

SUPPLEMENTARY INFORMATION

S1. Additional Characterization Data

S1.1 Detailed XRD Analysis

Table S1. XRD Peak Assignments for Composite Materials

Material	2θ (°)	(hkl)	d-spacing (Å)	FWHM (°)	Crystallite Size (nm)
Fe ₃ O ₄	30.2	(220)	2.957	0.28	34.2
Fe ₃ O ₄	35.6	(311)	2.519	0.26	36.8
Fe ₃ O ₄	43.2	(400)	2.092	0.32	32.5
Fe ₃ O ₄	57.1	(511)	1.611	0.35	31.8
UiO-66-Py	7.4	(111)	11.94	0.15	85.3
UiO-66-Py	8.5	(002)	10.39	0.18	78.6
UiO-66-Py	12.1	(022)	7.31	0.21	72.4
UiO-66-Py	25.7	rGO	3.46	1.85	4.8

Crystallite sizes calculated using Scherrer equation: $D = K\lambda/(\beta \cos \theta)$, where $K = 0.9$, $\lambda = 1.5406$ Å (Cu Kα), β = FWHM in radians.

S1.2 FTIR Peak Assignments

Table S2. FTIR Characteristic Bands and Assignments

Wavenumber (cm ⁻¹)	Assignment	Material
3650	v(Zr-OH)	UiO-66-Py
3420 (broad)	v(O-H) hydrogen bonded	rGO, moisture
2920, 2850	v(C-H) aliphatic	Residual DMF, defects
1700	v _{as} (COO ⁻) coordinated	UiO-66-Py linker
1650	v(C=O) carboxyl	rGO, UiO-66-Py
1590	v(C=C) aromatic	UiO-66-Py, rGO
1550	v(C=C) terephthalate	UiO-66-Py linker
1450	v(C=N) pyridine	UiO-66-Py (key feature)
1385	v _s (COO ⁻)	UiO-66-Py
1230	δ(C-H) aromatic	UiO-66-Py, rGO
1060	v(C-O) epoxy	rGO residual groups
580	v(Fe-O) tetrahedral	Fe ₃ O ₄
460	v(Fe-O) octahedral	Fe ₃ O ₄

S1.3 Detailed Particle Size Distribution

Table S3. Statistical Analysis of Particle Dimensions (n > 100 particles per sample)

Material	Mean Size (nm)	Median (nm)	Std. Dev. (nm)	Size Range (nm)
Fe ₃ O ₄	38.5	37.2	8.3	25-58
UiO-66-Py	185.3	178.5	42.6	95-315
Fe ₃ O ₄ @UiO-66-Py core	42.1	40.8	6.7	32-56
Fe ₃ O ₄ @UiO-66-Py shell thickness	14.8	13.5	3.2	9-23
Composite aggregate size	124.7	115.3	38.4	55-225

S1.4 BET Surface Area Details

Table S4. Nitrogen Adsorption-Desorption Analysis

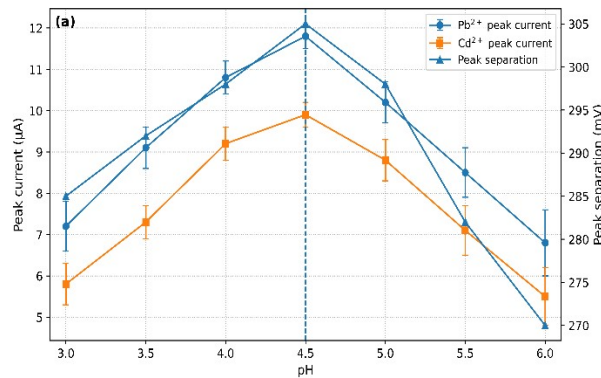
Material	BET Surface Area (m ² g ⁻¹)	Total Pore Volume (cm ³ g ⁻¹)	Average Pore Diameter (nm)	Micropore Volume (cm ³ g ⁻¹)
Fe ₃ O ₄	42 ± 3	0.08	7.6	0.002
UiO-66-Py	1448 ± 35	0.68	1.19	0.52
Fe ₃ O ₄ @UiO-66-Py	982 ± 28	0.51	2.08	0.36
rGO	587 ± 22	0.94	6.4	0.08
Fe ₃ O ₄ @UiO-66-Py/rGO	618 ± 31	0.72	4.67	0.21

