Trace manganese detection via differential pulse cathodic stripping voltammetry using disposable electrodes: additively manufactured nanographite electrochemical sensing platforms

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ESI Table 1. Optimisation of the manganese (II) detection using cathodic stripping voltammetry

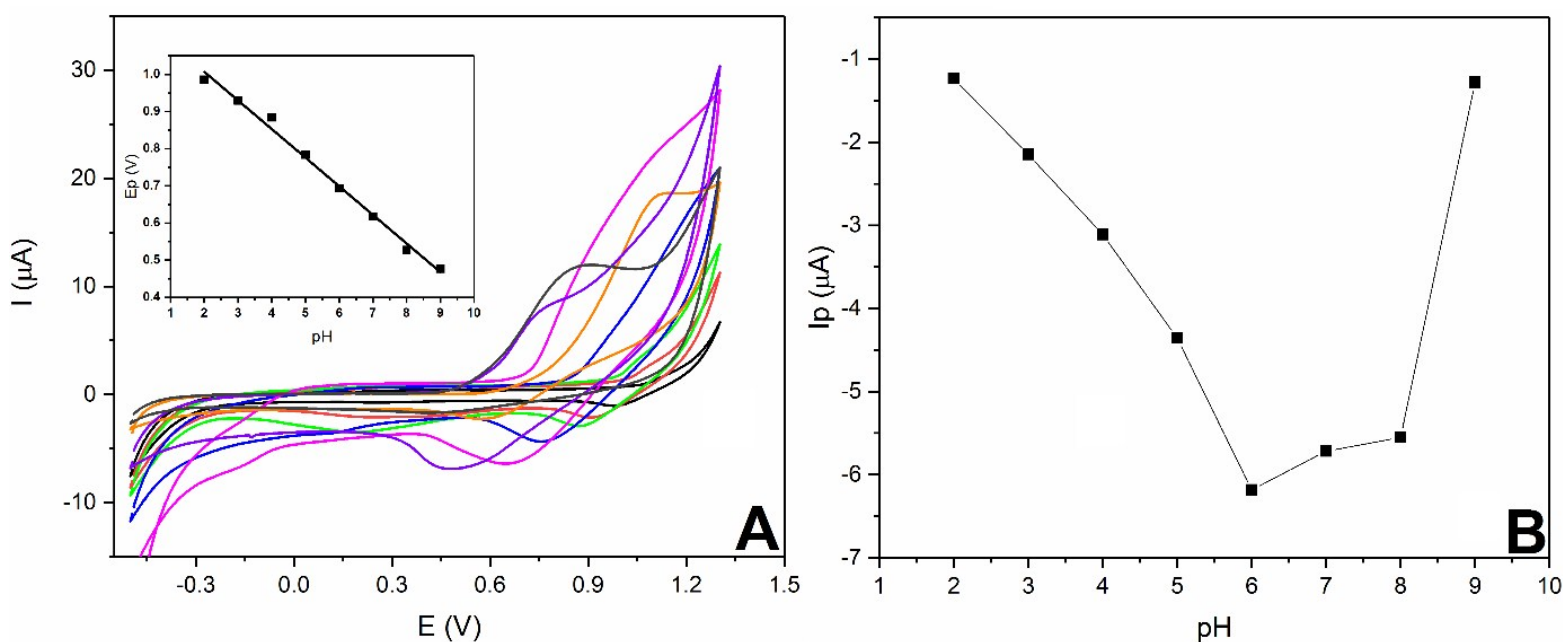| Variables	Studied range	Selected value
pH	2 – 9	6
Deposition potential (V)	0.8 – 1.2	1.05
Time of deposition (s)	0 – 450	350
Stirring rate (rpm)	0 – 2500	1500
Step potential (mV)	1 – 12	8
Modulation amplitude (mV)	25 – 500	250
Modulation time (s)	0.005 – 0.100	0.02

Figure ESI-1. (A) Cyclic voltammograms recordings containing 1.8×10^{-3} mol L^{-1} of

