Multilayer Paper-Based Device for Colorimetric and Electrochemical Quantification of Metals

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S *Supporting Information*

ABSTRACT: The release of metals and metal-containing compounds into the environment is a growing concern in developed and developing countries, as human exposure to metals is associated with adverse health effects in virtually every organ system. Unfortunately, quantifying metals in the environment is expensive; analysis costs using certified laboratories typically exceed $100/sample, making the routine analysis of toxic metals cost-prohibitive for applications such as occupational exposure or environmental protection. Here, we report on a simple, inexpensive technology with the potential to render toxic metals detection accessible for both the developing and developed world that combines colorimetric and electrochemical microfluidic paper-based analytical devices (mPAD) in a three-dimensional configuration. Unlike previous

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mPADs designed for measuring metals, the device reported here separates colorimetric detection on one layer from electrochemical detection on a different layer. Separate detection layers allows different chemistries to be applied to a single sample on the same device. To demonstrate the effectiveness of this approach, colorimetric detection is shown for Ni, Fe, Cu, and Cr and electrochemical detection for Pb and Cd. Detection limits as low as 0.12 μg (Cr) were achieved on the colorimetric layer while detection limits as low as 0.25 ng (Cd and Pb) were achieved on the electrochemical layer. Selectivity for the target analytes was demonstrated for common interferences. As an example of the device utility, particulate metals collected on air sampling filters were analyzed. Levels measured with the mPAD matched known values for the certified reference samples of collected particulate matter.

Human exposure to particulate matter (PM) air pollution has been established as a leading cause of human morbidity and mortality. Indoor and outdoor air pollution each rank among the top 10 risk factors contributing to disability-adjusted life years, a metric used by the World Health Organization to quantify the global burden of disease. Both the size and composition of airborne particles have been shown to play a role in PM toxicity.[1] Despite the well-established link between exposure and disease, the cellular mechanisms of PM-induced health effects are still not well-defined. Metals present in PM have been the subject of much research, as metals have known pathologies in many organ systems. In occupational settings, exposure to metal-containing PM is particularly concerning due to the tendency for higher exposures.[2] For

example, metals exposures (e.g., Be, Cd, Cr, Cu, Fe, Pb, Ni, and Hg) have been linked to increased hospitalization and mortality and to a variety of serious respiratory disorders including cancers of the lung, nose, and sinus cavity.[3−7] The Occupational Safety and Health Administration (OSHA) mandates permissible exposure limits (PELs) for workplace exposure to metals across a range of levels. For example, worker exposure to Pb and Ni is regulated at 30 and 1 μg/m³, respectively, for an 8 h workshift.[8] As a result, methods to measure aerosolized metals are important to understand and mitigate exposure.

In occupational settings, the approach for PM exposure assessment prescribes collection of an 8 h filter sample from within a worker's breathing zone followed by analysis using either inductively coupled plasma (ICP)[9] or atomic emission spectrometry (OES).[10] These analytic methods give very low detection limits and selective detection of multiple metals in a single sample. However, ICP and OES analyses require tedious sample preparation and highly trained personnel, and the equipment is both expensive and complicated. As a result, analytic costs are high, often more than $100 per sample.[11] The high cost makes large-scale studies economically infeasible and also prevents small businesses from routinely assessing worker exposure. As a result, there is a strong need for new approaches that are substantially less expensive and can be performed by minimally trained individuals or even everyday citizens.

Although many approaches have been proposed as point-of-need sensors,[12,13] paper-based analytical devices (PADs) have recently gained significant attention because they are simple and inexpensive, require minimal sample, and are readily disposable.[14−17] To date, PADs have been used for point-of-care diagnostic assays, food safety assessment,[18] and environmental monitoring.[19−21] The most common detection method used with PADs is colorimetry where specific reagents are applied to the device and the developed color intensity and/or hue correlates with analyte concentration.[22] Electrochemical detection has also been used with PADs to generate electrochemical paper-based analytical devices (ePADs).[22−27] Electrochemistry is attractive due to its portability, sensitivity, and selectivity. The use of ePADs for environmental analysis has been reported but only for limited applications.[26,27]