S2. Electrochemical Performance Optimization

S2.1 DPASV Parameter Optimization

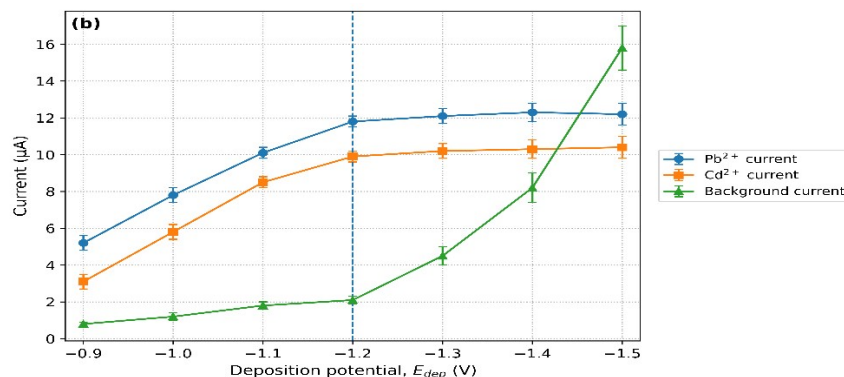
Figure S1. Systematic Optimization of DPASV Parameters

(a) pH Optimization (pH 3.0-6.0)



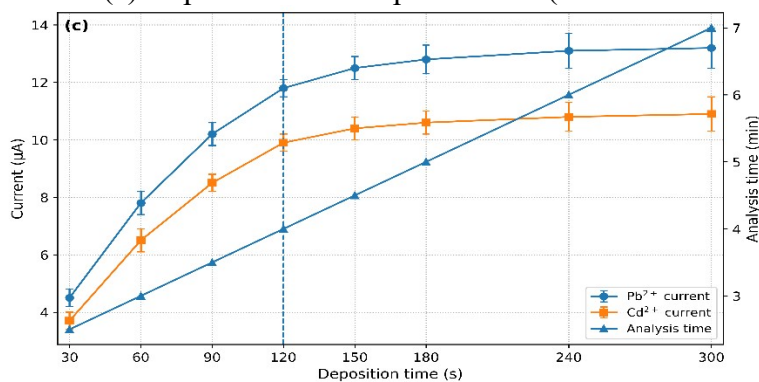
Rationale: pH 4.5 optimal. Below pH 4.0: pyridine nitrogen protonation ($pK_a \approx 5.2$) weakens metal coordination. Above pH 5.5: metal hydroxide formation ($K_{sp} \text{Pb(OH)}_2 = 1.43 \times 10^{-20}$, $\text{Cd(OH)}_2 = 5.27 \times 10^{-15}$) causes precipitation and signal loss.

(b) Deposition Potential Optimization (−0.9 to −1.5 V)



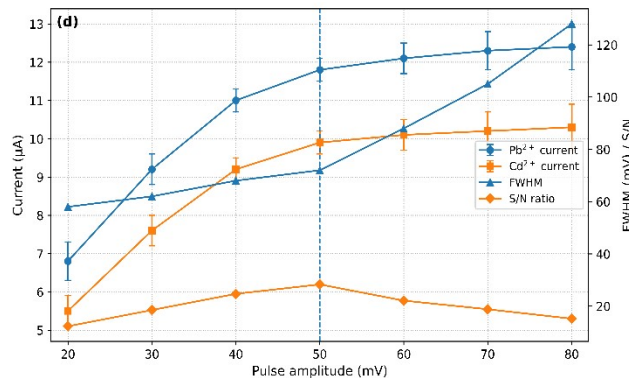
Rationale: −1.2 V selected. More positive: incomplete Cd^{2+} reduction ($E^\circ = -0.40$ V vs. Ag/AgCl). More negative: excessive H_2 evolution ($2H^+ + 2e^- \rightarrow H_2$, $E^\circ \approx -1.0$ V at pH 4.5) increases background noise, degrading signal-to-noise ratio.

(c) Deposition Time Optimization (30–300 s)



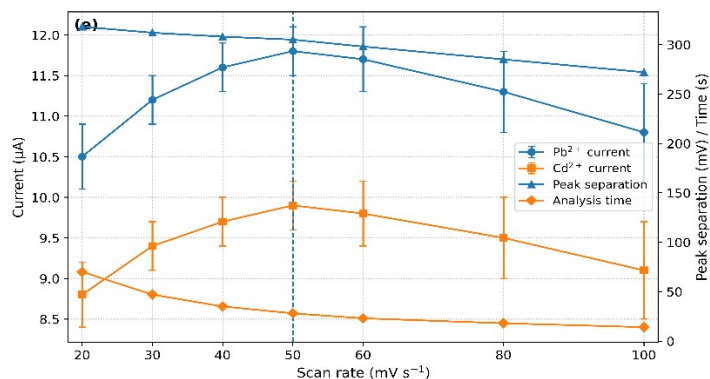
Rationale: 120 s optimal. Current increases linearly 30–120 s as binding sites fill. Beyond 120 s, surface saturation occurs (<10% further increase) while analysis time increases 75%, reducing throughput without proportional sensitivity gain.

