Supporting Information

3D-Printed Column with Porous Monolithic Packing for Online Solid-Phase Extraction of Multiple Trace Metals in Environmental Water Samples

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Table of Content

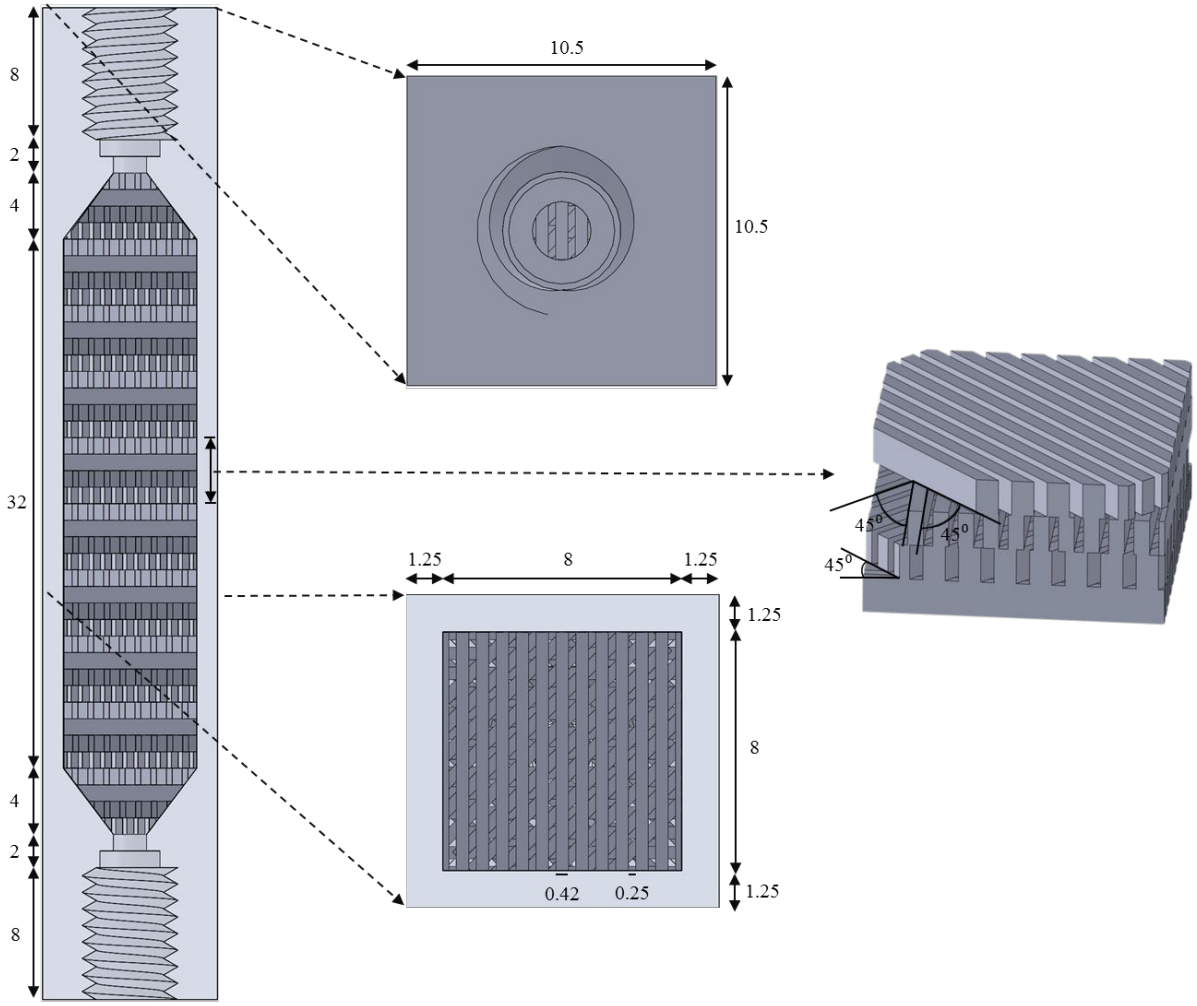
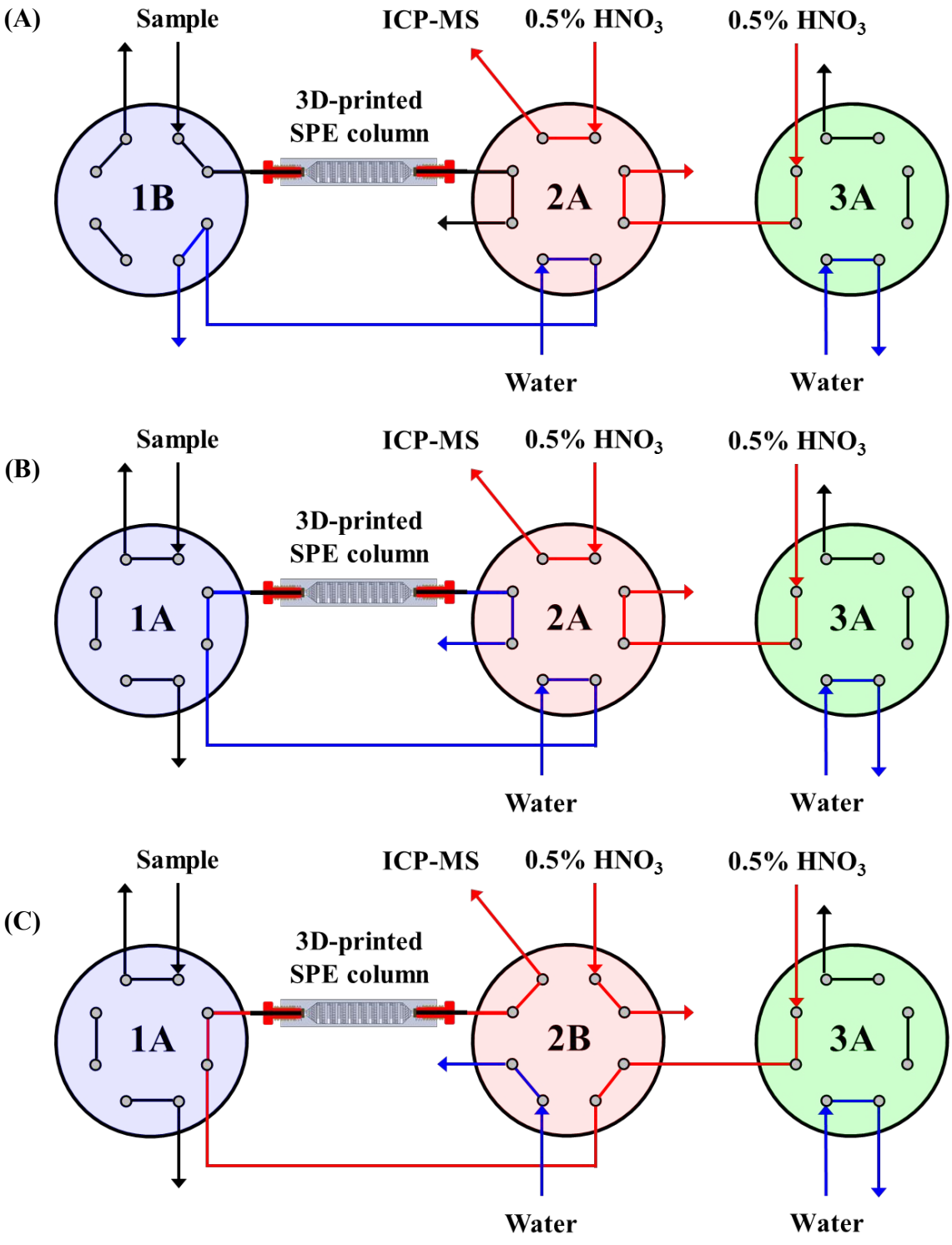


