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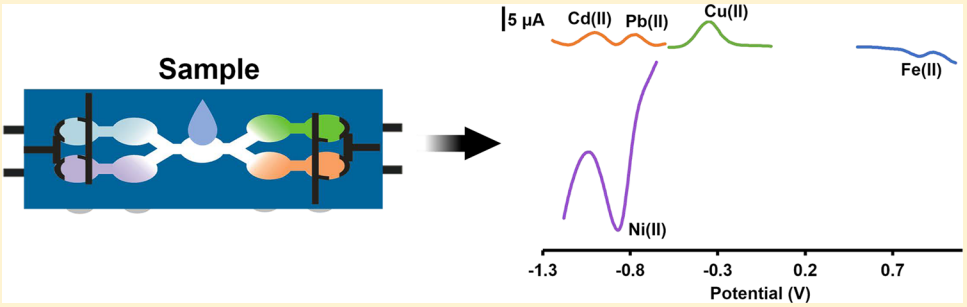
Janus Electrochemical Paper-Based Analytical Devices for Metals Detection in Aerosol Samples

Jaruwan Mettakoonpitak,[†,‡] John Volckens,[§] and Charles S. Henry*[,‡]

[†]Department of Chemistry, Faculty of Science and Technology, Rambhai Barni Rajabhat University, Chantaburi 22000, Thailand
[‡]Department of Chemistry, and [§]Department of Mechanical Engineering, Colorado State University, Fort Collins, Colorado 80523, United States

Supporting Information



ABSTRACT: Exposure to trace metals in airborne particulate matter (PM) has been linked to various adverse health effects. Quantifying metals in PM is important; however, current analytical tools tend to be bulky and expensive. A need therefore exists for more rapid, low-cost, portable tools for multiplexed determination of metals in PM. Electrochemical paper-based devices (ePADs) have been used for detecting metals in PM but require different devices and methods for different metals, making the systems more complicated than desired. Recently reported Janus ePADs offer a solution to this problem by allowing for multiple electrochemical experiments from a single sample. Here, we sought to determine if a Janus ePAD containing four independent channels and working electrodes could be used for simultaneous detection of multiple metals in PM. Online sample pretreatment in each channel during sample delivery yielded optimal conditions for each experiment. The design allows the device to conduct square-wave anodic stripping voltammetry (SWASV) and square-wave cathodic stripping voltammetry (SWCSV) for simultaneous detection of Cd, Pb, Cu, Fe, and Ni from a single sample. Two detection zones each with shared reference and counter electrodes were used for SWASV and SWCSV, respectively. The proposed sensors reached LODs down to 0.5, 0.5, 1.0, 0.5, and 1.0 μg L^{-1}, for Cd(II), Pb(II), Cu(II), Fe(II), and Ni(II), respectively. The linear working ranges were 0.5−400.0 μg L^{-1} for Cd(II), Pb(II), and Fe(II), 1.0−400.0 μg L^{-1} for Cu(II), and 0.5−200.0 μg L^{-1} for Ni(II). The devices were applied for Cd(II), Pb(II), Cu(II), Fe(II), and Ni(II) determination in PM samples, and the results agreed with those using traditional ICP-MS analyses at 95% confidence.

Metals are frequently present in ambient particulate matter (PM) at trace (i.e., ng/m^3) levels. Long-term or high-dose exposure to aerosolized trace metals, mainly released from oil fly ash and coal fly ash, is associated with increased mortality.[1−3] Further, inhalation of trace metals, such as Cd, Pb, Cu, Ni, and Fe, has been associated with damage to the respiratory and cardiovascular systems.[3−8] In addition to direct toxicity, some metals such as Fe and Cu are linked to oxidative stress in humans via reactive oxygen species (ROS) production from Fenton chemistry.[9−11] Oxidative stress from ROS in PM is widely hypothesized as a mechanism for adverse health effects stemming from oxidative protein damage, DNA mutation, and DNA-adduct formation.[12−14] Thus, trace metals analysis in PM is needed to monitor potential PM toxicity.

Analyzing the metal content of PM is traditionally performed using inductively coupled plasma mass spectrometry (ICP-MS) or atomic absorption spectrometry (AAS).[15−18] These methods require large, expensive instruments, complicated procedures, and trained users, which often precludes their use in resource-limited settings. More affordable, portable, and simpler devices such as microfluidic paper-based analytical devices (mPADs) have been developed to address the limitations of ICP-MS and AAS technologies (especially for application in developing countries where the risks of exposure to metal-containing PM is high).[19,20] The limits of detection (LODs) of mPADs using colorimetric detection are not sensitive enough, however, to detect trace metals in PM (at ng m^{-3} levels). Electrochemical detection has been integrated into low-cost devices for analyzing some toxic metals including Zn, Cd, Pb, Ni, and Co in PM at trace levels