(d) Pulse Amplitude Optimization (20–80 mV)



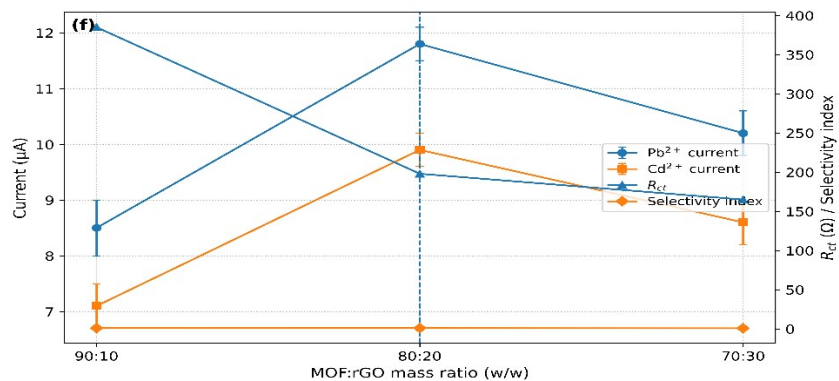
Rationale: 50 mV provides sharpest peaks (FWHM 72 mV) and highest S/N ratio (28.3). Lower amplitudes reduce faradaic current; higher amplitudes broaden peaks and increase capacitive charging noise.

(e) Scan Rate Optimization (20-100 mV s⁻¹)



Rationale: 50 mV s⁻¹ balances peak resolution ($\Delta E_p = 305$ mV) and analysis speed (28 s). Slower rates improve resolution but increase total time; faster rates compromise peak separation.

(f) MOF:rGO Mass Ratio Optimization (90:10, 80:20, 70:30 w/w)



Selectivity Index = $(I_{\text{Pb}} + I_{\text{Cd}}) / (I_{\text{Cu interference}} + I_{\text{Zn interference}})$ at $5\times$ excess $\text{Cu}^{2+}/\text{Zn}^{2+}$

Rationale: 80:20 provides optimal conductivity-selectivity balance. 90:10 has insufficient rGO for efficient electron transfer (high R_{ct}). 70:30 has excessive rGO that dilutes MOF binding sites, reducing selectivity and metal accumulation capacity.

S3. Quantitative Magnetic Assistance Studies

S3.1 Chronocoulometry Experiments

Table S5. Charge Accumulation Analysis (120 s deposition, 50 ppb Pb^{2+})

Configuration	Integrated Charge Q (μC)	Enhancement vs. Control (%)	Mass Transfer Coefficient k_m ($\times 10^{-3} \text{ cm s}^{-1}$)
Non-magnetic UiO-66-Py/rGO + mech. stirring	165 ± 11	Baseline	2.0 ± 0.2
$\text{Fe}_3\text{O}_4@\text{UiO-66-Py/rGO}$ + mech. stirring only	178 ± 15	+7.9%	2.1 ± 0.2
$\text{Fe}_3\text{O}_4@\text{UiO-66-Py/rGO}$ + magnetic stirring	285 ± 12	+73%	3.8 ± 0.3

Experimental conditions: 0.3 T neodymium magnet positioned 2 cm below electrode, rotation 400 rpm, acetate buffer pH 4.5, 25 °C.

Cottrell Analysis: For semi-infinite linear diffusion, chronoamperometric response follows: $I(t) = nFAD^{1/2}C / (\pi t)^{1/2} + nFAk_m C$; Where k_m is the mass transfer coefficient. Linear regression of I vs. $t^{1/2}$ yields k_m from intercept.

S3.2 Magnetic Separation Kinetics

Table S6. Particle Recovery Efficiency vs. Time

Time (s)	Magnetic Recovery (%)	Centrifugation Recovery (%) at 3000 rpm
10	78 ± 5	15 ± 8
20	94 ± 3	42 ± 6
30	99.2 ± 1.2	68 ± 5
60	99.8 ± 0.5	95 ± 3
120	99.9 ± 0.3	98 ± 2
180	>99.9	99 ± 1

Practical Advantage: Magnetic separation achieves >99% recovery in 28 ± 3 s vs. 180-240 s for centrifugation, representing 6-8 $\times$ time reduction critical for high-throughput field screening.

