The Response of Colorimetric Sensor Arrays to Chemical Warfare Agents

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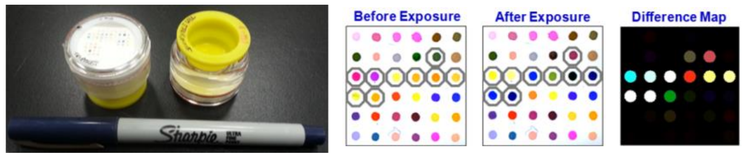
Abstract

Colorimetric sensor arrays (CSAs) are cheap, disposable, and have previously shown a powerful ability to identify a wide range of samples based on their volatile emissions. As such they are of interest as a tool for the Warfighter in multiple contexts. We have been testing CSAs against both headspace vapors and directly against liquids and have found that general, unoptimized arrays are capable of distinguishing between closely-related chemical warfare agents (CWAs) and are quite robust in 'red light/green light' detection at an early development stage. Design and manufacturing improvements have made direct exposure of the arrays to liquids more reliable and in this context they are both highly sensitive and nearly instantaneous in reacting. We are currently engaged in evaluating and optimizing both types of array for Warfighter-relevant targets and developing prototype hardware and mobile applications for sensing.

What is a Colorimetric Sensor Array?

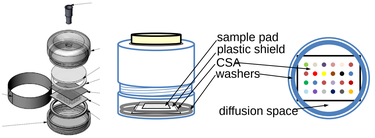
- CSAs are multiplexed chemical assays printed on a small (≈1 in^2) piece of paper.
- Each dot on the array is unique and responsive to a different moiety or property.
- This is NOT specific "1-for-1" chemistry – Read the Pattern!
- Analogous to our sense of smell – Hundreds of receptors recognize billions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



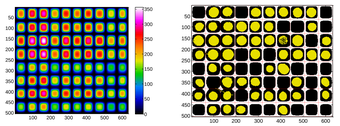
Left, CSAs installed in jars for confined headspace analysis, with a pen for scale. Right, a series of three ticket images. The first image is of the ticket before exposure to any analyte. The second image is after exposure to ammonia for 30 minutes. The final image is a representation of the color change, generated by subtracting after from before per-spot RGB values from each other, normalizing, and plotting a circle with the difference RGB value.

Headspace Vapor Analysis

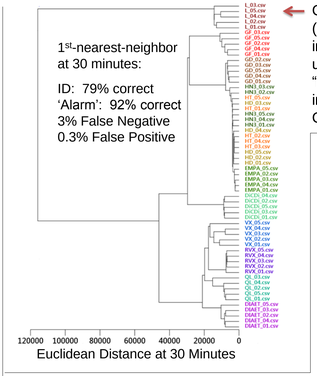
We evaluated the responses of CSAs to chemical agents and their precursors and degradation products, fuels, lubricants, cleaning products, solvents, agricultural chemicals, and personal care products. Our general test strategy was to co-confine each analyte and a CSA in a test fixture, capturing images every 5 minutes using an unmodified flatbed scanner.



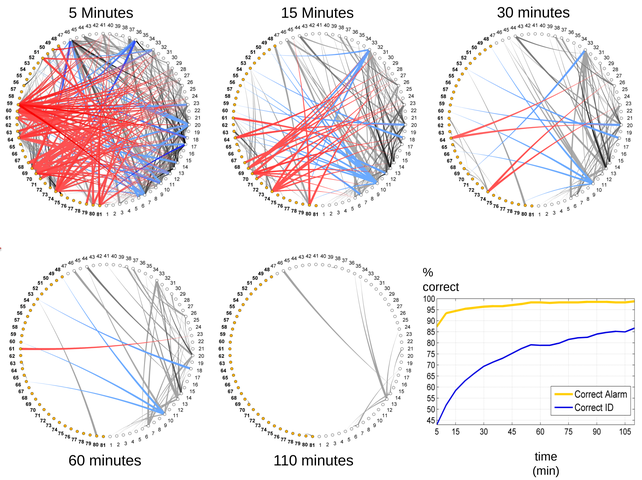
Spots are recognized from each image and RGB values are extracted by an automated algorithm.



Extracted RGB values form the 'signature database' for each tested analyte.



Clustering Analysis: Array performance can be visualized using hierarchical clustering analysis (HCA), and a 1st-nearest-neighbor algorithm operating on the Euclidean distance matrix generated in HCA yields reasonable performance in identification of analytes (assignment of identity to an unknown) and good performance for "alarm" purposes (correct assignment to either "threat" or "non-threat" classes). As we pursue engineering and materials improvements we are also investigating more robust means to make correct decisions based upon the data produced by CSAs.

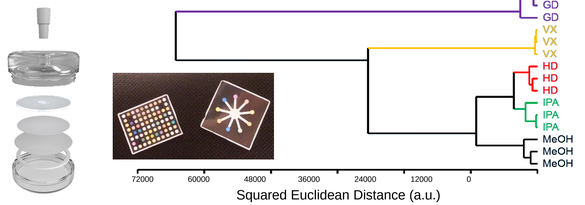


Detection graphs

Alarm and identification results from a distance to- and angle to- model principle component 'subspace' algorithm. Chemical IDs are divided into "threat" or "non-threat" categories with threats in orange. Connections indicate potential mis-identifications. Nodes with no connections are unambiguously and correctly identified. Inter-class mis-identifications (correct alarm, incorrect ID) are GRAY, False-negatives are RED, and false positives are BLUE. Darker lines indicate a stronger probability of mis-identification.

Liquid Analysis

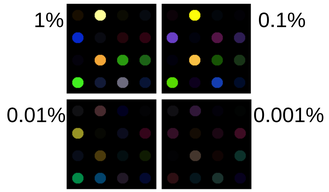
To accommodate direct liquid analysis, iSense developed a crosslinked CSA with a radial microfluidic design to "wick" analyte to indicators in polymer wells to avoid bleeding. The 'radial' design is performing well and is in active development to increase the number of indicators and finalize indicator identity.



Undiluted VX response on Liquid CSA

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.

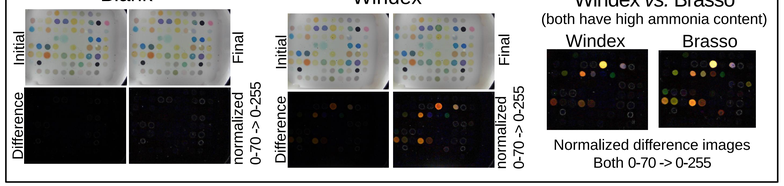
VX dilutions in isopropyl alcohol (iPA): differences after iPA blank subtraction



Hardware Development (The VOCkit)

A hardware concept (the VOCkit) is being developed to assist in the development of CONOPS and engage with potential users for technology transition. The device uses a replaceable sampling cartridge containing a sorbent pad and a CSA which docks onto an electronics unit containing an optics package, Bluetooth radio, and battery. The device functions stand-alone to capture before and after images of the CSA then provides the images on-demand to a phone or other device for analysis.

Prototype test: Exposure time: 2 minutes



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