Figure S1. Detailed dimensions of the SPE column designed with the inner packing stacked by interlacing cuboids. Units: mm.


(A)
Sample
ICP-MS
0.5% HNO3
0.5% HNO3
3D-printed
SPE column
1B
2A
3A
Water
Water
(B)
Sample
ICP-MS
0.5% HNO3
0.5% HNO3
3D-printed
SPE column
1A
2A
3A
Water
Water
(C)
Sample
ICP-MS
0.5% HNO3
0.5% HNO3
3D-printed
SPE column
1A
2B
3A
Water
Water

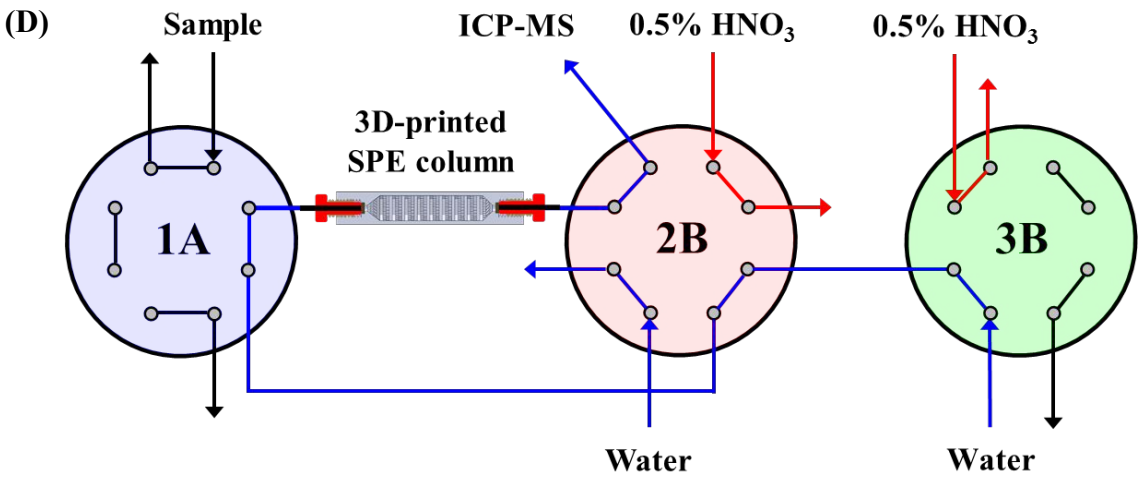


Figure S2. Schematic step-by-step representations of the operating sequence for the automatic sample pretreatment system using the 3D-printed SPE column featuring porous monolithic packing. (A) Step 1 (BAA): The conditioned sample (pH 8) was loaded into the column for extraction of the tested metal ions. (B) Step 2 (AAA): Residual sample matrices were evacuated, and the column was rinsed with pure water. (C) Step 3 (ABA): The extracted metal ions were eluted with 0.5% HNO_3 and delivered to the ICP-MS system. (D) Step 4 (ABB): The residual eluent in the column was replaced with pure water prior to loading of the next sample.