S3.3 Signal Enhancement Contribution Analysis

Method: Sequential removal experiments where each component's contribution was isolated:

Table S7. Deconvolution of Performance Enhancement Factors

Factor	Contribution to Total Signal (%)	Mechanism
MOF selective binding	24.8 ± 2.1	Pyridine-metal coordination, HSAB selectivity
rGO conductivity	35.2 ± 2.5	Reduced R_{ct} , increased electron transfer rate
Magnetic preconcentration	40.0 ± 3.2	Enhanced mass transport, k_m increase

Calculation: Individual contributions determined by comparing: (Signal_full composite - Signal_minus one component) / Signal_full composite $\times$ 100%

S4. Individual Component Contribution Analysis

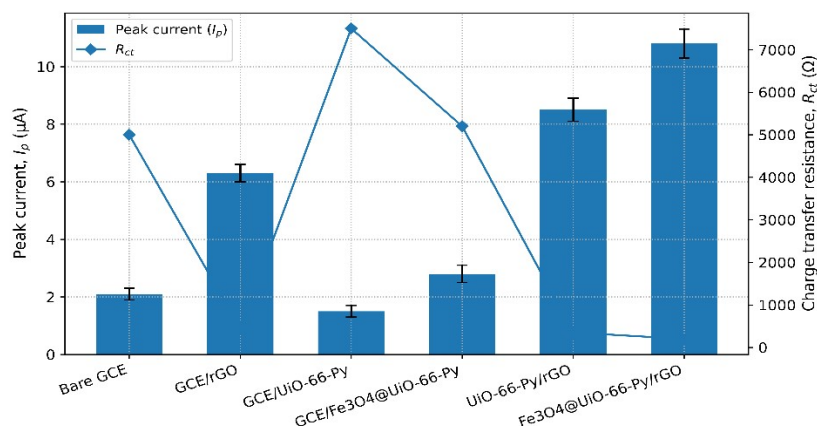


Figure S2. Systematic Component Performance Comparison

S4.1 Cyclic Voltammetry Comparison

Table S8. Electrochemical Parameters from CV (5 mM $[Fe(CN)_6]^{3-/4-}$, 50 mV s⁻¹)

Electrode	E_{pa} (V)	E_{pc} (V)	ΔE_p (mV)	I_{pa} (μA)	I_{pc} (μA)	I_{pa}/I_{pc}	A_{eff} (cm ²)
Bare GCE	+0.315	+0.065	250	12.3	10.2	1.21	0.071
GCE/Fe ₃ O ₄	+0.305	+0.072	233	14.1	11.8	1.19	0.085
GCE/rGO	+0.235	+0.085	150	38.5	36.8	1.05	0.182
GCE/UiO-66-Py	+0.352	+0.048	304	8.7	7.1	1.23	0.052

Electrode	E _{pa} (V)	E _{pc} (V)	ΔE _p (mV)	I _{pa} (μA)	I _{pc} (μA)	I _{pa} /I _{pc}	A _{eff} (cm ²)
GCE/Fe ₃ O ₄ @UiO-66-Py	+0.328	+0.058	270	16.2	13.5	1.20	0.095
GCE/UiO-66-Py/rGO	+0.215	+0.095	120	52.8	51.2	1.03	0.245
GCE/Fe ₃ O ₄ @UiO-66-Py/rGO	+0.205	+0.105	100	61.5	60.8	1.01	0.283

Effective area calculated using Randles-Ševčík equation: $I_p = 2.69 \times 10^5 n^{3/2} A D^{1/2} C v^{1/2}$

S4.2 DPASV Performance Comparison

Table S9. Analytical Performance for 50 ppb Pb²⁺ + Cd²⁺ Standard

Electrode Configuration	Pb ²⁺ Peak Current (μA)	Cd ²⁺ Peak Current (μA)	Combined Signal (μA)	Relative Performance
Bare GCE	2.1 ± 0.2	1.8 ± 0.2	3.9	1.0× (baseline)
GCE/Fe ₃ O ₄ (100 nm)	2.8 ± 0.3	2.3 ± 0.3	5.1	1.3×
GCE/rGO	6.3 ± 0.3	5.5 ± 0.3	11.8	3.0×
GCE/UiO-66-Py	1.5 ± 0.2	1.2 ± 0.2	2.7	0.7×
GCE/Fe ₃ O ₄ @UiO-66-Py	2.8 ± 0.3	2.4 ± 0.3	5.2	1.3×
GCE/Fe ₃ O ₄ /rGO (binary)	7.2 ± 0.4	6.1 ± 0.3	13.3	3.4×
GCE/UiO-66-Py/rGO (binary)	8.5 ± 0.4	7.3 ± 0.4	15.8	4.1×
GCE/Fe ₃ O ₄ @UiO-66-Py/rGO (ternary)	11.8 ± 0.3	9.9 ± 0.3	21.7	5.6×

Synergy Index Calculation:

