Paper on Demand: Inkjet Printing of Task-Specific Assays

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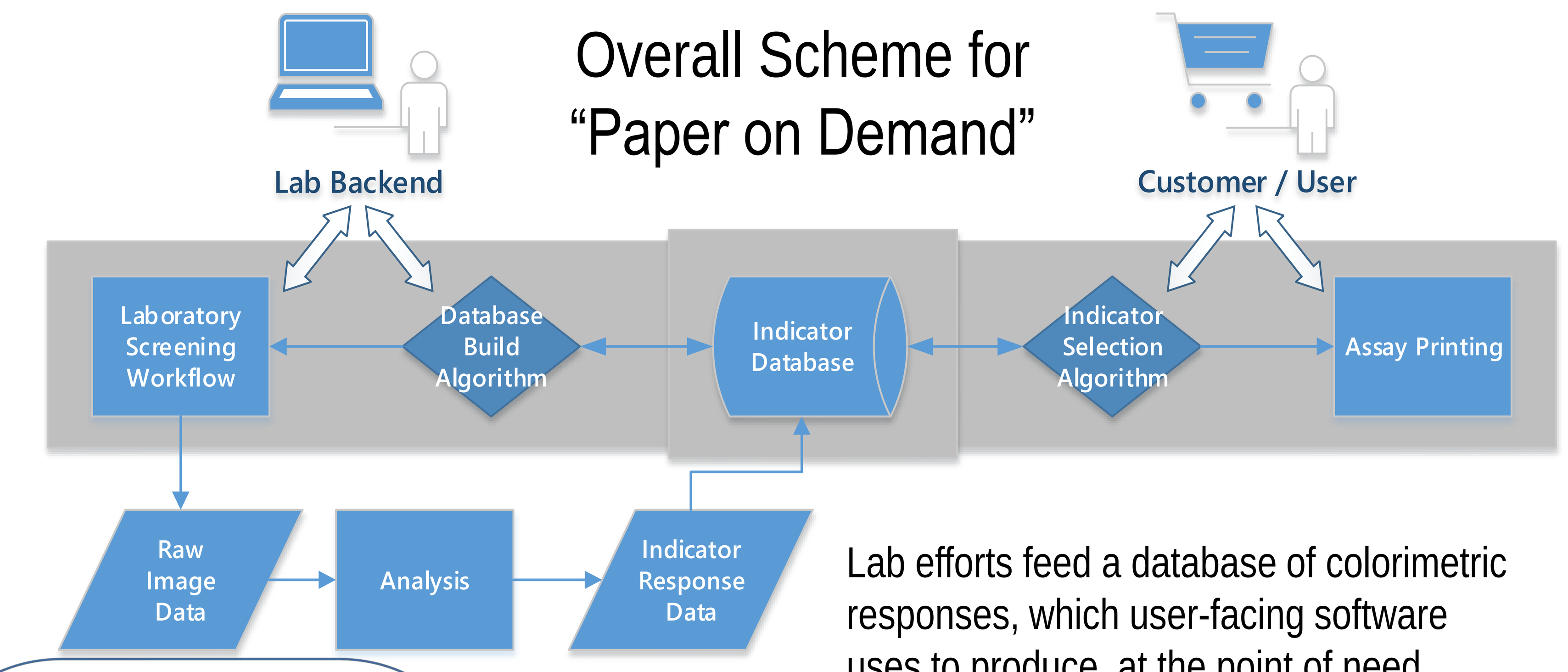
Abstract / Introduction

Colorimetric assays offer a low size, weight, power, cost (SWAP-C) and effective method for chemical threat detection and identification. Colorimetric assays may be machine-readable or human-readable depending on proposed application and response time required. Machine-readable assays offer high resolution capability over a wide range of chemicals, but the interpretation requires a powered device therefore increasing SWAP-C. Human-readable assays provide a quick response time and lower overall burden, which is highly sought after by the warfighter for decision making in the field. However, both methods are limited when a decision is based on subtle color changes; this may lead to misinterpretation and a false positive identification of a hazardous threat. Therefore, specific indicators with readily perceived color changes and specific analyte-targeting is highly desired. This in turn, also limits the design of the ticket and therefore improvement on the ticket design is also required.

Here we present a 'paper on demand' system that combines the specificity of machine-read assays with a human-readable CONOP. This system uses inkjet-printable chemical indicators, a COTS inkjet printer, and custom software to allow any end user to print a mission-specific, ticket-type chemical identification assay at the point of need. Rather than including many indicators on a single assay or relying on high specificity at the indicator or material level, we use a response database to select the best subset of indicators to discriminate between a target and an interferent, both specified by the end user as a part of the interactive assay design process. Here we present our methods for building our response database, our consideration of human perception of color in the ranking of indicator responses, and examples of how we demonstrated these concepts for both general chemicals, chemical simulants, and chemical warfare agents (CWAs). We believe this approach could find utility for first responders and other "burden-sensitive" users, and this technology may also serve as a platform for the deployment of more specific chemistries against threat agents as they are developed.



