance in spot size/shape which can cause false positives and negatives.



Revision 9



This is a newer array with better formulation (and 'cleaner' spots). The yields are better (fewer tickets discarded) and performance has improved.



Detection by 1st-nearest neighbor matches an unknown signature by its similarity to other signatures. The HCA dendrograms above provide a visual reference to this process: whatever a sample is nearest to in its connectivity on the chart is what it would be detected as if it were introduced as an unknown.

Hardware Development: The VOCkit

CSAs have the potential to bring a powerful chemical identification capability to the individual-user level. To explore this, we are developing a portable hardware CSA reader and an Android application to perform the image analysis and signature matching tasks.

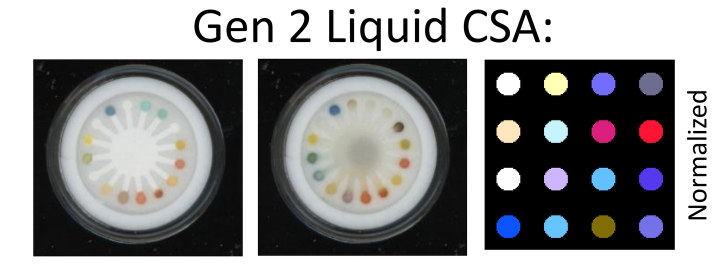
For more information on the VOCkit project, see Colin Graham's Poster!

Direct Liquid Analysis

There are some compounds of interest which cannot be addressed by vapor-phase sensing. To accommodate direct liquid analysis, iSense developed a crosslinked CSA with a radial microfluidic design to "wick" analyte to indicators in polymer wells to avoid bleeding. The 'radial' design is performing well and is in active development to increase the number of indicators and finalize indicator identity.

Gen 1 Liquid CSA (early prototype)

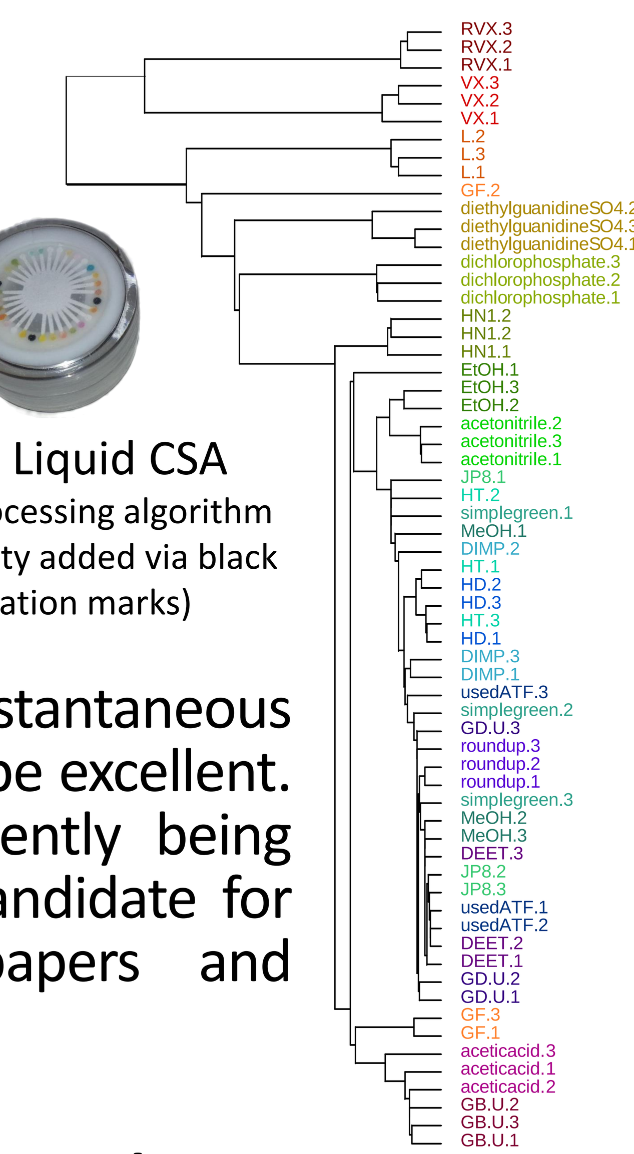
Undiluted VX response:
Gen 2 Liquid CSA:



Before After Difference

Gen 3 Liquid CSA
(image-processing algorithm compatibility added via black calibration marks)

Classification Performance: Gen 3



Liquid analysis is rapid (changes are instantaneous upon contact) and sensitivity appears to be excellent. Revised and expanded arrays are currently being tested at ECBC. This technology is a candidate for replacing or augmenting M8/M9 papers and integration with concentrator systems.

Acknowledgements

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TECHNOLOGY DRIVEN. WARFIGHTER FOCUSED.