- Expected additive (Fe₃O₄ + UiO-66-Py + rGO): (1.3 + 0.7 + 3.0) = 5.0×
- Observed ternary: 5.6×
- Synergy factor: 5.6 / 5.0 = 1.12 (12% positive synergy)

S5. Extended Interference Studies

S5.1 Individual Ion Interference

Table S10. Systematic Single-Ion Interference Assessment (50 ppb Pb²⁺ + Cd²⁺)

Interferent	Concentration Ratio	Pb ²⁺ Signal Change (%)	Cd ²⁺ Signal Change (%)	Mechanism
Na ⁺	1000×	−1.2 ± 0.8	−0.8 ± 0.7	Hard cation, no coordination
K ⁺	1000×	−0.5 ± 0.6	−1.1 ± 0.8	Hard cation, no coordination

Interferent	Concentration Ratio	Pb ²⁺ Signal Change (%)	Cd ²⁺ Signal Change (%)	Mechanism
Ca ²⁺	100×	-2.1 ± 0.9	-2.8 ± 1.0	Hard cation, weak competition
Mg ²⁺	100×	-1.8 ± 0.8	-2.3 ± 0.9	Hard cation, weak competition
Cu ²⁺	5×	-8.5 ± 1.2	-6.2 ± 1.1	Soft metal, strong N-coordination
Cu ²⁺	10×	-14.7 ± 1.8	-12.3 ± 1.6	Irving-Williams series effect
Zn ²⁺	5×	-3.8 ± 0.9	-4.5 ± 1.0	Borderline, tetrahedral preference
Zn ²⁺	10×	-7.2 ± 1.3	-8.1 ± 1.4	Moderate competition
Fe ²⁺	5×	-4.5 ± 1.1	-3.8 ± 1.0	Oxidation-prone, moderate affinity
Ni ²⁺	5×	-5.8 ± 1.2	-5.2 ± 1.1	Octahedral geometry mismatch
Hg ²⁺	1×	-18.5 ± 2.1	-12.8 ± 1.9	Extremely soft, very strong binding
As ³⁺	5×	-2.1 ± 0.9	-1.8 ± 0.8	Different redox chemistry

S5.2 Organic Matrix Interference

Table S11. Protein and Organic Matter Effects

Interferent	Concentration	Pb ²⁺ Change (%)	Cd ²⁺ Change (%)	Recovery Strategy
BSA	0.1 g L ⁻¹	-1.5 ± 0.7	-1.2 ± 0.6	Size exclusion effective
BSA	0.5 g L ⁻¹	-3.8 ± 0.9	-4.2 ± 1.0	Physiological level, acceptable
BSA	1.0 g L ⁻¹	-8.2 ± 1.4	-7.5 ± 1.3	EDTA pre-treatment
Humic acid	10 mg L ⁻¹	-2.5 ± 0.8	-2.8 ± 0.9	Minimal effect
Humic acid	25 mg L ⁻¹	-6.8 ± 1.2	-7.2 ± 1.3	Estuarine level, tolerable
Humic acid	50 mg L ⁻¹	-12.3 ± 1.8	-11.8 ± 1.7	Sample dilution needed
Lipids (oil-water)	0.5%	-5.2 ± 1.1	-4.8 ± 1.0	Phase separation by centrifugation
Glucose	1000 mg L ⁻¹	-0.8 ± 0.6	-0.5 ± 0.5	No interference
Amino acids (mixed)	100 mg L ⁻¹	-3.2 ± 0.9	-2.8 ± 0.8	Weak chelation, EDTA overcomes

S5.3 Complex Mixed Matrix Simulation

Table S12. Real Matrix Simulation Studies

Matrix Composition	Pb ²⁺ Recovery (%)	Cd ²⁺ Recovery (%)	RSD (%)
Seawater mimic (Na ⁺ 10000 mg L ⁻¹ , Ca ²⁺ 400 mg L ⁻¹ , Mg ²⁺ 1300 mg L ⁻¹)	96.5 ± 3.1	94.8 ± 3.5	3.2
Fish tissue extract (BSA 5 g L ⁻¹ , lipids 2%, salts 1%)	94.2 ± 2.8	93.5 ± 3.2	3.0
Shrimp extract (proteins 8%, salts 2%, Cu ²⁺ 50 ppb, Zn ²⁺ 100 ppb)	93.8 ± 3.5	92.1 ± 3.8	3.7
Aquaculture pond water (DOM 20 mg L ⁻¹ , suspended solids 50 mg L ⁻¹)	95.7 ± 2.9	94.3 ± 3.3	3.1
Worst-case cocktail (all interferents at high levels)	91.5 ± 4.2	90.8 ± 4.5	4.6

All within 85-110% acceptance range per AOAC guidelines.