Lab efforts feed a database of colorimetric responses, which user-facing software uses to produce, at the point of need, assays for specific detection or identification tasks.

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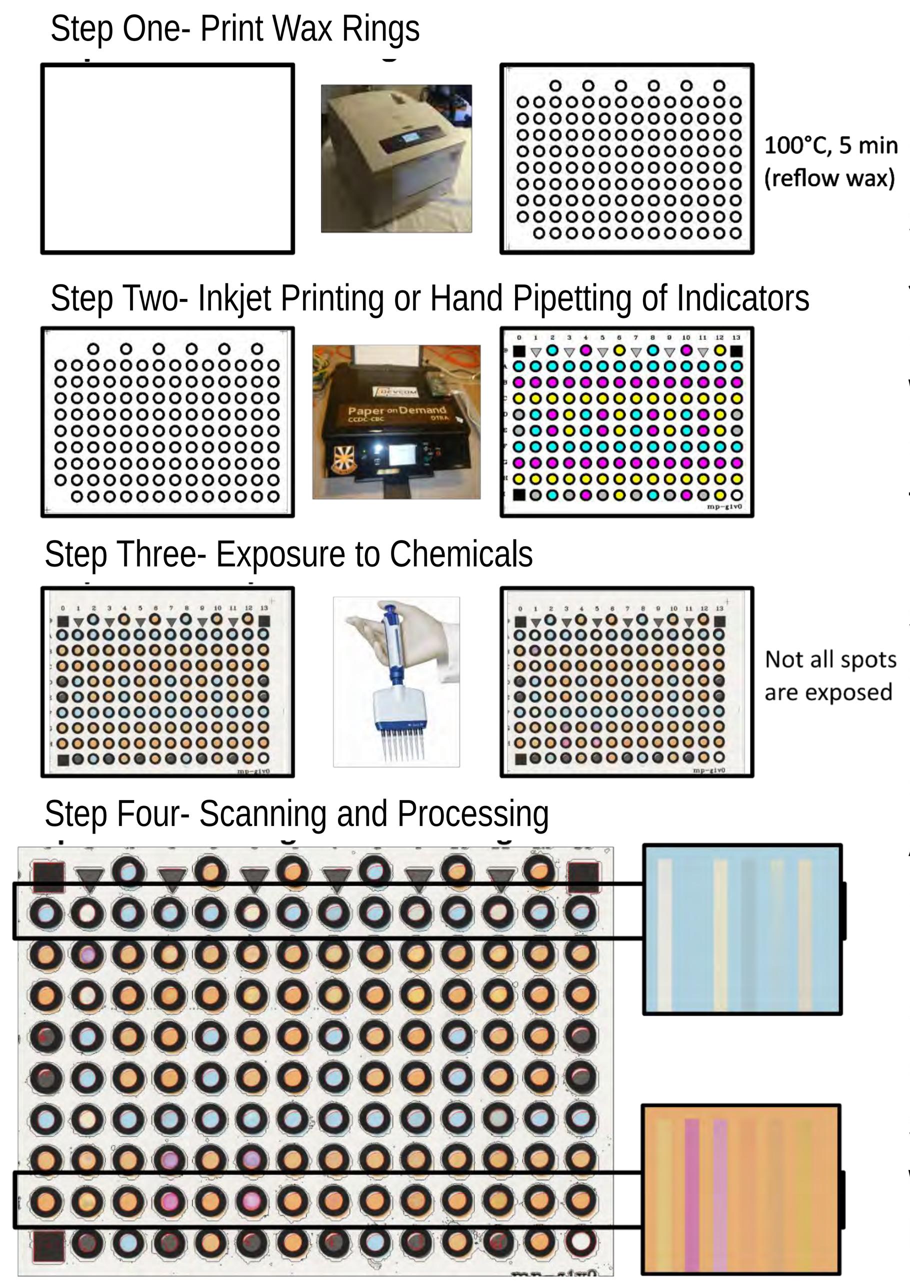
Screening System Design and Implementation

