## **Supplemental Information**

## Dual sample preconcentration for simultaneous quantification of metal ions using electrochemical and colorimetric assays

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Figure S1. Impact of heater system patterns on the preconcentration of blue food coloring. 500  $\mu$ L of blue food coloring was added to paper devices and heated at 100 °C of 20 min.



**Figure S2.** Impact of temperature (25–200 °C) on the preconcentration of blue food coloring after 10 min of heating.



**Figure S3.** The effect of sample volume (100–500  $\mu$ L) and heating time (5–20 min) on preconcentration of blue food coloring.



**Figure S4.** The effect of 1,10-phenanthroline concentration (4 to 12 g  $L^{-1}$ ) on the development of a colorimetric assay for Fe<sup>3+</sup>.



**Figure S5.** The effect of hydroxylamine concentration (0.05 to 0.9 g mL<sup>-1</sup>) on the development of a colorimetric assay for Fe<sup>3+</sup>.



**Figure S6.** The effect of ammonium hydroxide concentration (14%-28% w/w) on the development of a colorimetric assay for Ni<sup>2+</sup>.



Figure S7. The effect of DMG concentration (40–120 mM) on the development of a colorimetric assay for  $Ni^{2+}$ .



**Figure S8.** Optimizing conditions to detect lead and cadmium using anodic stripping voltammetry. (a) Effect of Bi concentration on the stripping peak currents of solutions containing 0.5 mg L<sup>-1</sup> Pb<sup>2+</sup> and Cd<sup>2+</sup>, which were eluted with 1 M HCl after 10 min of preconcentration. (b) Comparison of Bi film (8 mg L<sup>-1</sup>) and bare electrodes for the detection of Cd<sup>2+</sup> and Pb<sup>2+</sup> at 0.5 mg L<sup>-1</sup> *without* sample preconcentration, using HCl as background. (c) Comparison of Bi film (8 mg L<sup>-1</sup>) and bare electrodes for the detection of Cd<sup>2+</sup> and Pb<sup>2+</sup> at 0.5 mg L<sup>-1</sup> with sample preconcentration, using HCl as background.



**Figure S9.** Effect of deposition potential on the stripping peak currents of a solution containing  $0.5 \text{ mg L}^{-1} \text{ Pb}^{2+}$  and  $\text{Cd}^{2+}$  with 1 M HCl.



**Figure S10.** Effect of step potential on the stripping peak currents of a solution containing 0.5 mg L<sup>-1</sup> Pb<sup>2+</sup> and Cd<sup>2+</sup> with 1 M HCl.



**Figure S11.** Effect of amplitude on the stripping peak currents of a solution containing 0.5 mg  $L^{-1}$  Pb<sup>2+</sup> and Cd<sup>2+</sup> with 1 M HCl.



**Figure S12.** Effect of frequency on the stripping peak currents of a solution containing 0.5 mg  $L^{-1}$  Pb<sup>2+</sup> and Cd<sup>2+</sup> with 1 M HCl.



**Figure S13.** Effect of deposition time on the square-wave anodic stripping voltammetric peak currents used to detect 0.5 mg L<sup>-1</sup> of Cd<sup>2+</sup> and Pb<sup>2+</sup> eluted with 1 M HCl. This 500  $\mu$ L sample volume was subjected to 10 min of preconcentration.



**Figure S14.** Stability of paper-based devices used to detect  $Fe^{3+}$  and  $Ni^{2+}$  (0.20 mg L<sup>-1</sup>) when stored at 4 °C for up to 4 weeks.





Figure S15. Effect of interferents on assays for (a)  $Cd^{2+}$ , (b)  $Pb^{2+}$ , (c)  $Fe^{3+}$ , and (d)  $Ni^{2+}$ .