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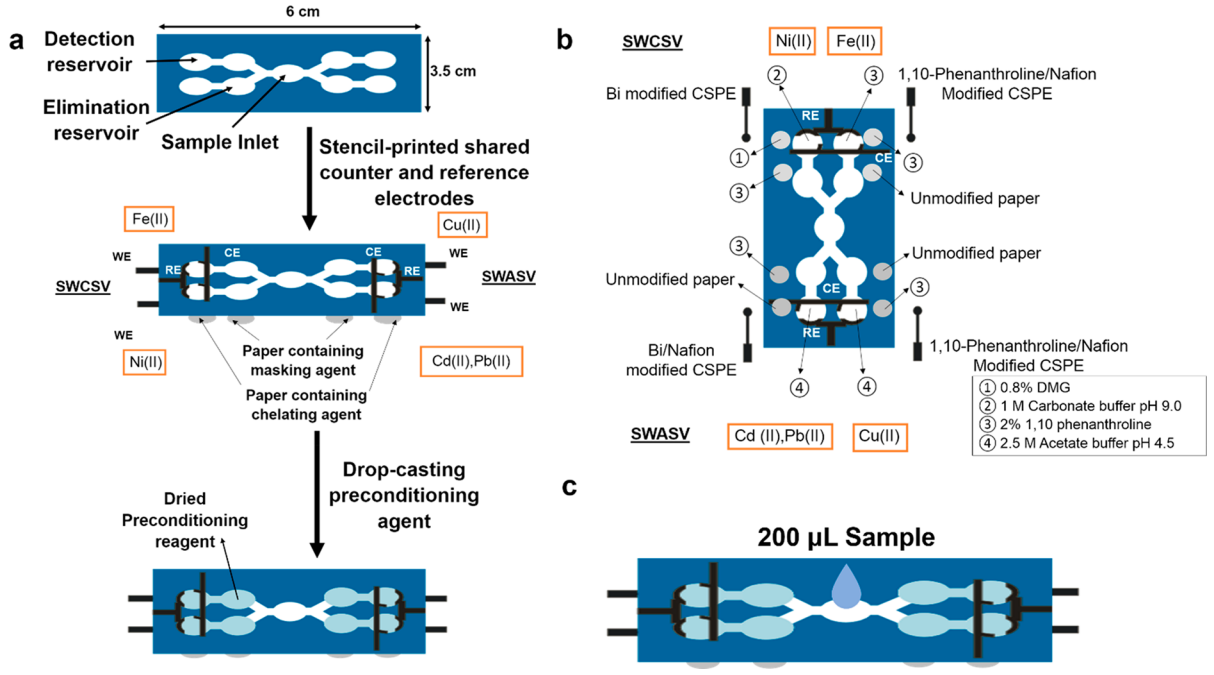

Figure 1. Schematic for (a) fabrication of Janus paper substrate showing manufacturing steps, (b) the details of working conditions, chelating agent, masking agent, and working electrodes positioned on Janus ePADs for simultaneous Cd(II), Pb(II), Cu(II), Fe(II), and Ni(II) detection, and (c) a ready-to-use Janus ePAD. The acronyms are defined as follows: SWCSV, square-wave cathodic stripping voltammetry; SWASV, square-wave anodic stripping voltammetry; DMG, dimethylglyoxime; CSPE, carbon stencil-printed electrode; WE, working electrode; RE, reference electrode; and CE, counter electrode.

to address this problem.[20−22] However, previous devices could detect a few metals in PM at once at most, limiting device utility.

Here, Janus ePADs are introduced for simultaneously detecting Cd, Pb, Cu, Fe, and Ni in collected samples of PM. Janus ePADs use multiple channels to create multiple unique solution conditions on a single device.[23] Working electrodes at the channel outlets allow simultaneous electrochemical detection of analytes at their optimal conditions while sharing a common reference and counter electrode. Prior Janus ePADs detected organic molecules; we sought to determine if the system could be used for simultaneous analysis of multiplexed metals using a single device. In the Janus ePADs, paper channels store reagents that pretreat sample before it reaches the electrochemical detection zones. Unlike normal ePADs, however, Janus ePADs have multiple channels and multiple working electrodes to enable detection of analytes at their optimal conditions while sharing reference and counter electrodes to reduce device complexity. The proposed design consisted of two regions for different forms of stripping voltammetry. Simultaneous operation between square-wave anodic stripping voltammetry (SWASV), for Pb, Cd, and Cu, and square-wave cathodic stripping voltammetry (SWCSV), for Fe and Ni, were carried out. Additionally, the design consisted of an interference elimination layer for removing interfering metals. The proposed Janus ePADs achieved LODs of 0.5, 0.5, 1.0, 0.5, and 1.0 μg L^{-1} (i.e., ng m^{-3} levels), for Cd(II), Pb(II), Cu(II), Fe(II), and Ni(II), respectively. As proof they could be used on real samples, the developed devices were applied for detecting metals in aerosol samples collected from wood-burning and coal-burning stoves. The proposed method was compared to inductively coupled plasma mass spectrometry (ICP-MS), and the techniques provided similar results at the 95% confidence level.

EXPERIMENTAL SECTION

Materials and Methods. Bismuth(III) oxide, sodium dodecyl sulfate (SDS), sodium acetate trihydrate, 1,10-phenanthroline, and trimethylsilylated Nafion were purchased from Sigma−Aldrich (St. Louis, MO). Iron(II) sulfate, sodium carbonate, cadmium(II) nitrate tetrahydrate, and lead(II) nitrate were purchased from Fisher Scientific (Waltham, MA). Copper(II) nitrate, ammonium hydroxide, sodium bicarbonate, and nitric acid were purchased from Mallinckrodt (St. Louis, MO). Nickel(II) sulfate hexahydrate was purchased from Acros (Morris, NJ). Dimethylglyoxime (DMG) was purchased from Fluka (St. Louis, MO). Glacial acetic acid and isopropanol were purchased from EMD Millipore (Billerica, MA). Ethanol was purchased from Pharmco-Aaper (Brookfield, CT). Milli-Q water from Millipore ($R \geq 18.2$ MΩ cm) was used for all experiments. All chemicals were used as received without further purification. Carbon ink purchased from Ercon (Wareham, MA), graphite powder (diameter < 20 μm, Sigma−Aldrich, St. Louis, MO), and transparency film PP2200 (3M, St. Paul, MN) were used for electrode fabrication. Paper substrates were created from Whatman Type 1 chromatography paper. A 30-W Epilog Zing Laser Cutter and Engraver (Golden, CO) was used to create electrode patterns on a transparency sheet using Corel Draw X4 program for stencil printing. A wax printer (Xerox Phaser 8860) was used for creating the wax pattern on the filter paper. A CHI1832 bipotentiostat (CH Instruments) was used for all electrochemical measurements.

