PAPER ANALYTICAL DEVICE FOR MEASURING TOXIC METALS IN AIR
David M. Cate, John Volckens, and Charles S. Henry
Colorado State University, USA

ABSTRACT
The goal of this research is to develop paper-based sensors for measuring aerosolized metals in ambient and occupational environments. We report a new method for simultaneous detection of transition metals that does not require external instrumentation, saving hundreds of dollars per test. The detection strategy (referred to as ‘distance-based detection’) is multiplexed for simultaneous measurement of Ni, Cu, and Fe from collected particulate matter. Device fabrication and reagent deposition is accomplished primarily via inkjet printing for improved detection sensitivity and assay reproducibility.

KEYWORDS: PADs, Transition Metals, Distance-based Detection, Microfluidics

INTRODUCTION
Colorimetry, electrochemistry, and electrochemiluminescence are commonly reported detection motifs for paper analytical devices (PADs) [1-3], however their reliance on external detectors (e.g., camera, scanner, potentiostat, etc.) for quantification can increase assay cost and complexity to the point where routine analyses are prohibited. While the material cost per PAD is typically pennies, the cost of the associated detector can range from hundreds to thousands of dollars [4]. Distance-based detection relies on reading the length of a colored reaction product along a paper channel with the unaided eye, dramatically simplifying sample measurement without sacrificing assay sensitivity [5].

EXPERIMENTAL
The device, depicted in Figure 1, contains a sample reservoir and wax channel patterned with a colorimetric indicator specific for the metal analyte of interest. Dissolved analyte flows down the channel and complexes with indicator reagent; the resulting complex precipitates and consequently generates a colored band with a length proportional to analyte mass [5]. Visual quantification is aided by a ruler printed on each device, which is read analogously to temperature on a thermometer. While detection is straightforward, the dynamic range of each assay is limited by the flow rate of analyte through the channel. Flow rate decreases nonlinearly with time/penetration distance in paper. To counteract this effect, the indicator reagents are printed along the channel at pre-determined gradients using a modified piezo-electric printer. The concentration of reagent deposited is highest near the sample zone and decreases along the flow axis. The printed gradient is significant because it improves the linearity and dynamic range of the analyte response curve.

Figure 1: Example of a distance-based PAD for metal detection. Operation consists of printing a hydrophobic barrier on filter paper, patterning reagents, and adding a sample for analysis.
RESULTS AND DISCUSSION

Results are demonstrated for Cu, Fe, and Ni (Figure 2a). Devices for distance-based detection of Ni from incineration ash have been fabricated and analytical results are approximately 10× more sensitive (0.1 vs. 1 µg limit of detection) than corresponding paper devices employing computer-aided intensity measurements with a desktop scanner [1]. Preliminary data also shows good reproducibility (≤ 7% relative standard deviation) between devices tested in the laboratory.

Figure 2: (a) Color length is linear for Cu, Fe, and Ni masses between 0.1–17, 0.1–7, and 0.1–10 µg respectively. Reagents deposited as a gradient increase the linearity of response (blue and green data points) vs. manual deposition with no gradient (open data points). Improvement in dynamic range is shown for (b) Ni, and (c) Cu.

In previous work, reagents were manually deposited on the paper, which reduces analytical precision and can introduce additional variability due to operator error [4]. In this work, reagents are deposited as a gradient via a desktop inkjet printer we modified for custom chemical inks. The significance of the gradient (Figure 2 b, c) is evident from the improvement in overall dynamic range for each stand-alone assay (50 and 24% for Ni and Cu detection respectively), and the linearity of the analyte response curve is also enhanced. Additionally, reagent printing improves device reproducibility compared to manual deposition methods such as nebulization (4% vs. 8% relative standard deviation, respectively). Small droplet volumes from the printer (~1.5 pL) lead to high patterning resolution and low overall reagent consumption (< 50 µL). Reagent printing is also amenable for large-scale device fabrication. Compared with manual deposition methods, reagent printing is precise, user friendly, and complex chemical patterns (e.g. linear/non-linear gradients) can be deposited on the device surface (Figure 3).
CONCLUSION

Paper-based analytical devices hold great potential for application at the point-of-need. The analytical technique presented here is minimally instrumented for device portability and is highly cost effective; excluding fabrication equipment (computer, drawing software, printer, pipette), a single assay costs approximately $0.04. Since analyte quantification is near real-time and can be performed on-site, processing time is dramatically reduced when compared to other centralized measurement techniques.

ACKNOWLEDGEMENTS

This work was supported by grants from the National Institute for Occupational Safety and Health (OH010050) and the National Institute of Environmental Health Sciences (ES019264).

REFERENCES


CONTACT
* Charles S. Henry, tel: +1-970-491-2852; chuck.henry@colostate.edu