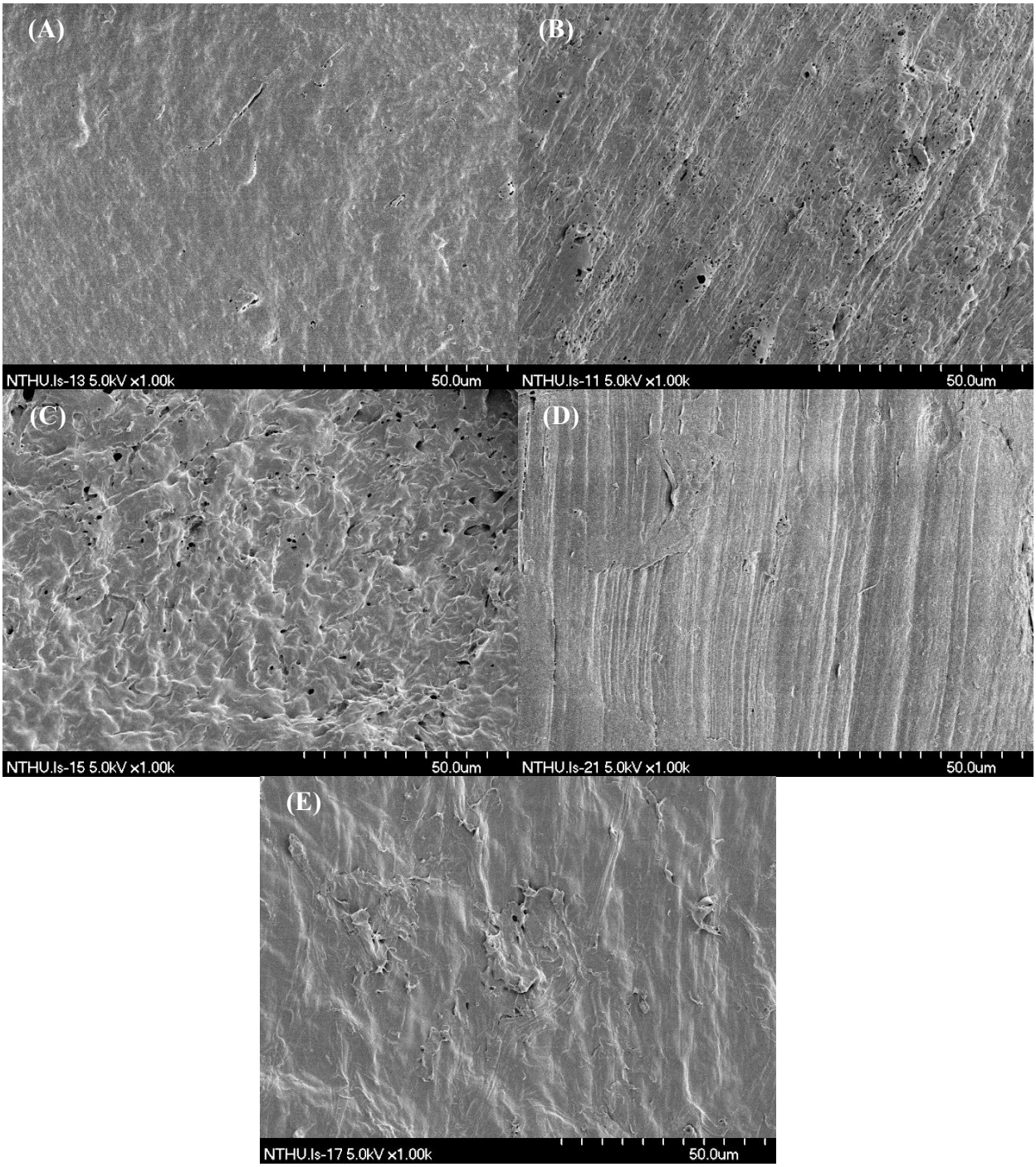


Figure S3. SEM images of the surfaces of the inner packings fabricated using (A) ABS, (B) Lay-Fomm 40, (C) Lay-Fomm 60, (D) Gel-Lay, and (E) Lay-Felt filament, recorded using a Hitachi HT7700 scanning electron microscope. All of these fabricated columns had been washed with a pure water stream for 24 h to remove their water-soluble components. Scale bar: 50 μm.