Fabrication of Carbon Stencil-Printed Electrodes (CSPEs). CSPEs were fabricated as previously described.[21,24−26] Stencil inks were prepared by adding 0.43 g of graphite to 1.00 g of the commercial carbon ink to increase electrochemical conductivity, followed by hand mixing until

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homogeneous. For electrode modification, working, counter, and reference electrodes were stencil printed on a polyethylene transparency (PET) sheet through a laser-cut stencil. The circle-shaped working electrode had a 3 mm diameter. The electrodes were dried at 65 °C for 1 h. A laser-cut, ring-shaped piece of adhesive tape was used for confining the solution droplet to the electrodes (Figure S1a). A photograph of a representative CSPE is shown in Figure S1b.

Electrode Modification. *Bi/Nafion-Modified CSPEs for Pb(II), Cd(II), and Ni(II) Detection.* Bi/Nafion-modified CSPE was performed as previously described.[21,25] 1 μL of 0.5% w/v Nafion dissolved in 50% v/v isopropanol/water was drop-cast coated onto the CSPE working electrode and allowed to dry. 50 μL of 50 mg mL^{-1} Bi_2O_3 in 0.1 M acetate buffer pH 4.5 was electrodeposited on the CSPE surface using an optimum deposition potential of −1.4 V vs carbon pseudoreference electrode and a deposition time of 5 min for Pb(II) and Cd(II) detection and 20 min for Ni(II) detection. After Bi modification, the CSPE was rinsed with 0.1 M acetate buffer pH 4.5 for Pb(II) and Cd(II) and 2 M carbonate buffer pH 9.0 for Ni(II) prior to use.

1,10-Phenanthroline/Nafion-Modified CSPEs for Cu(II) and Fe(II) Detection. 1,10-Phenanthroline/Nafion-modified CSPEs were prepared by drop-casting 1 μL of 0.5% w/v Nafion dissolved in 50% v/v isopropanol/water onto the CSPE working electrode and allowing the solvent to evaporate. 5.0 μL of the optimum 2% w/v 1,10-phenanthroline in 0.1 M acetate buffer pH 4.5 was then drop-cast onto the Nafion-modified CSPE and allowed to dry. The 1,10-phenanthroline/Nafion-modified CSPEs were rinsed with 0.1 M acetate buffer pH 4.5 prior to use.

A Janus Electrochemical Paper-Based Platform Fabrication and Operation. The Janus ePAD design is shown in Figure 1a. Device patterns were drawn with CorelDraw X4 and wax printed (Xerox ColorQube) on Whatman 1 filter paper. The patterned paper was heated at 150 °C on a hot plate for 90 s to melt the wax. The device consisted of a sample inlet and two regions for SWASV detection and SWCSV detection. Cd(II), Pb(II), and Cu(II) were measured using SWASV, while Fe(II) and Ni(II) were determined using SWCSV. Each region features shared electrode arms (counter and reference electrodes), which were carbon stencil-printed. The modified working electrodes were placed under the channel outlets using adhesive double-sided tape. Each arm included detection and elimination reservoirs, at which a chelating solution-containing paper disk and a masking agent-containing paper disk were placed underneath, respectively. The final device viewed from above and the bottom is shown in Figure S2.

The operational details are shown in Figure 1b. Three 9-μL aliquots of each preconditioning reagent, masking agent, and chelating agent were added for all of the steps. Between each reagent addition, the paper was dried at room temperature. The preconditioning solution was dried directly in each device channel. The following preconditioning agents were used for each assay: 2.5 M acetate buffer pH 4.5 for Cd(II), Pb(II), Cu(II), and Fe(II) detections and 1 M carbonate buffer pH 9.0 for Ni(II) detection. To remove interferences, a masking agent was added to a 5 mm disk of Whatman 1 paper, and the disk was placed under the elimination reservoirs. 2% w/v 1,10-phenanthroline dissolved in 2.5 M acetate buffer pH 4.5 was used as masking agent to remove Cu(II) for Cd(II) and Pb(II) detection and Fe(II) for Ni(II) detection. For complexing metals, a chelating solution was added onto a 5 mm disk of Whatman 1 filter paper and then placed between the detection reservoir and the working electrode layer. The following chelating agents were used for each assay: 2% w/v 1,10-phenanthroline dissolved in 2.5 M acetate buffer pH 4.5 for Cu(II) and Fe(II) detection, and 0.8% w/v DMG for Ni(II) detection. An unmodified Whatman 1 filter paper piece was additionally put under the detection reservoir of the Cd(II) and Pb(II) arm and the elimination reservoir of the Cu(II) and Fe(II) arm for balancing fluid flow rate. The additional parts of the ePAD, including paper pieces and working electrodes, were firmly attached to the ePAD using Scotch packing tape. Figure 1c shows the ready-to-use device. A 200 μL aliquot of sample solution was introduced into the sample inlet to start the analysis.