Here, a paper-based analytical device was developed that combines colorimetric and electrochemical quantification of six metals using two separate detection layers. Colorimetric detection was used for Fe, Ni, Cr, and Cu while square-wave anodic stripping voltammetry was used to measure Pb and Cd. Separating the colorimetric and electrochemical detection areas allowed for different sample preparation methods to be applied for each technique. Following sample collection, microwave-assisted acid digestion was performed directly on a filter punch to solubilize metals.[21] For analysis, the digested punch was placed on the center of the PAD, a drop of buffer was added, and metals were eluted outward to the colorimetric detection zones and downward to the electrodes. Ferricyanide and bismuth were added to the electrode surface prior to analysis to reduce the impact of Cu on Cd electrochemistry and to create an amalgam, respectively. Using the optimized PADs, detection limits of 0.12, 0.75, 0.75, and 0.75 μg for Cr, Fe, Cu, and Ni in colorimetric detection mode and detection limits of 0.25 ng (1 μg/L) for Pb and Cd were achieved, when analysis was performed on 2 mm and 10 mm filter punches, respectively. Finally, the PADs were used to measure metal content in resuspended baghouse dust samples, and results matched known quantities of each metal deposited on the filter.

■ EXPERIMENTAL SECTION

Materials and Methods. Standards for the six metals assays were prepared from lead(II) nitrate, cadmium(II) nitrate tetrahydrate, ammonium dichromate(VI), iron(III) chloride hexahydrate, nickel(II) sulfate hexahydrate, and copper(II) sulfate pentahydrate (Sigma-Aldrich, St. Louis, MO). Potential interferences (i.e., metals commonly found in PM) were prepared from barium(II) chloride, manganese(II) chloride tetrahydrate, zinc(II) nitrate hexahydrate, vanadium(III)

chloride, silver(II) nitrate, cobalt(II) chloride, and aluminum-(III) sulfate hydrate (Sigma-Aldrich, St. Louis, MO). For colorimetric assays, phthalic anhydride, cerium(IV) ammonium nitrate, 1,5-diphenylcarbazide, dimethylglyoxime, ammonium hydroxide, sodium chloride, bathocuproine, polydiallyl-dimethylammonium chloride (medium molecular weight), and sodium fluoride (Sigma-Aldrich, St. Louis, MO) were used as received. Hydroxylamine (Fisher Scientific, Pittsburgh, PA), 1,10-phenanthroline (Acros Organics, Fair Lawn, NJ), poly-(acrylic acid) (Polysciences, Warrington, PA), polyethylene glycol (PEG) (Calbiochem, LaJolla, CA), and chloroform (Macron,) were used as received. For electrochemical detection, carbon ink (E3178, Ercon Incorporated, Wareham, MA) and Graphite powder (diameter <20 μm, Sigma-Aldrich, St. Louis, MO) were used for electrode materials. Multiwalled carbon nanotubes (MWCNT), 1000 ppm Bi standard solution (Sigma-Aldrich, St. Louis, MO), and potassium ferricyanide (Fisher Scientific, Pittsburgh, PA) were used for electrode modification. The transparency film used for electrode fabrication was purchased from Apollo Presentation Products (Booneville, MS). Sodium acetate and glacial acetic acid were obtained from Fisher Scientific (Pittsburgh, PA). The certified metal sample of baghouse dust (RTC-CRM014) was purchased from LGC Standards (Teddington, UK). Milli-Q water from Millipore ($R \geq 18.2$ MΩ cm^{-1}) was used throughout these experiments. All chemicals were used as received without further purification.

Design and Fabrication of the PAD. A wax-printing technique was used to create PADs because this fabrication process is simpler, less expensive, and faster than other reported methods.[28,29] CorelDRAW software was used to create the device design shown in Figure S1, Supporting Information. Blue, yellow, and black wax colors were generated with RGB color codes using 0−153−255, 248−195−0, and 22−24−25, respectively. The colors were selected to be complementary to the colorimetric reactions. The wax-pattern was printed onto Whatman grade 1 filter paper (VWR) using a wax printer (Xerox Phaser 8860). The wax pattern was melted at 200 °C for 120 s on a hot plate to define the hydrophobic barriers and hydrophilic channels. The hydrophilic area consisted of sample reservoir, pretreatment zone, and detection zone with diameters of 1.2, 0.3, and 0.3 cm, respectively. One side of the device was covered with clear packing tape to prevent solution leakage through the device and to add structural integrity. Finally, a 6 mm diameter hole was punched in the middle of sample reservoir using a biopsy punch to provide a solution connection between the sample and the electrode surfaces.