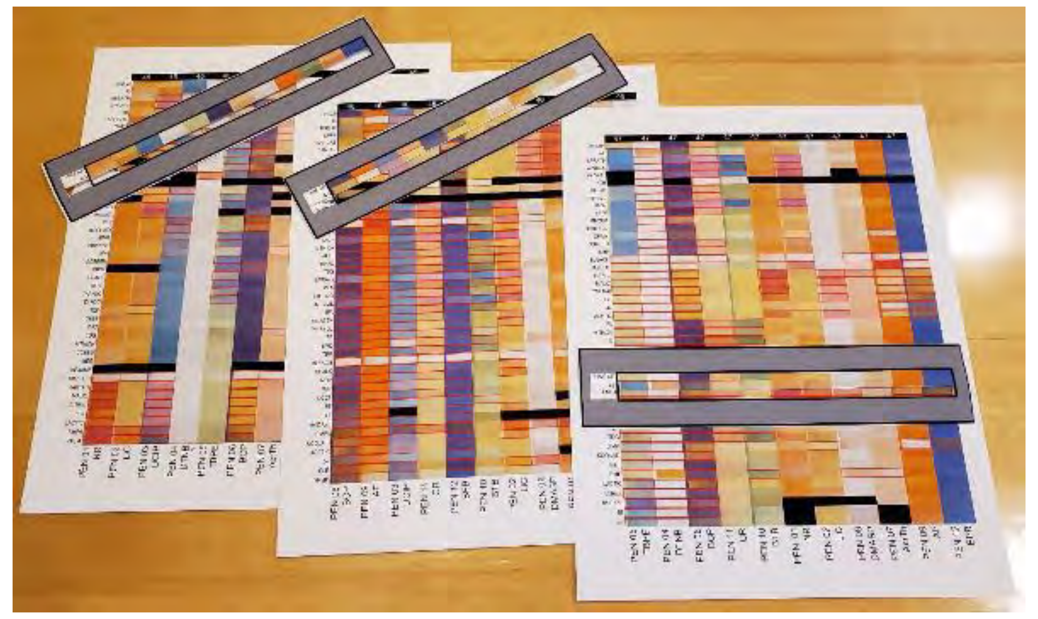


In order to create this system, detailed information about indicator color changes was required. To obtain this information quickly and accurately, we leveraged existing schemes for high-throughput screening. *(Our process is shown on the left.)* We screened several types of paper and found that COTS photo papers, in general, worked well. This is likely due to photo papers being polymer-coated to imbibe and stabilize inks, which is also beneficial for our intended application. Our printed targets were based on 96-well microplate geometries in order to use standard plates and pipettors for storage and transfer operations. We found that pre-printing our paper with wax rings contained both the indicators and analytes to a defined region of the paper, making analysis more reliable. Alternating wells were left unexposed to control for vapors evolved from the chemicals and wicking through the paper. Finally, machine vision was used to automate analysis, enabled by fiducial and 50% gray control marks printed on each screening target. In this manner, we were able to screen 24 chemicals at three dilutions against 18 indicators with 5X replicates using less than three person-weeks of labor at the bench. Our workflow and examples of the extracted color-change data are shown at left.

To demonstrate that this system could be generalized beyond the relatively innocuous chemicals and include chemical warfare agents, we developed a new CWA-appropriate screening workflow, and a move away from inkjet printing to direct deposition (via pipettes and marker pens). Our previous screening approach was to print three different indicators and expose it to a library of 12 chemicals using a pre-made chemical set plate and a multi-channel pipettor was unsuitable for agent work with the increase in engineering controls required. The chemical set plate approach requires additional handling steps which increases risk, generates additional waste plastics, and is incompatible with the best practice of working with only one agent at a time in operations. To keep throughput up while using best practices for agent work, a new screening target was developed. The "agent" target is printed (or pipet-deposited) with 12 indicators and then screened against one agent at a time. An example of the improved chemical agent tickets is shown to the right. In year two, a new screening target was designed to accommodate agent operations.

Results/ 'End User' Tools

With the change to pipetting indicators and using pens from the earlier inkjet printing, our team reconsidered the entire 'end user experience'. No power or electronics would be required to apply indicators from a collection of pens, ideal for users out in 'the field'. An unpowered, chart-based approach to indicator pen selection was prototyped and is presented in the above photograph. The down-selected set of 12 indicators is provided in highlighter-type pens, labeled 1-12. For each chemical agent, a chart and a card key is provided. The chart contains the responses of all 12 pens against all chemicals in our database. The key contains the unexposed colors of each pen, above the color corresponding to the response to the agent, above a cut-out through which the chart can be viewed. By sliding the card key down the chart, the user can examine "A/B vs unexposed" colors for the agent in question versus any chemical in the database. The charts also contain time-domain data: unexposed is always present as a bar to the left of each color block, and moving from left to right represent the time from immediate exposure to 10 minutes after exposure. This provides a cue for the users to know if responses are intended to be immediate or if they might require some time to develop. This will aid the user in selecting the "best" indicators, bearing in mind that "best" may in fact be somewhat relative due to differences in color perception.



Our on-demand approach to create human-readable chemical-agent identifiers is, in general, feasible. We have demonstrated the ability to formulate and apply by several means indicators to paper, and have constructed a human-interpretable and unpowered "decoder key" which allows the use of many indicators to achieve confidence in identification and allow separation of chemical agents from other chemicals. The methods we have developed are amenable to relatively fast expansion of either analyte chemicals or chemical indicator libraries, so the system can rapidly evolve to treat emerging threats and serve a multitude of users, including first responders and other "burden-sensitive" users,

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