Electrochemical Detection. *Cu(II) and Fe(II) Detection Optimization.* For Cu(II), SWASV was performed by pipetting 50.0 μL of standard Cu(II) in 0.1 M acetate buffer pH 4.5 (used as supporting electrolyte) containing the optimum 0.7 mM 1,10-phenanthroline onto the 1,10-phenanthroline/Nafion-modified CSPE. The potential was swept from −0.70 to 0.0 V versus a carbon pseudoreference electrode. The electrochemical conditions for potential increment, amplitude, and frequency were 5 mV, 75 mV, and 20 Hz, respectively. An optimum deposition potential and an optimum deposition time were set at −0.5 V and 150 s, respectively. SWASV was performed after a 10 s equilibration time.

For Fe(II), SWCSV was performed by pipetting 50.0 μL of standard Fe(II) in 0.1 M acetate buffer pH 4.5 (used as supporting electrolyte) containing the optimum 0.7 mM 1,10-phenanthroline onto the 1,10-phenanthroline/Nafion-modified CSPE. The potential was swept from 1.1 to 0.4 V versus a carbon pseudoreference electrode. The optimum electrochemical parameters for potential increment, amplitude, and frequency were 5 mV, 75 mV, and 5 Hz, respectively. An optimum deposition potential and time were set at −0. V and 240 s, respectively. SWCSV was performed after a 10 s equilibration time.

Simultaneous Cd(II), Pb(II), Cu(II), Fe(II), and Ni(II) Detection Using Janus ePADs. Simultaneous metal determination was carried out using two bipotentiostats operating in a four-electrode configuration. For Cd(II), Pb(II), and Cu(II) simultaneous detection using SWASV, the potential was swept from −1.8 to 0 V versus a carbon pseudoreference electrode. The optimum electrochemical parameters for potential increment, amplitude, and frequency were 15 mV, 75 mV, and 10 Hz, respectively. The optimum deposition potential and time were set at −1.7 V and 360 s, respectively. SWASV was performed after a 10-s equilibration time.

For Fe(II) and Ni(II) simultaneous detection using SWCSV, the potential was swept from 1.1 to −1.4 V versus a carbon pseudoreference electrode. The optimum electrochemical parameters for potential increment, amplitude, and frequency were 5 mV, 75 mV, and 5 Hz, respectively. An optimum deposition potential and time were set at −0.85 V and 360 s, respectively. SWCSV was performed after a 10-s equilibration time.

Sample Collection and Sample Preparation. Aerosol samples from wood-burning and coal-burning stoves were collected using ultrasonic personal aerosol samplers (UPAS) on 37 mm diameter MTL Teflon filters (Minneapolis, MN).[27] The masses of the PM aerosol samples are shown in Table S1.

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A 5 mm diameter punch was removed from the 37 mm diameter filter for electrochemical analysis. Before quantifying metals, punches were digested using microwave assisted digestion as previously described.[28] The digestion was achieved by adding 8 μL of 5% w/v SDS in Milli-Q water to aid in filter wetting and 2 μL of concentrated nitric acid onto the 5 mm diameter punch. The punch was then placed in a microwave on high power for 15 s and repeated twice (i.e., a total of three heated digestions for 45 s total). A 15 μL aliquot of 5% w/v SDS was added to the punch between each heating step. Each punch was neutralized with 2 M Na_2CO_3 after the last digestion step. Verification that the punch was neutralized was performed with pH paper. Milli-Q water was used to elute metals from the digested filter and the digestion container. 50 μL of the eluent was simultaneously analyzed for Pb(II), Cd(II), Cu(II), Fe(II), and Ni(II) from three punches of each sample filter to create replicate measurements. The completeness of microwave assisted digestion was verified using the incinerator ash certified reference materials (CRM012-100). 0.1 g of the incinerator ash was dispersed in 0.1 mL of Milli-Q water using a vortex mixer (Scientific Industries, Inc., Bohemia, NY) for 1 min. The dispersed solution was dropped on a 5 mm diameter punch of a MTL Teflon filter and allowed to dry. The digestion procedures were performed as previously described[28] and analyzed Pb(II), Cd(II), Cu(II), Fe(II), and Ni(II) using the Janus ePADs.

RESULTS AND DISCUSSION

Cu(II) and Fe(II) Detections Using Individual CSPEs. Cu(II) and Fe(II) in PM are believed to impact human health via ROS production,[9−11,29−31] but their measurements using ePADs have not been reported. Here, the methods for Cu(II) and Fe(II) measurements using adsorptive stripping voltammetry were investigated prior to applying them to Janus ePADs. 1,10-Phenanthroline was used as a chelating agent for complexing Cu(II)[32] and Fe(II).[33] Nafion was used as a coating because the sulfonate group in Nafion allows selective preconcentration of cations leading to improved electrochemical signal.[34] Cu(II) was determined using adsorptive SWASV as shown in Figure S3a. The voltammograms show a peak potential of −0.36 ± 0.02 V. The peak current for 200 μg L^{-1} Cu(II) using 1,10-phenanthroline/Nafion-modified CSPEs (4.54 ± 0.09 μA) improved as compared to the unmodified CSPEs (0.37 ± 0.10 μA) by a factor of 12. The effect of 1,10-phenanthroline concentration for chelating Cu(II) was studied as shown in Figure S4a. The anodic peak current increased with increasing 1,10-phenanthroline concentration to 0.7 mM, at which the maximum adsorbed Cu(II)-1,10-phenanthroline complex was established.[35,36] The decrease of peak current at 1,10-phenanthroline concentrations greater than 0.7 mM is a result of competitive adsorption of free ligand.[37] Therefore, the optimum 1,10-phenanthroline concentration was 0.7 mM.