For electrochemical detection, a three-electrode system was screen printed onto polyester film. Unmodified carbon ink (Gwent) was printed onto the substrate to make a conductive pad and a pseudoreference electrode. Ink modified with a mixture of MWCNTs, graphite powder, and carbon ink (5:5:200) was printed three times onto the substrate to make the working and counter electrodes. To cure the inks, the transparency film was baked at 65 °C for 30 min after each screen-printing step. To complete the device, patterned paper, double sided adhesive tape, a screen-printed electrode, and 6 mm-punched double-sided adhesive tape were assembled by folding as shown in Figure 1.[30]

Colorimetric Detection of Fe, Ni, Cr, and Cu. Previously reported methods for Fe, Ni, Cr, and Cu detection on PADs were combined here.[21,31] These methods employ addition of
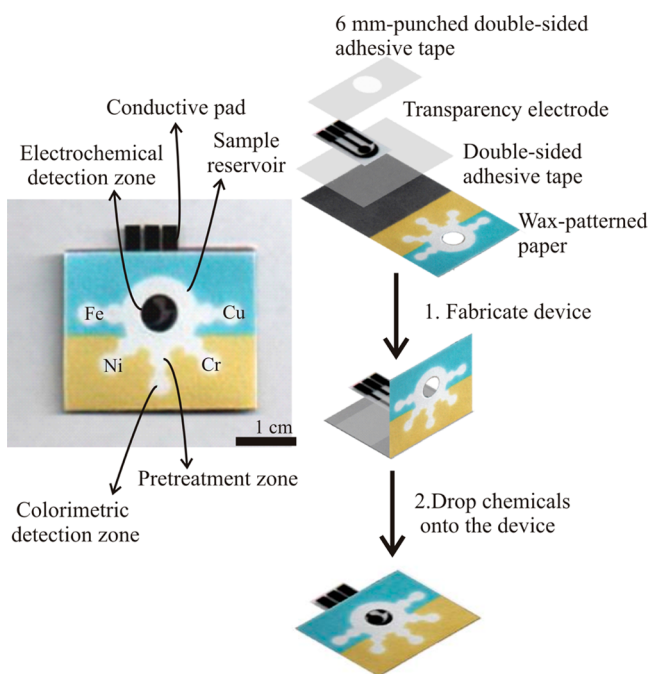
Figure 1. (Left) Photograph of a microfluidic paper-based analytical device with the different regions labeled. (Right) Schematic drawing of the fabrication procedure for the PAD.

nonvolatile reagents direct to the paper to define sample pretreatment and detection zones as described previously.[21] For colorimetric detection of Fe, the detection zone was prepared by adding 1 μL of hydroxylamine (0.1 g/mL) in 6.3 M acetate buffer. Next, 0.5 μL of poly(acrylic acid) (0.7 mg/mL) was added, followed by two 0.5 μL aliquots of 1,10-phenanthroline (8 mg/mL) in 6.3 M acetate buffer. The poly(acrylic acid) was added to immobilize the Fe−phenanthroline complex. For Ni detection, devices were prepared by adding two 0.5 μL aliquots of NaF in DI water (0.5 M), followed by 0.4 μL of acetic acid (6.3 M, pH 4.5) to define a sample pretreatment zone. Five 0.5 μL aliquots of DMG in methanol were then added to the colorimetric detection zone, followed by two 0.5 μL aliquots of ammonium hydroxide (0.03 mM pH 9.5). For Cr detection, the PAD was prepared by adding two 0.5 μL of ceric(IV) ammonium nitrate (0.35 mM), followed by 0.5 μL of poly(diallyldimethylammonium chloride) (PDDA) (5% w/v) to the pretreatment zone. Two 0.25 μL aliquots of a 1,5-diphenylcarbazide (1,5-DPC) and phthalic anhydride (15 and 40 mg, respectively, in acetone 1 mL) mixture were also added to the colorimetric detection zone. For Cu, a 1 μL aliquot of hydroxylamine (0.1 g/mL), followed by a 0.5 μL aliquot of acetic acid/NaCl buffer (10 mM, pH 4.5) was first added to the colorimetric detection zone. The Cu detection solution was prepared from 50 mg/mL bathocuproine and 40 mg/mL PEG 400 dissolved in chloroform. Two 0.5 μL aliquots of the bathocuproine/PEG detection solution were then added to the colorimetric detection zone. Between each addition of reagent, the device was allowed to dry at room temperature (22 $\pm$ 1 °C).

Electrode Modification of Bi and Ferricyanide. A mixture of Bi (100 ppm) and potassium ferricyanide (5 mM) was prepared in acetate buffer pH 4.5 (0.1 M). A 2.5 μL aliquot of this mixture was added directly to the screen-printed carbon

nanotube electrode surface and allowed to dry. The final device is shown in Figure 1B.