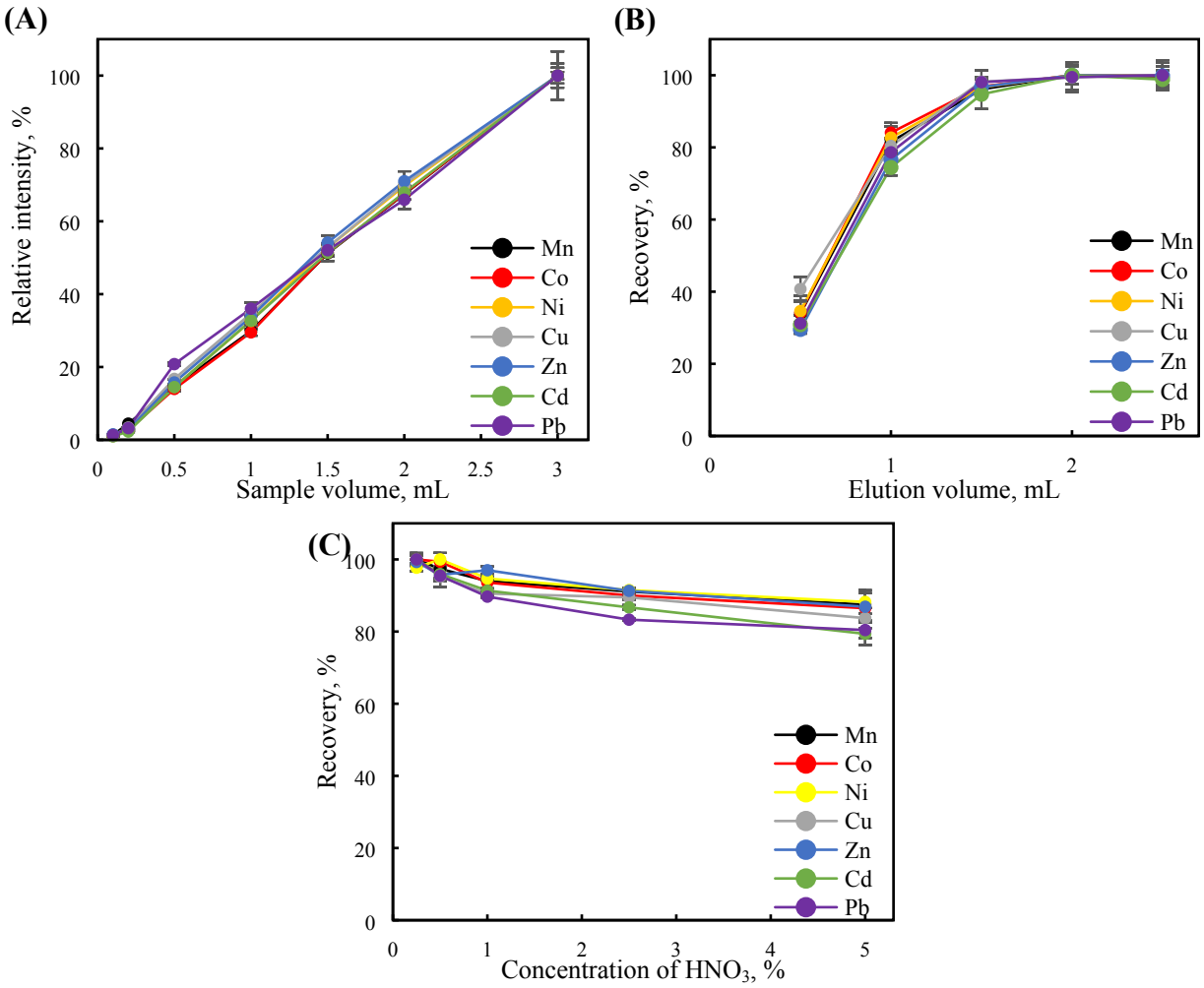


Figure S4. Signal intensities of the extracted metal ions, plotted with respect to (A) the sample volume, (B) the elution volume, and (C) the HNO_3 concentrations in the eluent. Data in (A) are normalized to their respective maxima; data in (B) and (C) are expressed as the extraction recoveries of these metal ions (10 μg L^{-1}). Error bars represent standard deviations (n = 5). The sample loading flow rate and elution flow rate were 1.0 mL min^{-1}; the rinsing flow rate was 0.5 mL min^{-1}.

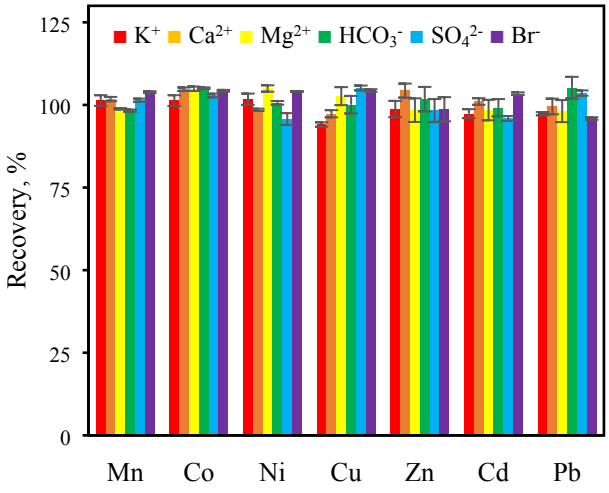


Figure S5. Relative signal intensities of the extracted metal ions, plotted with respect to the co-existing matrix ions [K^+ (1000 mg L^{-1}; added as KCl), Ca^{2+} (1000 mg L^{-1}; added as $CaCl_2$), Mg^{2+} (1000 mg L^{-1}; added as $MgCl_2$), HCO_3^- (500 mg L^{-1}; added as $NaHCO_3$), SO_4^{2-} (2000 mg L^{-1}; added as Na_2SO_4), and Br^- (500 mg L^{-1}; added as NaBr)]. All data are expressed as the extraction recoveries of these metal ions (10 μg L^{-1}). Error bars represent standard deviations (n = 5). The sample loading flow rate and elution flow rate were 1.0 mL min^{-1}; the rinsing flow rate was 0.5 mL min^{-1}.