Parameters	Cd(II)	Pb(II)	Fe(III)	Ni(II)
Linear range (mg L <sup>-1</sup> )	0.005 - 0.100	0.005 - 0.100	0.050 - 0.250	0.050 - 0.250
$\mathbf{R}^2$	0.9962	0.9975	0.9920	0.9908
Linear equations	y = 1067.5x + 1.7628	y = 875.15x - 4.3192	y = 274x + 47.9	y = 206x + 39.9
$LOD (mg L^{-1})$	0.00233 (2.33 μg L <sup>-1</sup> )	0.00097 (0.97 μg L <sup>-1</sup> )	0.03	0.04
$LOQ (mg L^{-1})$	0.005	0.005	0.05	0.05
%RSD	7.25% (0.050 ppm) 5.39% (0.075 ppm)	8.01% (0.050 ppm) 6.89% (0.075 ppm)	8.23% (0.05 ppm) 7.26% (0.20 ppm)	5.76% (0.05 ppm) 10.12% (0.20 ppm)

**Table S1.** Analytical performance of assays for  $Pb^{2+}$ ,  $Cd^{2+}$ ,  $Fe^{3+}$ , and  $Ni^{2+}$ .

<b>Table 52.</b> Survey of methods to detect FD <sup>-</sup> and Cd <sup>-</sup> using electrochemical as	Table S2	. Survey	of methods to	detect Pb <sup>2+</sup>	and Cd <sup>2+</sup>	using	electrochem	nical assays
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Electrode	Method	Analyte	Linearity (µg L <sup>-1</sup> )	LOD (µg L <sup>-1</sup> )	Sample	Ref.
Glassy-carbon with bismuth film	SWASV	$\begin{array}{c} Pb^{2+}\\ Cd^{2+}\end{array}$	40 - 200	1.1	-	(43)
Glassy carbon and multifiber microelectrodes with bismuth film	SWASV Double deposition using two electrodes	$Pb^{2+}$ $Cd^{2+}$	0.1 - 1 0.02 - 0.6	0.040 0.005	Synthetic freshwater sample	(44)
Sputtered-bismuth screen-printed sensors	SWASV	$\begin{array}{c} Pb^{2+}\\ Cd^{2+}\end{array}$	20 – 150 20 – 80	6.1 11.8	Atmospheric particulate matter	(45)
Bismuth bulk electrode	SWASV	$\begin{array}{c} Pb^{2+}\\ Cd^{2+}\\ Zn^{2+}\end{array}$	10 - 100	0.093 0.054 0.396	River water	(50)
Stencil-printed transparency electrodes with bismuth film	SWASV	$Pb^{2+}$ $Cd^{2+}$	1 - 200	0.3 0.2	Seawater	(49)
Dendritic bismuth film electrodes	SWASV	$\begin{array}{c} Pb^{2+}\\ Cd^{2+}\end{array}$	5 - 50	0.1 0.4	Wastewater	(46)
Glassy carbon disc electrode with bismuth film	SWASV	$Pb^{2+}$ $Cd^{2+}$	10 - 100	6.9 1.4	Surface water	(47)
carbon-based sensor with Bi	SWASV	$\begin{array}{c} Pb^{2+}\\ Cd^{2+}\end{array}$	5 - 100	1.8 1.2		(48)
Screen printed electrode with heating preconcentration	SWASV	$\begin{array}{c} Pb^{2+}\\ Cd^{2+}\end{array}$	5 - 100	0.97 2.33	Drinking, pond, tap water and wastewater	Our work

Method	Reagent	Analyte	Linearity (mg L <sup>-1</sup> )	LOD (mg L <sup>-1</sup> )	Sample	Ref.
Colorimetric	1,10-phen Dimethylglyoxime	Fe Ni Cu	188 – 1,250 125 – 213 125 – 188	188 125 125	Particulate metals	(40)
Electrochemical and colorimetric	1,10-phen Dimethylglyoxime Electrochemical Electrochemical	Fe Ni Cu Cr Pb Cd	$\begin{array}{r} 30-300\\ 30-300\\ 60-300\\ 7.6-120\\ 0.005-0.150\\ 0.005-0.150\end{array}$	15 15 15 2.4 0.001 0.001	Particulate metals	(26)
Colorimetric (distance)	Bathophenanthroline Dimethylglyoxime Dithiooxamide	Fe Ni Cu	20 - 1,300 100 - 1,100 100 - 1,300	1 2 2	Particulate metals	(54)
Colorimetric	1,10-phen	Fe	100 - 1000 40 - 350	20	Natural hot spring water	(55)
Colorimetric	Ferrozine	Fe	0.005 - 0.100	0.004	Fortified foods	(56)
Smartphone	AgNPs/CTAB	Fe	0.05 - 0.90	0.20	Water and blood plasma	(57)
Colorimetric with heating	1,10-phen Dimethylglyoxime	Fe Ni	0.05 - 0.25	0.03	Drinking, pond tap water and	This