Analytical Procedure. For calibration, a series of 10 mm diameter punches were cut from either Whatman #1 filter paper or mixed cellulose ester (MCE) filters using a CO_2 laser cutter (Zing). Standards were added to punches and allowed to dry. The punch was placed at the center of the sample reservoir. As shown in Figure S2, Supporting Information, a polydimethylsiloxane (PDMS) lid consisting of one 2 mm-diameter hole over the sample reservoir and five 5 mm-diameter holes over the colorimetric detection zones was then aligned over the device, and the device was connected to the potentiostat. The lid reduced evaporation during analyte transport from the sample to detection zones. The PDMS cover also provides consistent pressure across the surface of the device, maintaining conformal contact between the filter and device across the entire filter punch. 50 μL of 0.1 M acetate buffer (pH 4.5) was added to the center hole of the PDMS lid causing the soluble metals to flow through the channels to the colorimetric detection zones and down to the electrodes.

Square-Wave Anodic Stripping Voltammetric Detection. Electrochemical measurements were made at room temperature (22 $\pm$ 1 °C) using a potentiostat (CHI 660B, CH Instruments, Austin, TX). Square-wave anodic stripping voltammetry was performed for sample measurement using the following (optimized) conditions: conditioning potential (E_{cond}) +0.0 V for 5 s, deposition potential (E_{dep}) −1.5 V for 240 s, equilibration time (t_{eq}) 5 s, SW amplitude (E_{amp}) 15 mV, step potential (E_{step}) 5 mV, frequency (f) 15 Hz, and scanning potential −1.5 to 0.0 V. All measurements were made against a carbon pseudoreference counter electrode on the PAD.

Image Processing. After electrochemical detection, a scanner (XEROX DocuMate 3220) was used to capture the device image for colorimetric measurements. Collected images were saved in JPEG format at 600 dpi and analyzed using ImageJ software (National Institutes of Health) using previously developed methods from our laboratory.[21,32] The software was used to measure the mean intensity of the color for each colorimetric reaction. As shown in Figure S3, Supporting Information, the hue of interest was selected by applying a color threshold window specific for each metal/reagent complex. The optimum threshold color ranges for removing the blue and yellow background colors were (20,210) and (0,180), respectively. Images were then converted to gray scale and inverted. The mean intensity was then measured and imported into Origin (v 8.0, MicroCal) for analysis. Alternative methods that do not rely on conversion to grayscale are also available and gave similar results.[33,34]

Particulate Metal Collection and Digestion. Dust samples were generated in a 1 m^3 chamber. Using an aerosol photometer (TSI, Model 8250), the average concentration in the chamber was measured at 0.73 mg m^{-3}. The relative humidity (RH) was monitored and remained <50% RH during all experiments. The dust was reaerosolized and collected at a flow rate of 10 L/min for 4 h onto 37 mm Pallflex or mixed cellulose ester (MCE) filters. For the Pallflex filter, gravimetric analysis was used to measure the dust mass by weighing the filter before and after sampling using a Mettler-Toledo analytical microbalance (MX5), yielding an average of 1.25 mg ash per cm^2 on the filter. A 20 μL aliquot of sodium dodecyl sulfate (1 mM) was added to each 10 mm MCE punch to make it more hydrophilic prior to metal digestion. Microwave-assisted acid digestion was performed by adding 5 μL of

concentrated nitric acid followed by 30 μL of water to the filter punches. The punches were placed in a household microwave on high power (1100 W). The filter was heated for 15 s three times, and 30 μL of water was added to the punches between each heating step. Finally, 10 μL of sodium bicarbonate (0.5 M pH 9.5) was added to neutralize the digested sample. After adding the sodium bicarbonate, the filter was heated again for 15 s. Finally, the digested filter was placed on the center of the PAD and analyzed as described above.

■ RESULTS AND DISCUSSION

Device Design. Simultaneous profiling of multiple metals using both colorimetric and electrochemical methods is
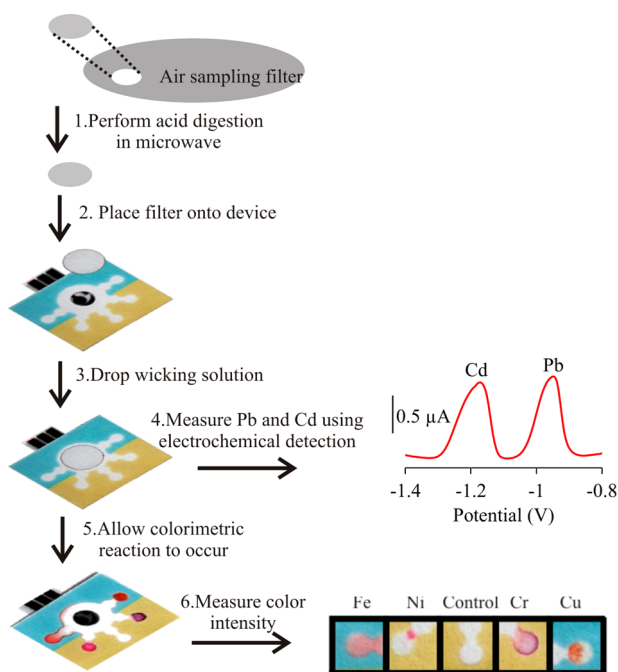