Mn^{2+} in BR 0.04 mol L^{-1} at pH 2 (black line), pH 3 (red line), pH 4 (green line), pH 5

(blue line), pH 6 (pink line), pH 7 (orange line), pH 8 (purple line) and pH 9 (grey line). (B) Voltammetric response vs pH of the supporting electrolyte for the voltammograms in (A). The inset in (A) corresponds the dependence of MnO_2 reduction potential (Ep) on pH of background electrolyte.
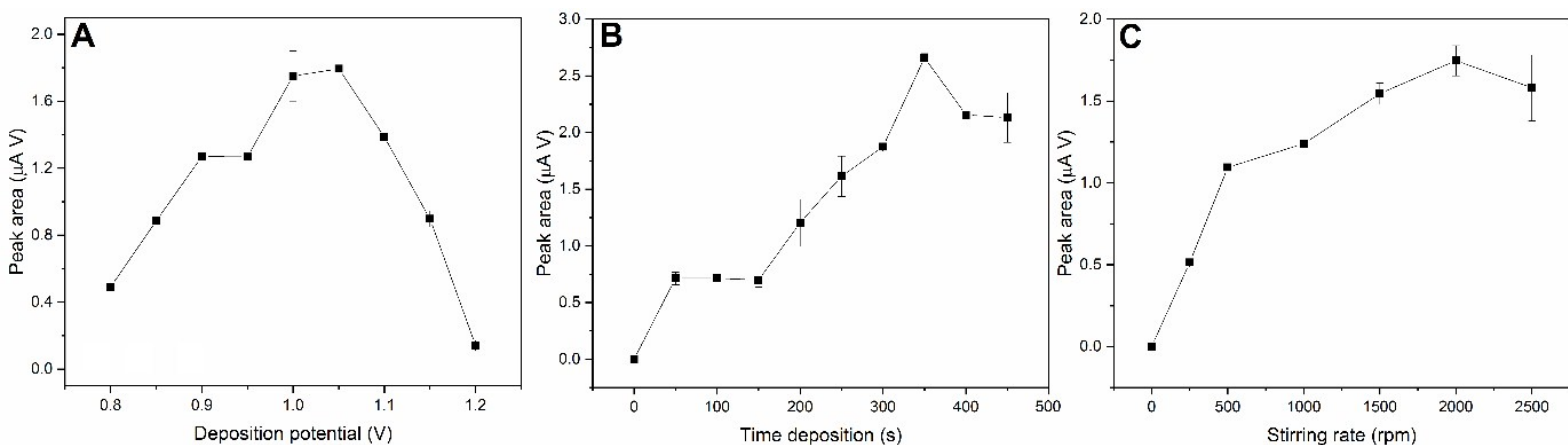