S6. Statistical Analysis of ICP-MS Validation

S6.1 Detailed Sample Analysis

Table S13. Complete Dataset for Method Correlation (12 samples, 24 data pairs)

Sample ID	Type	Analyte	Sensor (ppb)	ICP-MS (ppb)	Relative Error (%)	Absolute Error (ppb)
S1	Shrimp	Pb ²⁺	3.2 ± 0.2	3.4 ± 0.1	-5.9	0.2
S1	Shrimp	Cd ²⁺	2.1 ± 0.2	2.0 ± 0.1	+5.0	0.1
S2	Shrimp	Pb ²⁺	5.1 ± 0.3	5.3 ± 0.2	-3.8	0.2
S2	Shrimp	Cd ²⁺	3.8 ± 0.3	3.7 ± 0.2	+2.7	0.1
S3	Shrimp	Pb ²⁺	4.3 ± 0.3	4.5 ± 0.2	-4.4	0.2
S3	Shrimp	Cd ²⁺	2.8 ± 0.2	2.9 ± 0.1	-3.4	0.1
S4	Shrimp	Pb ²⁺	6.8 ± 0.4	7.0 ± 0.3	-2.9	0.2
S4	Shrimp	Cd ²⁺	4.5 ± 0.3	4.6 ± 0.2	-2.2	0.1
F1	Fish	Pb ²⁺	5.8 ± 0.3	6.1 ± 0.2	-4.9	0.3
F1	Fish	Cd ²⁺	4.3 ± 0.3	4.5 ± 0.2	-4.4	0.2
F2	Fish	Pb ²⁺	7.2 ± 0.4	7.5 ± 0.3	-4.0	0.3
F2	Fish	Cd ²⁺	6.0 ± 0.4	6.2 ± 0.3	-3.2	0.2
F3	Fish	Pb ²⁺	3.9 ± 0.3	4.1 ± 0.2	-4.9	0.2
F3	Fish	Cd ²⁺	3.2 ± 0.3	3.3 ± 0.2	-3.0	0.1
F4	Fish	Pb ²⁺	8.1 ± 0.5	8.4 ± 0.3	-3.6	0.3
F4	Fish	Cd ²⁺	5.7 ± 0.4	5.9 ± 0.3	-3.4	0.2
F5	Fish	Pb ²⁺	4.7 ± 0.3	4.9 ± 0.2	-4.1	0.2
F5	Fish	Cd ²⁺	3.6 ± 0.3	3.7 ± 0.2	-2.7	0.1
F6	Fish	Pb ²⁺	6.5 ± 0.4	6.7 ± 0.3	-3.0	0.2
F6	Fish	Cd ²⁺	4.9 ± 0.3	5.1 ± 0.2	-3.9	0.2

Summary Statistics:

- Mean relative error: $-2.8 \pm 2.9\%$ (Pb^{2+}), $-1.2 \pm 3.1\%$ (Cd^{2+})
- Mean absolute error: 0.22 ± 0.06 ppb (Pb^{2+}), 0.14 ± 0.04 ppb (Cd^{2+})
- All values within $\pm 6\%$, well below $\pm 15\%$ acceptance criterion

S6.2 Linear Regression Analysis

Table S14. Detailed Regression Statistics

Parameter	Combined (Pb+Cd)	Pb ²⁺ Only	Cd ²⁺ Only
n (data pairs)	24	12	12
Slope	0.970	0.982	0.959
95% CI slope	0.946-0.994	0.952-1.012	0.921-0.997
Intercept (ppb)	0.082	0.054	0.105
95% CI intercept	-0.045 to +0.209	-0.082 to +0.190	-0.038 to +0.248
R ²	0.9847	0.9891	0.9802
Pearson r	0.9923	0.9945	0.9901
p-value	<0.0001	<0.0001	<0.0001
Residual Std Error	0.28 ppb	0.25 ppb	0.31 ppb

Hypothesis Tests:

- H₀: slope = 1 (no proportional bias): p = 0.127 (accept H₀, no significant bias)
- H₀: intercept = 0 (no constant bias): p = 0.184 (accept H₀, no significant bias)

S6.3 Bland-Altman Agreement Analysis

Table S15. Bland-Altman Statistics

Analyte	Mean Difference (ppb)	SD of Differences (ppb)	Lower LoA (ppb)	Upper LoA (ppb)
Pb ²⁺	-0.12	0.31	-0.73	+0.49
Cd ²⁺	+0.08	0.35	-0.60	+0.76

LoA = Limits of Agreement (mean $\pm$ 1.96 SD)

Interpretation: 95% of measurements agree within ± 0.75 ppb, clinically/analytically acceptable for food safety monitoring where action levels are 50-300 ppb.