Figure 2. Analytical procedure for metal assays using the PADs. The assay requires three steps, (i) microwave-assisted acid digestion, (ii) anodic stripping voltammetric detection of Pb and Cd, and (iii) colorimetric detection of Fe, Ni, Cr, and Cu.

challenging because each method requires different sample pretreatment steps. As a result, it is more common to analyze a small subset of metal species using any one technique when applying these detection modalities. To reduce overall analysis cost and complexity, a PAD was designed to allow detection of multiple metals using both modalities simultaneously. Key to this development is the ability to isolate each colorimetric step from the electrochemical detection steps to allow distinct chemical reactions to occur for each analysis. The PAD design and fabrication steps used to accomplish this goal are shown in Figure 1, and the operational procedure is shown in Figure 2. The top layer contains five wax-defined channels extending outward from an open sample reservoir. Each channel contains unique sample pretreatment and detection zones that give both metal selectivity and sensitivity. For electrochemistry, MWCNT modified carbon inks were screen-printed onto polyester and then modified with Bi and ferricyanide to enhance stripping signals and reduce Cu interference, respectively.[35,36] The electrodes were aligned below the colorimetric detection layer and isolated by double sided adhesive tape. Upon sample
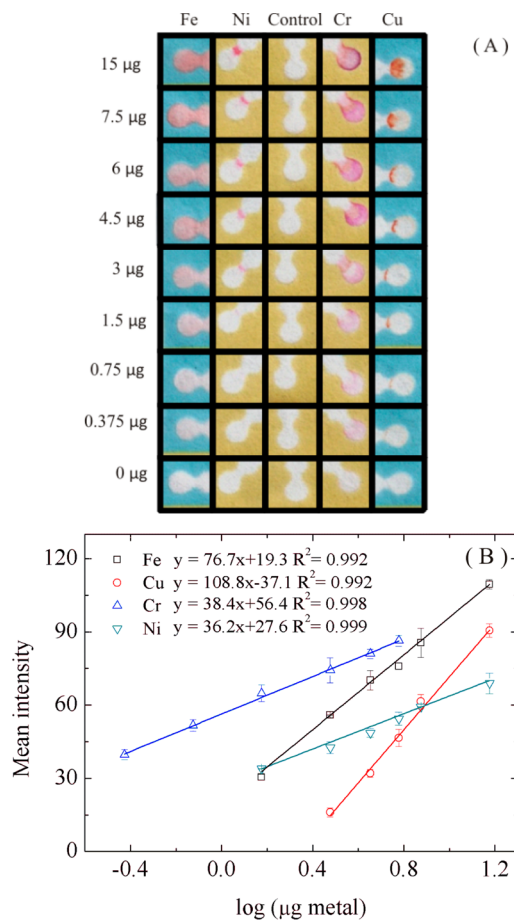

Figure 3. (A) Visual color changes obtained from detection of Fe, Cu, Cr, and Ni. (B) Representative calibration graph for each metal using a logarithmic metal concentrations and mean intensity.

addition, solution moved downward to wet the electrodes in the bottom layer while also moving outward to wet the colorimetric detection channels. The device shown here represents the first integration of all four colorimetric methods along with electrochemical methods for Pb and Cd.