Figure ESI-2. (A) Deposition potential optimization. DPCSV conditions: 240 s of MnO_2 deposition; stirring rate: 1000 rpm; scan from +1.4 to -0.4 V; step potential = 10 mV, interval time = 0.1 s, modulation amplitude = 150 mV; modulation time = 0.02 s and standby potential = 0.0 V. **(B) Deposition time optimization.** DPCSV conditions: deposition potential: +1.05 V; other conditions are the same of Fig. ESI-2 (A). **(C) Stirring rate optimization.** DPCSV conditions: time deposition: 350 s; other conditions are the same of Fig. ESI-2 (B). The deposition potential optimization, time deposition optimization and stirring rate optimization were carried out in the presence of 1.1 μmol L^{-1} of Mn^{2+} using BR buffer (pH 6.0) as supporting electrolyte.
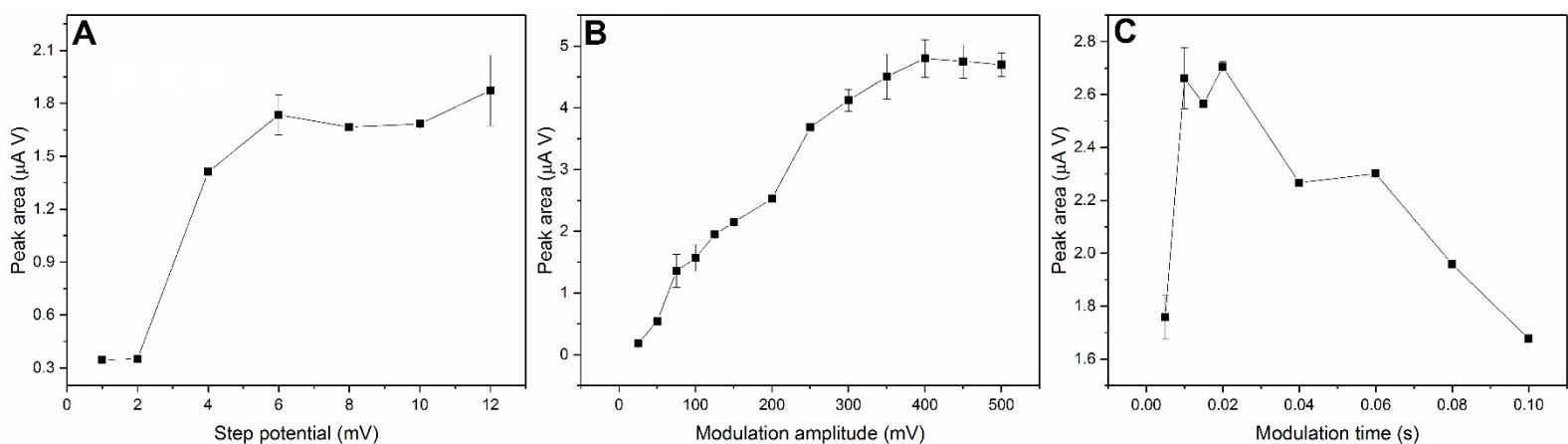
Figure ESI-3. (A) Step potential optimization. DPCSV conditions: deposition potential: +1.05 V; time deposition: 350 s; scan from +1.4 to -0.4 V; stirring rate: 1500 rpm; interval time = 0.1 s, modulation amplitude = 150 mV; modulation time = 0.02 s and standby potential = 0.0 V. **(B) Modulation amplitude optimization.** DPCSV conditions: step potential = 8 mV; other conditions are the same of Fig. ESI-3 (A). **(C) Modulation time optimization.** DPCSV conditions: modulation amplitude = 250 mV; other conditions are the same of Fig. ESI-3 (B). The optimization studies of step potential, modulation amplitude and modulation time were made using 1.1 μmol L^{-1} of Mn^{2+} in BR buffer (pH 6.0) as supporting electrolyte.

ESI Table 2. Trace metals contents in reference material of drinking water (Level 2, ALPHA APS-1075).

Element	Concentration ($\mu g\ mL^{-1}$)	Element	Concentration ($\mu g\ mL^{-1}$)
Aluminium	120	Manganese	40
Arsenic	80	Molybdenum	100
Antimony	10	Nickel	60
Barium	50	Potassium	2500
Beryllium	20	Rubidium	10
Bismuth	10	Selenium	10
Cadmium	10	Silver	2
Calcium	35000	Sodium	6000
Chromium	20	Strontium	250
Cobalt	25	Tellurium	3
Copper	20	Thallium	10
Iron	100	Uranium	10
Lead	40	Vanadium	30
Lithium	20	Zinc	70
Magnesium	9000		