0.03 0.04

water and

wastewater

work

preconcentration

**Table S3.** Survey of methods to detect  $Fe^{3+}$  and  $Ni^{2+}$  using colorimetric assays.

	Concentration ratio of -	<b>Recovery of analyte signal (%)</b>				
Interferences	analyte : interference	Cd(II)	Pb(II)	Fe(III)	Ni(II)	
Fe <sup>2+</sup>	1:1	97	98	-	101	
	1:100	80	117		120	
Fe <sup>3+</sup>	1:1	98	105	-	104	
	1:100	74	104		109	
Ni <sup>2+</sup>	1:1	102	95	97	-	
	1:100	85	76	106		
	1:1		98	95	106	
$Cd^{2+}$	1:100	-	95	90	110	
	1.1	102		98	105	
$Pb^{2+}$	1:100	97	-	109	110	
Ca <sup>2+</sup>	1:1	95	102	99	105	
	1:100	91	103	102	109	
	1:1000	90	104			
$Mg^{2+}$	1:1	89	100	102	104	
	1:100	91	92	106	111	
	1:1000	95	105			
Na <sup>+</sup>	1:1	100	108	101	101	
	1:100	90	107	105	109	
	1:1000	70	107			
$K^+$	1:1	88	94	98	103	
	1:100	87	90	106	107	
	1:1000	82	90			
$\mathrm{Co}^{2+}$	1:1	90	104	97	102	
	1:100	83	136	108	110	
Cu <sup>2+</sup>	1:1	80	87	98	105	
	1:100	62	70	110	109	
$Zn^{2+}$	1:1	94	104	102	106	
	1:100	114	118	109	110	
Cl-	1:1	102	93	95	105	
	1:100	97	96	106	108	
	1:1000	83	96			
$SO_4^{2-}$	1:1	97	104	105	103	
	1:100	93	110	110	111	
	1:1000	68	127			
NO <sub>3</sub> -	1:1	95	101	97	106	
	1:100	86	93	105	109	
	1:1000	77	89			
CO <sub>3</sub> <sup>2-</sup>	1:1	99	98	98	103	
	1:100	80	73	90	110	

**Table S4.** Effect of interfering ions on the voltammetric and colorimetric response of Cd<sup>2+</sup>, Pb<sup>2+</sup>, Fe<sup>3+</sup>, and Ni<sup>2+</sup>.

Samples	Temperature (°C)	pН	DO (mg/L)
Drinking water	26.4	7.1	0.3
Tap water	26.2	6.7	0.5
Pond water 1	26.5	6.4*	2.5
Pond water 2	27.1	6.2*	3.0
Wastewater	27.5	5.9*	3.9

 Table S5. General parameters for water samples.

\*Pond water and wastewater were preserved with HNO<sub>3</sub> (pH<1) after measurement of temp, pH, and dissolved oxygen (DO).

**Table S6.** Statistical comparison between our electrochemical method and ICP-AES to detect

 Pb<sup>2+</sup> and Cd<sup>2+</sup>.

	Variable 1	Variable 2
Mean	40.929	40.402
Variance	5.326921111	9.266084444
Observations	10	10
<b>Pearson Correlation</b>	0.18659605	
Hypothesized Mean		
Difference	0	
df	9	
t Stat	0.481663533	
P(T<=t) one-tail	0.320770405	
t Critical one-tail	1.833112933	
P(T<=t) two-tail	0.64154081	
t Critical two-tail	2.262157163	

**Table S7.** Statistical comparison between our colorimetric method and ICP-AES to detect  $Fe^{3+}$  and  $Ni^{2+}$ .

	Variable 1	Variable 2
Mean	119.032	117.753
Variance	69.77152889	67.59926778
Observations	10	10
<b>Pearson Correlation</b>	0.121593624	
Hypothesized Mean		
Difference	0	
df	9	
t Stat	0.325843089	
P(T<=t) one-tail	0.375995745	
t Critical one-tail	1.833112933	
P(T<=t) two-tail	0.751991489	
t Critical two-tail	2.262157163	