Colorimetric Detection of Fe, Ni, Cr, and Cu. On-device images of colorimetric reaction products and associated calibration curves for all four species are shown in Figure 3A,B, respectively. The specifics of the chemistry for each analysis has already been reported.[21,31] For Fe, Fe(III) was reduced to Fe(II) at the sample pretreatment zone using ascorbic acid. The resulting linear range of 1.5−15 μg was established for total on-filter Fe, and a visual detection limit of 0.75 μg was achieved. For Ni, we adjusted the pH to ∼9.0 and added NaF and acetic acid as masking agents for Fe to the pretreatment zone. The resulting linear range for Ni was 1.5− 15 μg for total on-filter Ni with a visible detection limit of 0.75 μg. The visible detection limit is defined as the lowest mass for which the complexation product was still visible against the substrate background with the unaided eye. To control user bias, untrained individuals were asked to identify which device contained a colored product with the lowest (yet still visible) intensity. Detection of Cu was performed at acidic pH 4.5, and the surface of the detection zone was modified with polyethylene glycol to trap the hydrophobic Cu−bathocuproine complex. The operating range and detection limit of Cu were 3.0−15 μg and 0.75 μg, respectively. For Cr, soluble Cr(III)
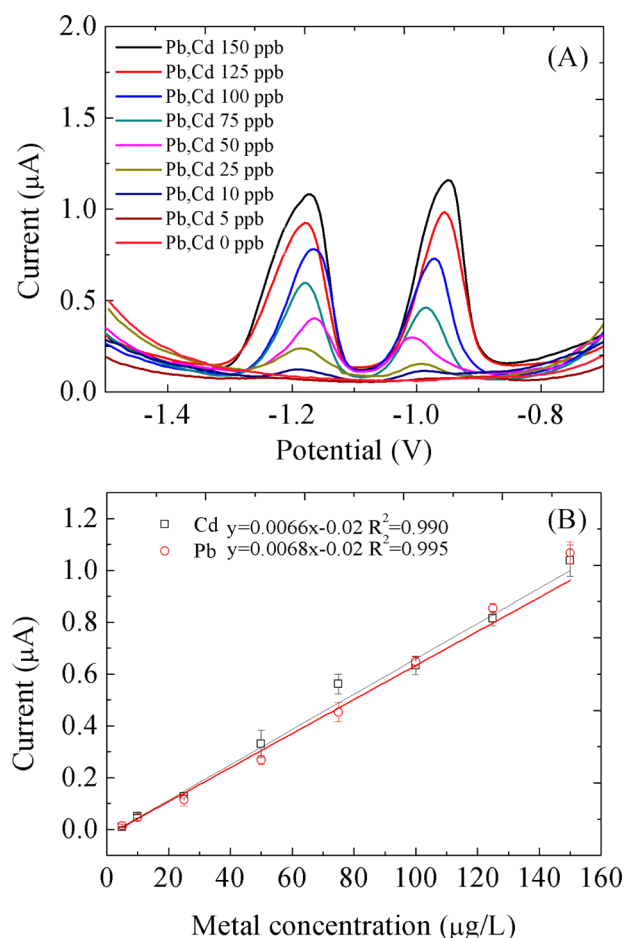
Figure 4. (A) Square-wave voltammogram showing electrochemical detection of Cd and Pb. (B) Representative calibration graph between metal and anodic current of Cd and Pb.

Table 2. Tolerance Ratio of Interfering Ions in the Electrochemical Determination of 2.5 ng (50 $\mu g/L$) of Pb(II) and Cd(II)

interfering ion	5% tolerance ratio	
	Cd	Pb
Mn(II)	10 000	10 000
Mg(II)	1000	1000
Zn(II)	1000	1000
Fe(II)	1000	1000
Fe(III)	1000	100
Al(III)	100	100
Ba(II)	100	100
V(III)	100	100
Ni(II)	100	10
Cr(VI)	50	50
Co(III)	10	10
Cu(II)	2	5

metry (ASV) is frequently used.[37,38] Due to the low levels of Pb and Cd in most types of PM, ASV was used in conjunction with Bi and ferricyanide additives. Bi improves ASV performance because it forms a metal-Bi alloy at the electrode surface during preconcentration and allows for the stripping measurement to be performed without deoxygenation.[35] Furthermore, bimodified electrodes have lower toxicity than mercury-modified electrodes.[35] Under optimized conditions, anodic peaks for Cd and Pb were obtained at -1.10 ± 0.04 and -0.91 ± 0.04 V ($n = 4$) versus pseudoreference carbon electrode. Under the optimized conditions, the anodic peak currents were proportional to Cd and Pb levels in the range of 0.25−7.5 ng (5−150 $\mu g/L$) with regression coefficients of 0.990 and 0.995, respectively (Figure 4A,B). The relative standard deviation for the method was found to be 9.79% and 7.02% for Cd and Pb, respectively. The detection limit was found to be 0.25 ng (1 $\mu g/L$) for both Cd and Pb. Analytical performance data for all six metals are summarized in Table 1, and the multilayer PAD can provide sensitive, selective analysis of multiple metals simultaneously. Furthermore, this system has the ability to isolate each analytical reaction so that simultaneous detection of multiple metals can be conducted in a single device. Table S2, Supporting Information, provides a comparison of microfluidic paper-based analytical device (mPAD) performance versus existing methods as well as the reported minimum detectable level (MDL) and minimum detectable level for an 8 h time-weighted average.[21,39−44] The results clearly show our ability to make measurements in relevant concentration ranges.