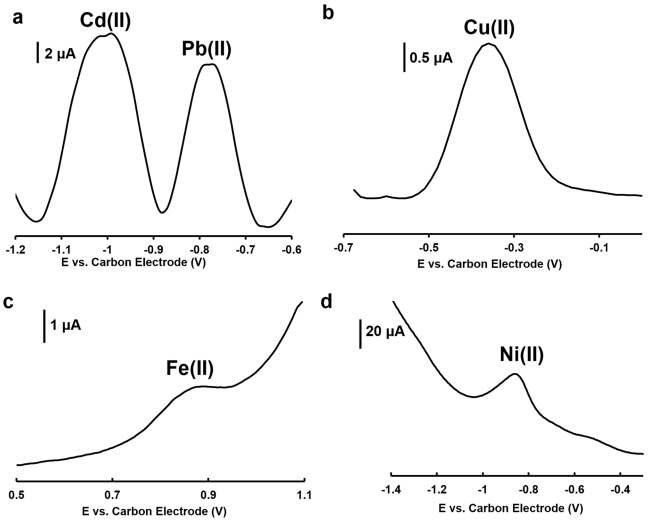

Figure 2. Voltammograms of (a) 50 μg L^{-1} Cd(II) and Pb(II), (b) 50 μg L^{-1} Cu(II), (c) 50 μg L^{-1} Fe(II), and (d) 50 μg L^{-1} Ni(II) separately detected on Janus ePADs with optimum working conditions and specific working electrodes.

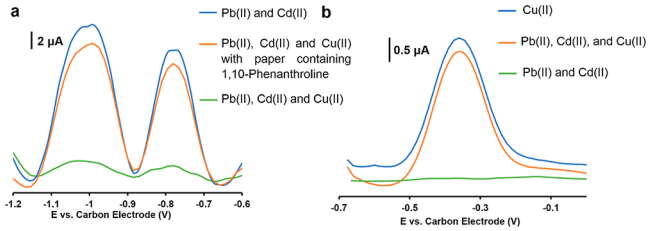

Figure 3. (a) Suppression of peak current when adding Cu(II) into 50 μg L^{-1} Cd(II) and Pb(II) detection and influence of 1,10-phenanthroline-containing paper disk added for Cu(II) elimination. (b) Voltammograms of 50 μg L^{-1} Cu(II) when adding Pb(II) and Cd(II).

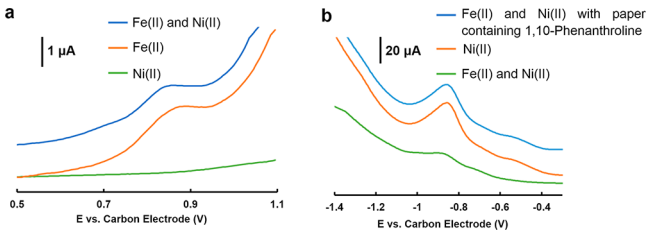

Figure 4. (a) Voltammograms of 50 μg L^{-1} Fe(II) when adding Ni(II). (b) Suppression of peak current when adding Fe(II) into 50 μg L^{-1} Ni(II) detection and influence of 1,10-phenanthroline-contained paper disk added for Fe(II) elimination.

Fe(II) was also determined using adsorptive SWCSV (Figure S3b). The peak potential of 200 μg L^{-1} Fe(II) was 0.82 ± 0.05 V. 1,10-Phenanthroline-modified CSPEs gave a peak current (0.07 ± 0.01 μA) greater than that of the unmodified CSPEs (0.02 ± 0.01 μA). The optimum 1,10-phenanthroline concentration was also 0.7 mM (Figure S4b) likely because both Cu(II) and Fe(II) behave as two-coordinate complexes with 1,10-phenanthroline.[35,38] The improvements in Cu(II) and Fe(II) detection using 1,10-phenanthroline-modified electrodes were attributed to 1,10-phenanthroline's ability to complex the metals more selectively, thereby enhancing the adsorption of Cu and Fe complexes onto the electrode surface.

Janus ePADs for Individual Cd(II), Pb(II), Cu(II), Fe(II), and Ni(II) Detection. We next sought to determine if we could measure all five metals at once from standard solutions. Simultaneous electrochemical analysis of Cd(II), Pb(II), Cu(II), Fe(II), and Ni(II) has not been achieved previously; however, this analysis requires four different working conditions. We hypothesized that Janus ePADs could be used to address this technological limitation through online sample preconditioning using different reagents in different channels. Figure 2 shows results from all of the metals,