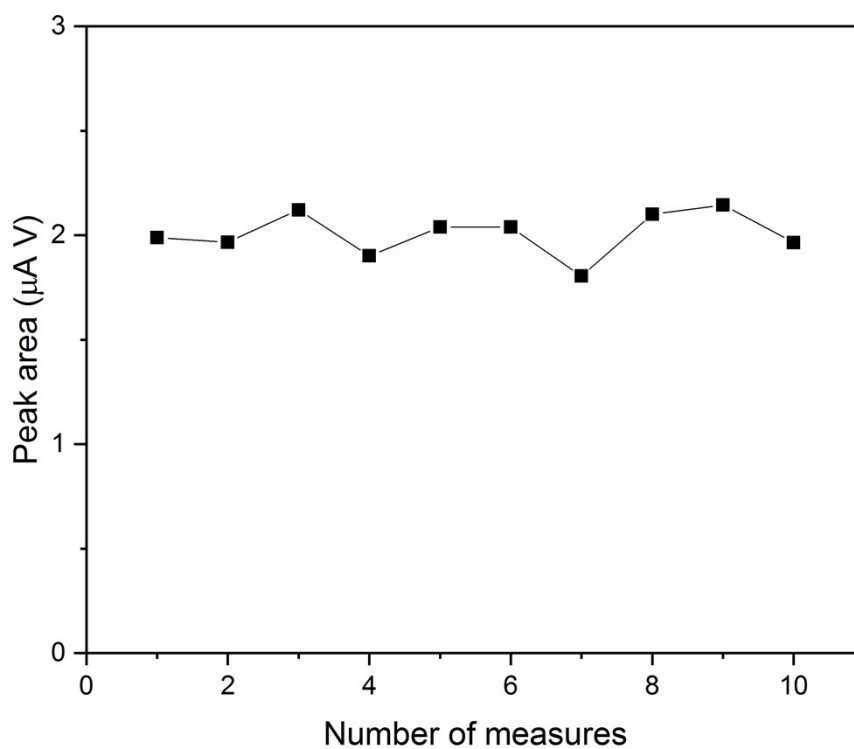**Figure ESI-4.** Repeatability study (N = 10) for 1 μmol L^{-1} of manganese (II) using the AM-electrodes. DPCSV conditions: deposition potential: +1.05 V; time deposition: 350 s; scan from +1.4 to -0.4 V; stirring rate: 1500 rpm; interval time = 0.1 s, step potential = 8 mV; modulation amplitude = 250 mV, modulation time = 0.02 s and standby potential = 0.0 V. Supporting electrolyte: BR buffer (pH 6.0).
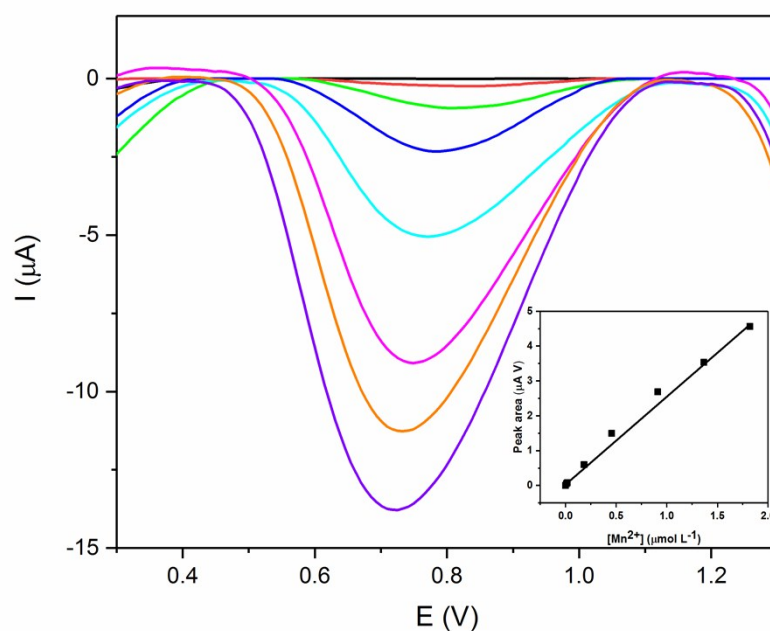
Figure ESI-5. Background-corrected differential-pulse cathodic stripping voltamograms of increasing concentrations of manganese (II) using SPEs: blank (black line); red line (9.10×10^{-9} mol L^{-1} / 0.5 µg L^{-1}); green line (1.82×10^{-8} mol L^{-1} / 1.0 µg L^{-1}); blue line (1.82×10^{-7} mol L^{-1} / 10.0 µg L^{-1}); cyan line (4.55×10^{-7} mol L^{-1} / 25.0 µg L^{-1}); pink line (9.10×10^{-7} mol L^{-1} / 50.0 µg