Interference Study for Cd and Pb. Because airborne PM contains many different metals that could interfere with ASV, the tolerance ratio for interfering metal species was measured.

was oxidized to Cr(VI) using Ce(IV) on the PAD and then reacted with 1,5-diphenylcarbazide.[31] A linear calibration curve was obtained in the range of 0.38−6.0 μg, and the visible detection limit was found to be 0.12 μg. The linear working ranges and detection limits reported here are appropriate for measuring integrated 4 to 8 h filter samples from occupational settings. Variability in the detection limits is largely the result of the molar absorptivity of each final complex. The upper end of each range occurred where the paper became saturated with the complex, and additional complexation did not result in additional increases in color intensity.

Electrochemical Detection of Cd and Pb. For monitoring low levels of heavy metals in biological, food, fuel, and/or environmental samples, anodic stripping voltam-

Table 1. Summarized Analytical Performance of Proposed 3DPAD for Each Metal Assay

metal	linearity	MDL[a]	%RSD ($n = 3$)[b]	detection mode
Fe	1.5−15 μg	0.75 μg	8.84	colorimetric detection
Cu	3.0−15 μg	0.75 μg	9.54	colorimetric detection
Ni	1.5−15 μg	0.75 μg	8.52	colorimetric detection
Cr	0.38−6.0 μg	0.12 μg	4.01	colorimetric detection
Pb	5−150 $\mu g/L$	0.25 ng (1 $\mu g/L$)	7.02	electrochemical detection
Cd	5−150 $\mu g/L$	0.25 ng (1 $\mu g/L$)	9.79	electrochemical detection

[a]Minimum detectable level (MDL) was observed from the lowest level of metals detected on a 10 mm filter punch. [b]Relative standard deviation (% RSD) was calculated from triplicate ($n = 3$) calibration curves.
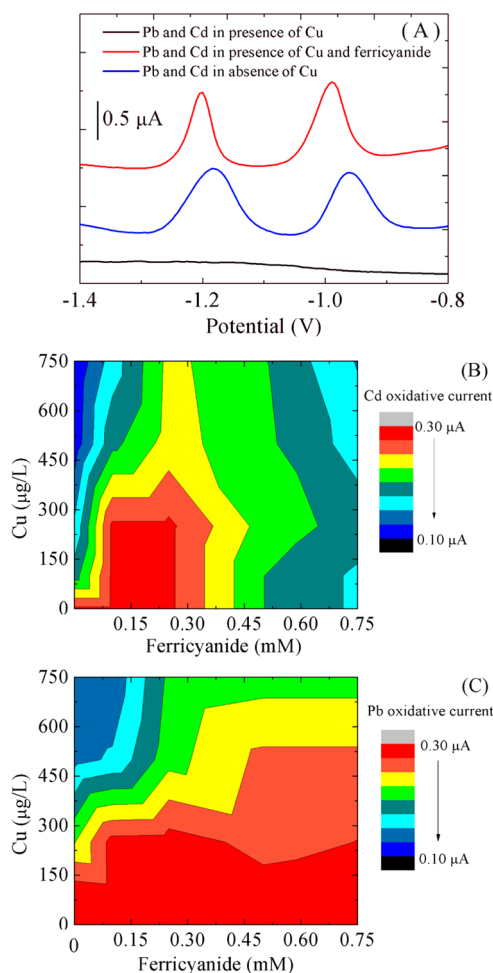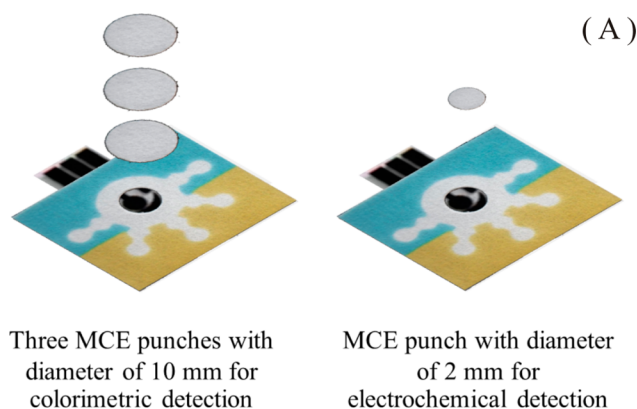
Figure 5. (A) Influence of ferricyanide concentration for elimination of Cu effect in square-wave anodic stripping voltammetric detection of Cd and Pb. Contour plot between Cu concentration and ferricyanide affecting (B) Cd detection and (C) Pb detection electrochemically.