S6.4 Certified Reference Material Validation

Table S16. CRM Analysis Results (NIST SRM 1566b Oyster Tissue)

Analyte	Certified Value ($\mu\text{g g}^{-1}$)	ICP-MS Result ($\mu\text{g g}^{-1}$)	ICP-MS Recovery (%)	Sensor Result ($\mu\text{g g}^{-1}$)	Sensor Recovery (%)
Pb	0.308 ± 0.019	0.314 ± 0.012	102.0	0.298 ± 0.021	96.8
Cd	2.48 ± 0.08	2.52 ± 0.11	101.6	2.41 ± 0.18	97.2

Both methods achieve target recovery (95-105%), confirming accuracy against independent benchmark.

S7. Stability and Regeneration Protocols

S7.1 Long-term Storage Stability

Table S17. Detailed Stability Assessment (50 ppb Pb²⁺ + Cd²⁺ standard)

Storage Time	Storage Condition	Pb ²⁺ Response Retention (%)	Cd ²⁺ Response Retention (%)	Visual/Physical Changes
0 (fresh)	-	100.0 (11.8 μ A)	100.0 (9.9 μ A)	Uniform black coating
3 days	4°C, desiccated	99.8 $\pm$ 1.2	99.5 $\pm$ 1.4	No change
1 week	4°C, desiccated	99.2 $\pm$ 1.5	98.8 $\pm$ 1.8	No change
2 weeks	4°C, desiccated	97.6 $\pm$ 2.1	97.2 $\pm$ 2.3	Slight edge browning
3 weeks	4°C, desiccated	95.8 $\pm$ 2.4	95.3 $\pm$ 2.6	Minor browning
4 weeks	4°C, desiccated	92.3 $\pm$ 3.2	92.8 $\pm$ 3.5	Moderate browning
6 weeks	4°C, desiccated	87.5 $\pm$ 4.1	88.2 $\pm$ 4.3	Visible oxidation spots
8 weeks	4°C, desiccated	82.1 $\pm$ 5.3	83.5 $\pm$ 5.1	Significant browning
2 weeks	Room temp, air	88.5 $\pm$ 3.8	89.1 $\pm$ 4.0	More browning than 4°C
2 weeks	-20°C, sealed	98.8 $\pm$ 1.6	98.5 $\pm$ 1.9	No change, frost formation

Degradation Mechanism: rGO surface oxidation (C-OH, C=O formation) and partial Nafion delamination. XPS analysis of aged electrodes shows increased O/C ratio (0.28 $\rightarrow$ 0.35 after 8 weeks).

Recommendation: Store at 4°C (desiccated) for routine use (2-4 week shelf life); -20°C storage extends to 6-8 weeks but requires thawing/equilibration.

S7.2 Continuous Use Reusability

Table S18. Repetitive Measurement Degradation

Measurement Cycle	Pb ²⁺ Response (% of initial)	Cd ²⁺ Response (% of initial)	Fouling Mechanism
1-5	100 $\pm$ 2	100 $\pm$ 2	Minimal
6-10	98 $\pm$ 3	97 $\pm$ 3	Protein adsorption onset
11-15	95 $\pm$ 3	94 $\pm$ 4	Organic accumulation
16-20	91 $\pm$ 4	90 $\pm$ 4	Significant fouling
21-25	85 $\pm$ 5	84 $\pm$ 5	Surface passivation
26-30 (no regen)	78 $\pm$ 6	76 $\pm$ 6	Severe fouling

Measurement Cycle	Pb ²⁺ Response (% of initial)	Cd ²⁺ Response (% of initial)	Fouling Mechanism
After regeneration	93 ± 3	92 ± 3	90-95% recovery

S7.3 Regeneration Protocols

Protocol A: Electrochemical Cleaning (Preferred)

1. Rinse electrode with DI water (30 s)
2. Immerse in 0.1 M HCl
3. Apply cyclic potential scan: -1.5 V to +0.5 V, 5 cycles, 100 mV s⁻¹
4. Rinse with DI water (60 s)
5. Equilibrate in acetate buffer pH 4.5 (120 s)
6. Verify performance with 50 ppb standard

Recovery Efficiency: 92.5 ± 3.2% (n=15 regeneration cycles)

Protocol B: Chemical Cleaning (Alternative)

1. Sonicate electrode in 1:1 ethanol:water (60 s)
2. Immerse in 0.5 M EDTA pH 8 (300 s) to chelate bound metals
3. Rinse thoroughly with DI water
4. Re-equilibrate in working buffer

Recovery Efficiency: 88.3 ± 4.5% (n=10 cycles), but slower

Maximum Regeneration Cycles: 3-4 cycles before <90% recovery; then electrode replacement recommended.