L^{-1}); orange line (1.37×10^{-6} mol L^{-1} / 75.0 µg L^{-1}); purple line (1.82×10^{-6} mol L^{-1} / 100.0 µg L^{-1}). Insert is a plot of peak area verses manganese (II) concentrations. CSDPV conditions: deposition potential: +1.05 V; time deposition: 350 s; scan from +1.4 to -0.4 V; stirring rate: 1500 rpm; interval time = 0.1 s, step potential = 8 mV; modulation amplitude = 250 mV, modulation time = 0.02 s and standby potential = 0.0 V. Supporting electrolyte: BR buffer (pH 6.0).
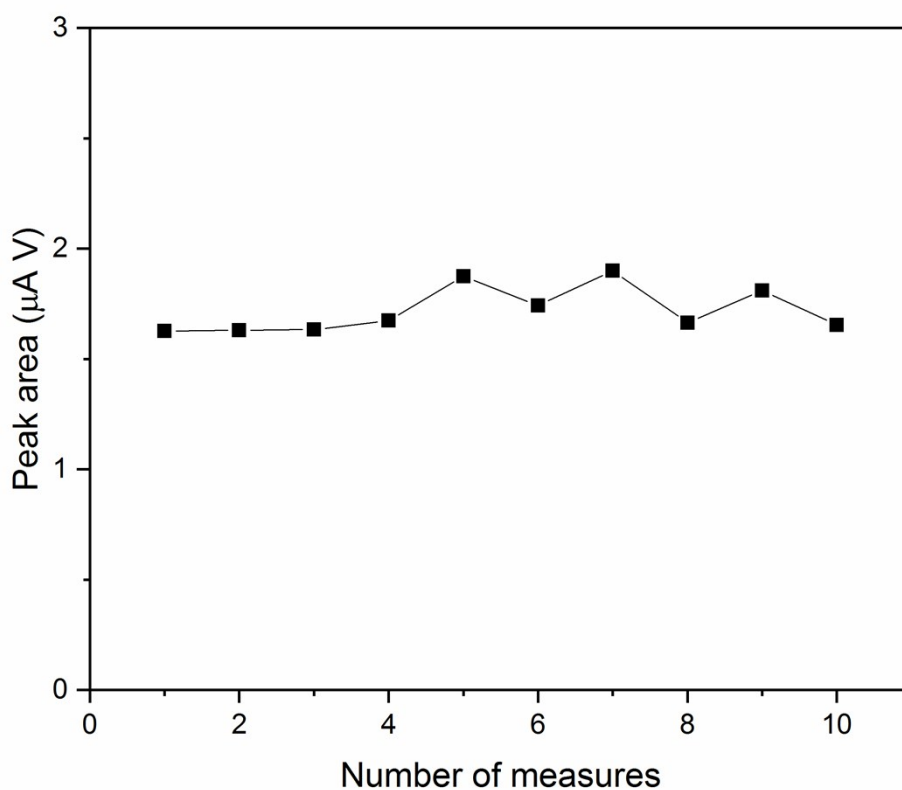
Figure ESI-6. Repeatability study ($N = 10$) for 1 μmol L^{-1} of manganese (II) using SPEs. DPCSV conditions: deposition potential: +1.05 V; time deposition: 350 s; scan from +1.4 to -0.4 V; stirring rate: 1500 rpm; interval time = 0.1 s, step potential = 8 mV; modulation amplitude = 250 mV, modulation time = 0.02 s and standby potential = 0.0 V. Supporting electrolyte: BR buffer (pH 6.0).