Figure 6. (A) Variation of the size and number of filter punches for determination of metals using the PAD. A single 2 mm punch was used for electrochemical methods while three 10 mm punches were best suited for colorimetric measurements. (B) Results from electrochemical and colorimetric detection by our proposed 3DPAD. [1]Measured level obtained from three dependent measurements (n = 3); [2]ND, not detectable.

The tolerance ratio is defined as the concentration of metals ions that generates a change in the peak height of less than 5% for Pb and Cd anodic peaks.[45] The maximum concentrations of interfering metals are shown in Table 2 when using 2.5 ng (50 μg/L) of Pb and Cd as the sample. From the results, it was concluded that Mn(II), Mg(II), Zn(II), Fe(III), Fe(II), Al(III), Ba(II), and V(III) ions did not affect Pb and Cd detection. On the other hand, Ni(II), Co(II), Cu(II), and Cr(VI) significantly impacted sensitivity. To minimize this problem, two solutions are possible: (i) diluting the aerosol sample by decreasing the size of the sampling filter while simultaneously maintaining extraction volume and (ii) complexation of Cu(II) using ferricyanide. Dilution represents a simple solution for ASV since the deposition step allows for preconcentration and was used for Ni(II), Co(II), and Cr(VI) interferences. Furthermore, these ions should be at very low levels in the proposed samples.[46] Cu levels are anticipated to be much higher, however, and thus additional optimization was required.

Minimizing the Cu(II) Interference Using Ferricyanide. The well-known Cu(II) interference has been previously described and attributed to the formation of intermetallic compounds of the target metals with deposited Cu.[47] The suppression of the ASV signal for Pb and Cd in the presence of Cu results from competition between electrodeposited bismuth

and copper intermetallic compounds at the electrode surface because the reduction potential of Cu is close to the reduction potential of Bi. In the absence of Cu(II), well-defined Pb(II) and Cd(II) peaks were observed as shown in Figure 5A. In the presence of 25 ng (500 μg/L) of Cu(II), ASV responses for both Pb(II) and Cd(II) were significantly diminished. To suppress the effect of Cu(II) on Pb and Cd detection, various compounds have been used to complex the Cu(II) including ferrocyanide[48] and cyanide.[49] In our experiment, ferricyanide was selected to complex with Cu(II) because it is less toxic than cyanide.[50] Suppression of the Cu signal was presumably due to the strong complexation between Cu and cyanide, leading to shift of the Cu oxidation potential to more negative potential over the potential range of −1.5 to 0.0 V. The optimum ferricyanide concentration was determined from contour plots of Cu and ferricyanide concentrations shown in Figure 5A,B. In the presence of 30 μg (500 μg/L) of Cu(II), complete recovery of Pb(II) and Cd(II) anodic peak currents was achieved when 0.25 mM of ferricyanide was added to the device prior to Pb and Cd measurements. These results demonstrate the importance of separating the detection modes because the highly colored ferricyanide would interfere with any of the colorimetric reactions.

Metal Determination in Resuspended Baghouse Dust. To validate the multilevel PAD approach, a baghouse dust

sample certified for Cd, Cr, and Pb and containing unknown amounts of Al, Sb, As, Ba, B, Be, Ca, Co, Cu, Fe, Mg, Mn, Hg, Mo, Ni, P, K, Ag, Se, Na, Sr, Tl, Sn, Ti, V, and Zn was analyzed from a filter sample. To generate a PM sample filter, dust was nebulized in an aerosol chamber and collected onto MCE filters at 10 L/min for 4 h. Sodium dodecyl sulfate (SDS) was used to pretreat the hydrophobic MCE filter after sample collection but before acid digestion.[19] Adding SDS to the MCE punch reduced its hydrophobicity, allowing aqueous solutions to penetrate through the MCE punch for elution. Metal concentrations measured from resuspended baghouse dust samples are shown in Figure 6B. As shown in the Figure 6A, a single 2 mm punch could be used for electrochemical detection, while three 10 mm punches were needed for colorimetric detection. The measured values were not statistically different from the known masses on the filters and demonstrate the accuracy of the system reported here.

CONCLUSIONS

A PAD was developed to measure particulate metals as part of an effort to reduce the overall cost and operation complexity of this measurement. The key development reported here is the use of two separate detection layers, one for colorimetric detection and one for electrochemical detection. Separating detection layers allowed for each layer to contain unique chemistries to improve sensitivity and selectivity. Using the method, six metals (Cd, Pb, Fe, Cu, Ni, and Cr) were determined simultaneously from PM collected on sample filters. Metal levels measured using the PAD matched those using traditional approaches.

ASSOCIATED CONTENT

⑤ Supporting Information

Additional information as noted in text. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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