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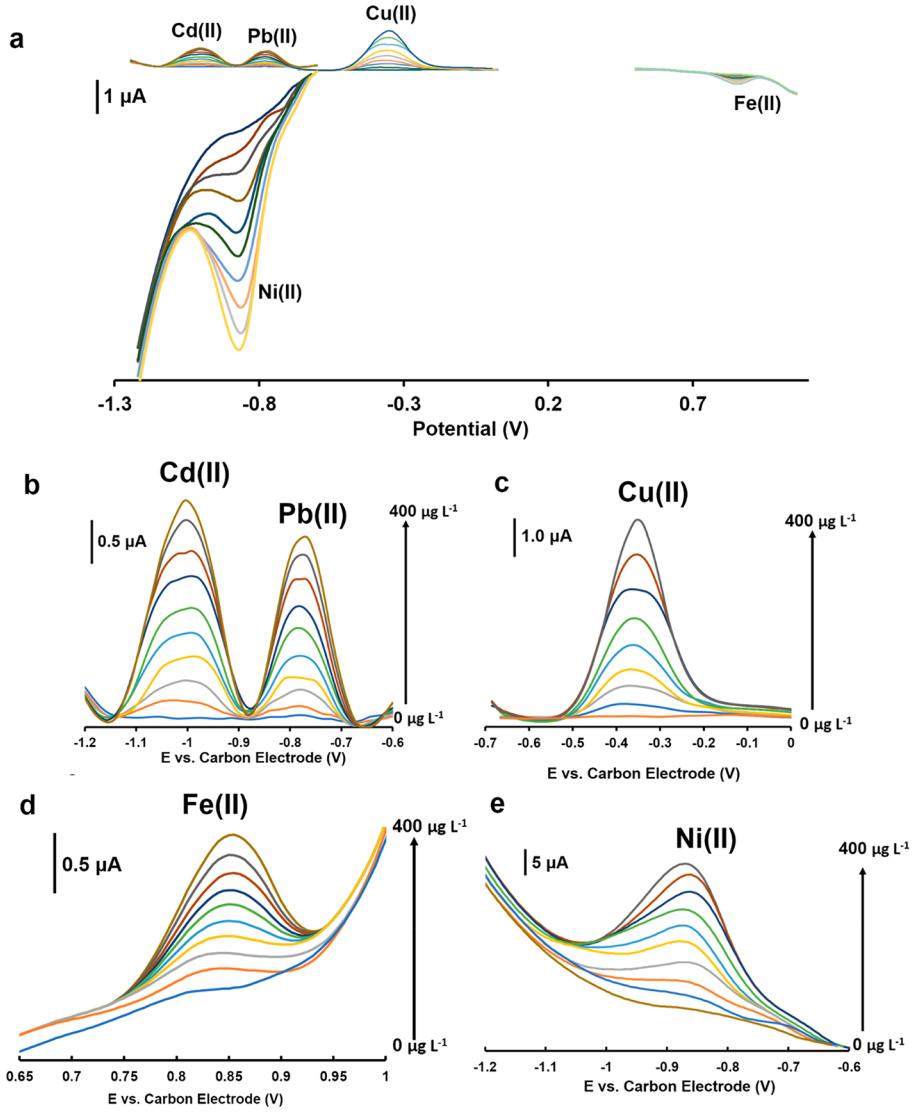

Figure 5. (a) Voltammograms of simultaneous Cd(II), Pb(II), Cu(II), Fe(II), and Ni(II) detection at various concentrations of 0−400.0 μg L^{-1}. Expansion of voltammograms of (b) Cd(II) and Pb(II), (c) Cu(II), (d) Fe(II), and (e) Ni(II).

displayed separately due to scaling requirements despite being collected in the same run. For Cd(II) and Pb(II) detection using the optimum buffer as a preconditioning reagent,[21] anodic peak currents (2.04 ± 0.4 and 1.59 ± 0.3 μA) appeared at −1.01 ± 0.05 and −0.78 ± 0.03 V (vs pseudo carbon reference) for Cd(II) and Pb(II), respectively, as shown in Figure 2a. Electrode modification with Bi and Nafion was performed prior to integrating electrodes into the device. Bi was utilized for its ability to form metal amalgams that yield well-defined, reproducible stripping peaks,[39−41] while the sulfonate group of Nafion selectively preconcentrates metal ions onto the electrode surface for improving detection performance.[34] While Cd(II) and Pb(II) did not require a chelating agent-modified paper, unmodified paper was placed under the detection zone to balance flow rate with the other arms. For Cu(II), 2.5 M acetate buffer was also used as the preconditioning reagent, and 1,10-phenanthroline on a separate paper disk was used for complexing Cu(II). The voltammograms of Cu(II) showed an anodic peak current of 2.84 ± 0.06 μA at −0.36 ± 0.05 V (Figure 2b). For Fe(II), 2.5 M acetate buffer was required as preconditioning agent, and a 1,10-phenanthroline-containing paper disk was used for complexing Fe(II). The cathodic peak current (0.70 ± 0.05 μA) of Fe(II) presented at 0.89 ± 0.07 V (Figure 2c). In terms of Ni(II), 1 M carbonate buffer pH 9.0 was used as the preconditioning agent, and a DMG-modified paper disk was used for complexing Ni(II). The voltammogram from Figure 2d shows a cathodic peak current of 23.0 ± 1.2 μA for Ni(II) at −0.85 ± 0.04 V. The results shown in Figure 2 demonstrate that in situ sample pretreatment with integrated electrochemical features allows a single Janus ePAD to measure up to five metals at once. The proposed device revealed technology utility of a single low-cost ePAD to do multiplexed metals detection.

Interfering Effects and Elimination for Simultaneous Detection Using Janus ePADs. After demonstrating the capability for multimetal determination, we sought to determine the impact of interfering metals on the Janus ePAD. Interference was studied by calculating a tolerance ratio for select metals (Table S2), defined as the mass ratio (interferant:analyte) causing a change in peak current of ±5%.[32] In the case of Cd(II) and Pb(II) detection, only Cu(II) interfered (tolerance ratio of 1). Cu(II) suppression of Cd(II) and Pb(II) anodic peak currents is shown in Figure 3a.