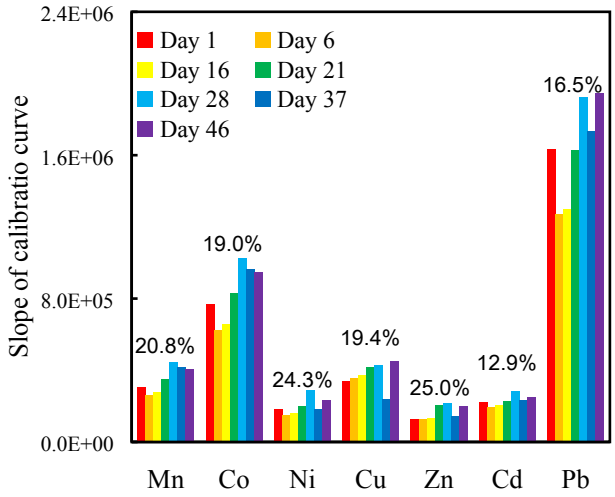


Figure S6. The fluctuations of the daily calibration slopes for these tested metal ions within 46 days.

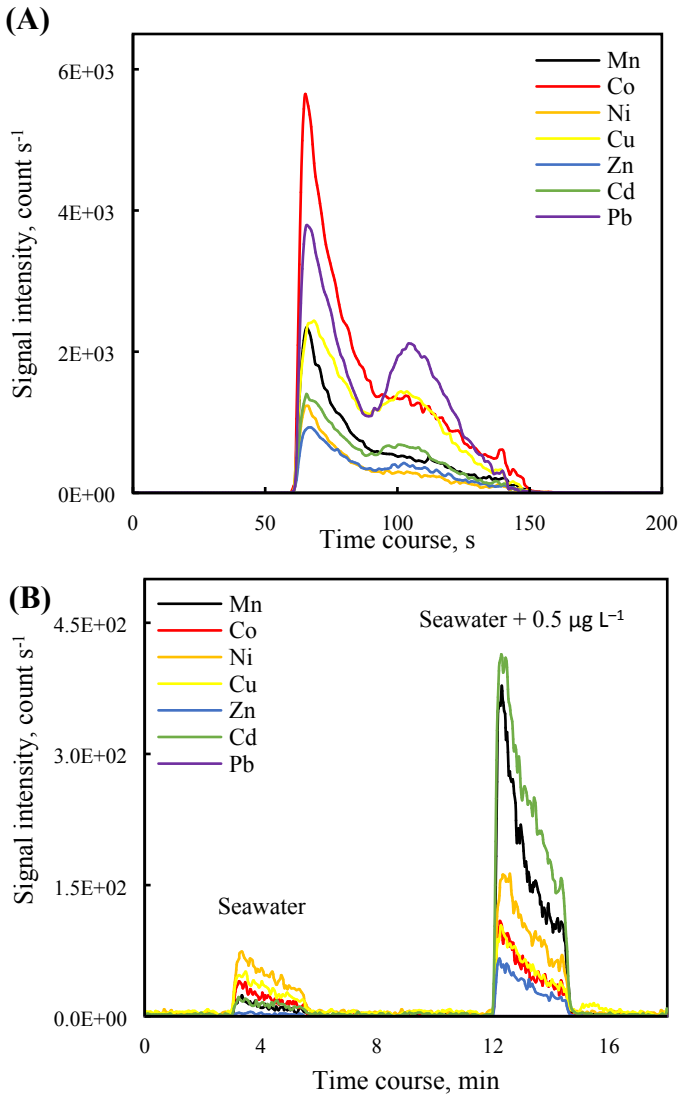


Figure S7. Elution profiles of these tested metal ions in (A) a standard solution (5 µg L^{-1}) and (B) a seawater sample (Keelung) with its spike analysis from the automatic sample pretreatment system incorporating the 3D-printed SPE column featuring porous monolithic packing.