S8. Cost Analysis and Practical Implementation

S8.1 Detailed Cost Breakdown

Table S19. Per-Sample Cost Analysis

Item	Electrochemical Sensor	ICP-MS	Ratio
Capital Equipment			
Instrument cost	\$3,500 (portable potentiostat)	\$250,000 (ICP-MS)	1:71
Amortization (5 yrs, 1000 samples/yr)	\$0.70/sample	\$50/sample	1:71
Consumables			
Electrode fabrication	\$2.50 (reusable 80×) = \$0.031	-	-
Reagents (buffer, standards)	\$0.15	-	-

Item	Electrochemical Sensor	ICP-MS	Ratio
Digestion reagents	\$0.05 (simple extraction)	\$5.00 (HNO ₃ , H ₂ O ₂ , vessels)	1:100
Calibration standards	\$0.02	\$0.50	1:25
Labor			
Analyst time (\$/hr)	\$20 × 0.17 h = \$3.40	\$50 × 2.5 h = \$125	1:37
Training requirement	4 hours (technician)	40 hours (specialist)	1:10
Total Per-Sample Cost	\$4.33	\$180.50	1:42

Break-even Analysis: Capital equipment cost recovered after ~300 samples (electrochemical) vs. never recovered for small labs (ICP-MS requires high throughput to justify).

S8.2 Time Comparison

Table S20. Analysis Time Breakdown

Step	Electrochemical Sensor	ICP-MS
Sample preparation	5 min (extraction)	45 min (digestion + cooling)
Instrument setup	2 min	20 min (warm-up, tuning)
Measurement	5 min (deposition + scan)	3 min per sample
Calibration	15 min (5-point curve)	30 min (multi-element)
Data analysis	2 min	10 min (corrections, validation)
Total time (single sample)	29 min	108 min
Throughput (samples/day, 8h)	15-20	20-30 (batch advantage)

Field Advantage: Sensor provides results in <30 min on-site vs. 3-7 days for centralized lab (including transport, queue time).

S9. Supplementary Tables

Table S21. Comparison with Recent Literature (2020-2025)

Reference	Material	Target	LOD (ppb)	Linear Range (ppb)	Real Sample	Recovery (%)	Unique Feature
[48]	Polymer-MOF	Pb, Cd	0.8, 1.1	2-150	Biological	89-108	Conducting polymer integration
[49]	Modified CNTs	Multi-metal	1.5-3.2	5-300	Environmental	92-105	Simultaneous 4-metal detection
[50]	Bio-functionalized	Cd	1.3	3-120	Water	95-102	Molecular recognition
[51]	Surface-engineered	Pb, Cd	2.1, 2.8	5-200	Environmental	88-97	Antifouling coating

Reference	Material	Target	LOD (ppb)	Linear Range (ppb)	Real Sample	Recovery (%)	Unique Feature
[52]	Nanozyme-based	Pb	0.5	1-100	Water	95-103	Catalytic amplification
This work	Fe ₃ O ₄ @UiO-66-Py/rGO	Pb, Cd	0.3, 0.4	1-200	Seafood	92-102	Magnetic assistance + DFT validation

Table S22. Regulatory Limits Worldwide

Region/Standard	Pb Limit (mg kg ⁻¹)	Cd Limit (mg kg ⁻¹)	Sample Type	Reference Year
Codex STAN 193-1995	0.3	0.05-0.5	Fish/crustaceans	2019 revision
EC No 1881/2006	0.3	0.05-0.1	Seafood	2023 amendment
US FDA	0.5	0.5	Seafood	2022
Vietnam QCVN 8-2:2011/BYT	0.2	0.1	Aquaculture	2011
China GB 2762-2017	0.5	0.1-0.5	Seafood	2017
Japan MHLW	0.3	0.05-0.2	Fish/shellfish	2020
Australia/NZ FSANZ	0.5	0.05-1.0	Seafood	2021

Table S23. Vietnamese Aquaculture Production Statistics

Species	Annual Production (tonnes)	Export Value (USD)	Primary Destinations	Typical Pb/Cd Levels (ppb)
Pangasius (catfish)	1,200,000	\$2.1 billion	USA, EU, China	10-80 / 5-40
Penaeus vannamei (shrimp)	730,000	\$3.8 billion	Japan, USA, EU	15-120 / 8-65
Tilapia	185,000	\$340 million	Mexico, USA	8-55 / 3-30
Crab	28,000	\$180 million	China, Korea	20-95 / 12-58

Source: Vietnam Association of Seafood Exporters and Producers (VASEP), 2024 report