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Table 1. Simultaneous Cd(II), Pb(II), Cu(II), Fe(II), and Ni(II) Detections in Aerosol Samples Using Janus ePADs (n = 3)

samples	metals	Janus ePADs (ng)	ICP-MS (ng)	certified values (ng)
1 (CRM012-100)	Cd(II)	3.23 ± 1.01	3.54 ± 0.09	3.62 ± 0.06
	Pb(II)	1.02 ± 0.08	1.17 ± 0.08	1.20 ± 0.06
	Cu(II)	26.40 ± 1.89	28.50 ± 1.50	30.02 ± 0.47
	Ni(II)	122.50 ± 3.20	126.50 ± 2.70	133.00 ± 1.50
	Fe(II)	268.50 ± 6.32	274.50 ± 5.82	287.00 ± 4.23
2	Cd(II)	$(1.8 \pm 0.5) \times 10^{-2}$	$(2.0 \pm 0.3) \times 10^{-2}$	
	Pb(II)	$(0.9 \pm 0.3) \times 10^{-2}$	$(1.0 \pm 0.2) \times 10^{-2}$	
	Cu(II)	$(5.7 \pm 0.6) \times 10^{-2}$	$(6.0 \pm 0.5) \times 10^{-2}$	
	Ni(II)	$(8.9 \pm 0.5) \times 10^{-2}$	$(9.2 \pm 0.5) \times 10^{-2}$	
	Fe(II)	<LOD	<LOD	
3	Cd(II)	$(0.6 \pm 0.2) \times 10^{-2}$	$(0.7 \pm 0.1) \times 10^{-2}$	
	Pb(II)	$(0.9 \pm 0.2) \times 10^{-2}$	$(1.0 \pm 0.2) \times 10^{-2}$	
	Cu(II)	$(4.1 \pm 0.7) \times 10^{-2}$	$(4.4 \pm 0.6) \times 10^{-2}$	
	Ni(II)	$(5.2 \pm 0.6) \times 10^{-2}$	$(5.6 \pm 0.6) \times 10^{-2}$	
	Fe(II)	<LOD	<LOD	
4	Cd(II)	$(2.6 \pm 0.4) \times 10^{-4}$	$(2.9 \pm 0.3) \times 10^{-4}$	
	Pb(II)	$(2.1 \pm 0.3) \times 10^{-3}$	$(2.3 \pm 0.2) \times 10^{-3}$	
	Cu(II)	$(3.3 \pm 0.5) \times 10^{-2}$	$(3.8 \pm 0.5) \times 10^{-2}$	
	Ni(II)	$(2.5 \pm 0.4) \times 10^{-4}$	$(2.9 \pm 0.3) \times 10^{-4}$	
	Fe(II)	<LOD	<LOD	
5	Cd(II)	$(8.7 \pm 0.5) \times 10^{-2}$	$(9.0 \pm 0.5) \times 10^{-2}$	
	Pb(II)	$(4.8 \pm 0.4) \times 10^{-2}$	$(5.0 \pm 0.3) \times 10^{-2}$	
	Cu(II)	$(26.0 \pm 1.4) \times 10^{-2}$	$(28.0 \pm 1.3) \times 10^{-2}$	
	Ni(II)	$(40.6 \pm 2.0) \times 10^{-2}$	$(42.3 \pm 1.8) \times 10^{-2}$	
	Fe(II)	$(2.5 \pm 0.3) \times 10^{-3}$	$(2.8 \pm 0.2) \times 10^{-3}$	
6	Cd(II)	<LOD	$(8.5 \pm 0.6) \times 10^{-4}$	
	Pb(II)	$(7.1 \pm 0.4) \times 10^{-3}$	$(7.4 \pm 0.2) \times 10^{-3}$	
	Cu(II)	$(10.9 \pm 0.6) \times 10^{-2}$	$(11.9 \pm 0.7) \times 10^{-2}$	
	Ni(II)	$(8.9 \pm 0.6) \times 10^{-4}$	$(9.3 \pm 0.5) \times 10^{-4}$	
	Fe(II)	$(1.8 \pm 0.3) \times 10^{-3}$	$(2.1 \pm 0.2) \times 10^{-3}$	

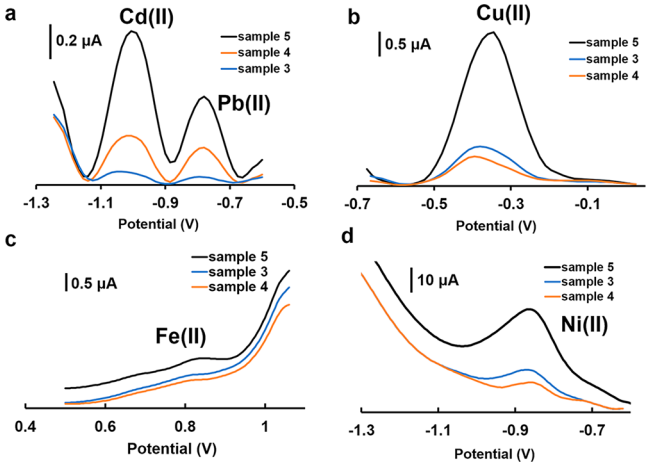

Figure 6. Voltammograms of some aerosol samples using Janus ePADs for (a) Cd(II) and Pb(II), (b) Cu(II), (c) Ni(II), and (d) Fe(II).

1,10-Phenanthroline has been used to remove Cu(II) interference by forming a Cu(II)-1,10-phenanthroline complex.[42] Adding a paper disk containing 1,10-phenanthroline in the flow channel allowed the device to detect Cd(II) and Pb(II) without suppression from Cu(II). In the case of Cu(II) analysis using SWASV, no other metals were found to impact Cu(II) detection with a tolerance ratio of up to 50 (Table S2 and Figure 3b). Although Cd(II) interfered with Cu(II) at a tolerance ratio above 50 (Table S2), that level is not normally found in PM samples.[43] To balance flow, a modified paper disk was inserted under the elimination reservoir. For Fe(II) measurements, no interference was observed up to a tolerance ratio of 100 (Table S2). Again, an unmodified paper disk was placed under the elimination reservoir for balancing flow rate with the other arms. Selective Fe(II) detection in this zone was demonstrated by the absence of cathodic peak current when adding Ni(II) solution to the device (Figure 4a). In the case of Ni(II) analysis using SWCSV, Fe(II) was found to suppress Ni(II) peak current at a tolerance ratio of 1 (Table S2). A 1,10-phenanthroline-containing paper piece was used to eliminate Fe(II) by a flow-though insert.[44] The addition of a masking agent-containing paper piece allowed for Ni peak in the presence of Fe(II) in the sample (Figure 4b). Therefore, addition of a paper disk containing masking agents was demonstrated as a simple method to eliminate the interfering metals and allow for simultaneous, interference-free SWASV and SWCSV.