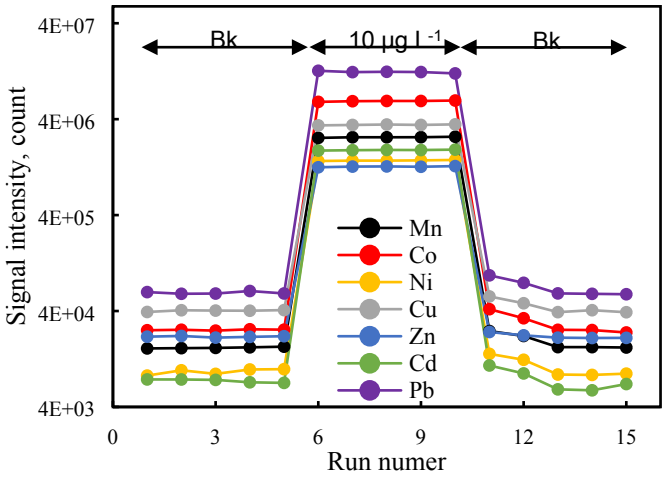


Figure S8. Temporal response of the proposed automatic sample pretreatment system incorporating the 3D-printed SPE column with porous monolithic packing for switching samples from the blank to the standard (10 μg L^{-1}) and then from the standard back to the blank. Sampling frequency: 12 h^{-1}.

Table S1. Operating sequence of the automatic sample pretreatment system

Step	Valve position (1 → 3)	Time interval	Function
1 (Fig. S2A)	BAA	0:00–1:00	loading of the conditioned sample into the column
2 (Fig. S2B)	AAA	1:00–3:00	evacuating sample matrices and rinsing the column with pure water
3 (Fig. S2C)	ABA	3:00–4:30	eluting these extracted metal ions with 0.5% HNO_3 and delivering to the ICP-MS system
4 (Fig. S2D)	ABB	4:30–5:00	replacing the residual eluent with pure water

Table S2. Specific surface area (BET), pore volume, and pore diameter of these monolithic packings after removal of water-soluble component

	Specific surface area, $m^2\ g^{-1}$	Pore volume, $cm^3\ g^{-1}$	Average pore diameter, nm
Lay-Fomm 40	5.7	0.008	8.4
Lay-Fomm 60	3.7	0.008	7.6
Lay-Felt	4.5	0.007	5.9
Gel-Lay	4.5	0.008	6.7

Table S3. Optimized conditions for the automatic sample pretreatment system

3D-Printed SPE column with porous monolithic packing	
Porous composite	Lay-Fomm 40
Interlacing cuboids	40 layers
Sample pretreatment using the 3D-printed SPE column	
Sample loading flow rate and volume	1.0 mL min^{-1}, 1.0 mL
Rinsing medium	H_2O
Rinsing flow rate and volume	0.25 mL min^{-1}, 0.5 mL
Eluent	0.5% HNO_3
Elution flow rate and volume	1.0 mL min^{-1}, 1.5 mL
ICP-MS	
ICP mass spectrometer	Agilent 7700x
Plasma forward power	1500 W
Ar gas flow rate	
Plasma gas	15 L min^{-1}
Auxiliary gas	0.9 L min^{-1}
Carrier gas	0.95 L min^{-1}
Makeup gas	0.20 L min^{-1}
Sampling cone	Pt, 1-mm orifice
Skimmer cone	Pt, 0.4-mm orifice
Analysis mode	Time-resolved analysis
Integration time	50 ms
Isotopes monitored	^{55}Mn, ^{59}Co, ^{60}Ni, ^{65}Cu, ^{66}Zn, ^{114}Cd, ^{208}Pb

Table S4. Analytical characteristics of the sample pretreatment systems respectively incorporating the column packed with the polyurethane filaments and the column packed with the polyurethane foam

	Polyurethane filament-packed column		Polyurethane foam-packed column	
	Extraction efficiency, %	MDL, ng L^{-1}	Extraction efficiency, %	MDL, ng L^{-1}
^{55}Mn	98.3	24.4	15.8	61.2
^{59}Co	98.6	6.1	18.0	11.4
^{60}Ni	98.3	31.0	15.3	30.8
^{65}Cu	98.8	72.7	37.5	84.5
^{66}Zn	98.8	40.1	35.2	58.9
^{114}Cd	98.3	4.4	12.6	17.4
^{208}Pb	98.2	2.7	37.1	4.2