Analytical Performance. The analytical performance for simultaneous Cd(II), Pb(II), Cu(II), Fe(II), and Ni(II) detection using the Janus ePADs was determined next. The voltammograms at various metal concentrations of Cd(II), Pb(II), Cu(II), Fe(II), and Ni(II) are shown in Figure 5. Online pretreatment allowed the device to simultaneously analyze metals, such as Cd(II), Pb(II), and Ni(II), which would otherwise have overlapping peak potentials as shown in Figure 5a. The Janus ePADs had linear working ranges of 0.5−400.0 μg L^{-1} for Cd(II), Pb(II), and Fe(II), 1.0−400.0 μg L^{-1} for Cu(II), and 0.5−200.0 μg L^{-1} for Ni(II) as shown in

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Figure S5. The decrease of peak current at high concentration of Ni(II) (>200 μg L^{-1}) was caused by electrode fouling leading to incomplete Ni(II)DMG reduction.[45] The Janus ePAD obtained LODs of 0.5, 0.5, 1.0, 0.5, and 1.0 μg L^{-1}, for Cd(II), Pb(II), Cu(II), Fe(II), and Ni(II), respectively. The achieved LODs are low enough to apply the device for the metals monitoring in PM (i.e., ng/m^3 level).[16−18,46] Further improvements in electrode chemistry could further improve LODs in the future.

Cd(II), Pb(II), Cu(II), Fe(II), and Ni(II) Detection in Aerosol Samples. Finally, the Janus ePADs were used to detect the metals in PM samples. For analyzing trace metals using the Janus ePADs, a digestion step was required prior to electrochemical analysis. A simple microwave-assisted digestion was proposed to reduce target metals on the filters.[47] The effectiveness of a simple digestion method was evaluated using the incinerator ash certified reference materials as the results show in Table 1. A paired Student's *t*-test with a two-tailed distribution was used to compare the certified values and the results from the ICP-MS. The *t*-value (−0.055) is less than the critical *t*-value (2.132, $P = 0.05$) for four degrees of freedom ($n = 5$), implying that the null hypothesis is not rejected. Simultaneous determination of Cd(II), Pb(II), Cu(II), Fe(II), and Ni(II) in PM samples from wood-burning and coal-burning stoves was performed using the Janus ePADs with ICP-MS for validation (Table 1). Voltammograms of a couple aerosol samples for simultaneous Cd(II), Pb(II), Cu(II), Fe(II), and Ni(II) detection are shown in Figure 6. A paired Student's *t*-test with a two-tailed distribution was also used to compare the results from the proposed devices and the ICP-MS. The *t*-value (−0.079) is less than the critical *t*-value (1.708, $P = 0.05$) when $n = 26$, implying that the null hypothesis is not rejected. The results demonstrate that Cd(II), Pb(II), Cu(II), Fe(II), and Ni(II) in PM samples can be determined simultaneously using the Janus ePADs with results that are not significantly different from those of the standard method (ICP-MS) at 95% confidence. The Janus ePADs extended the low-cost, portable devices' ability to simultaneously detect all five toxic metals in PM at trace level. The proposed method could ultimately be used in other sample analyses.

CONCLUSION

The use of Janus ePADs for simultaneous measurement of Cd(II), Pb(II), Cu(II), Fe(II), and Ni(II) in PM was demonstrated. The devices concurrently perform SWASV for Cd(II), Pb(II), and Cu(II) detection and SWCSV for Fe(II) and Ni(II) detection. To the best of our knowledge, no other paper-based analytical devices have achieved this level of integration and function in a single system. Preconditioning disks were added into individual paper channels for in situ adjusting optimum working conditions to the sample prior to electrochemical detection and for removing interferences. While the concept was developed for metals specifically, we believe the concept is general and could be applied to other types of devices and for other analytes. The Janus ePADs obtained LODs of 0.5, 0.5, 1.0, 0.5, and 1.0 μg L^{-1}, for Cd(II), Pb(II), Cu(II), Fe(II), and Ni(II), respectively. The proposed method provided working ranges of 0.5−400.0 μg L^{-1} for Cd(II), Pb(II), and Fe(II), 1.0−400.0 μg L^{-1} for Cu(II), and 0.5−200.0 μg L^{-1} for Ni(II). Finally, the device was applied for Cd(II), Pb(II), Cu(II), Fe(II), and Ni(II) detection in PM, and the results were validated with the ICP-MS. The results from the two methods were not significantly different at the 95% confidence level. Therefore, the Janus ePADs allow low-cost, portable, and simple tools for simultaneously analyzing the toxic metals in PM. While the methods developed here are specifically for metal determination, we believe the overall principle could be much more broadly applied to both environmental and biological analyses.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.analchem.9b04632.

Figures S1−S5 and Tables S1 and S2 (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: chuck.henry@colostate.edu.

ORCID

John Volckens: 0000-0002-7563-9525

Charles S. Henry: 0000-0002-8671-7728

Notes

The authors declare no competing financial interest.

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