

1. The Cyclic Voltammetry of the Hexacyanoferrate System with Different Scan Rates

A potassium ferrocyanide/ferricyanide system was employed as it is known that it follows a diffusion-controlled reaction for a reversible system. Thus, the GCE response should follow four characteristics, as described below. If this was not present, the GCE preparation procedure was repeated. During the forward scan (from more positive to towards more negative potentials), the $[\text{Fe}(\text{CN})_6]^{3-}$ is reduced to $[\text{Fe}(\text{CN})_6]^{4-}$, which results in a cathodic peak formation. During the reverse scan (from more negative towards more positive potentials), the $[\text{Fe}(\text{CN})_6]^{4-}$ is reoxidized to $[\text{Fe}(\text{CN})_6]^{3-}$, which results in an anodic peak formation. A reversible system that is diffusion controlled should follow four characteristics for cyclic voltammogram measurements: (i) the CV peak current for a reversible system is given by the Randles–Sevcik equation, i.e., $I_{\text{peak}} = (2.69 \cdot 10^5) \cdot n_{\text{el}}^{3/2} \cdot A \cdot c \cdot D^{1/2} \cdot \nu^{1/2}$, where, A is the area of the electrode in cm^2 , c is the concentration in mol/L , D is the diffusion coefficient in cm^2/s , and ν is the scan rate in V/s . Therefore, with an increase of $\nu^{1/2}$, the I_{peak} (for both anodic and cathodic CV peaks) should increase linearly; (ii) the ratio of the anodic (I_{pa}) vs. cathodic (I_{pc}) CV peak currents is unity, i.e., $| \frac{I_{\text{pa}}}{I_{\text{pc}}} | = 1$; (iii) the potential difference between the anodic (E_{pa}) and cathodic (E_{pc}) peak potentials should follow $\Delta E = E_{\text{pa}} - E_{\text{pc}} = \frac{0.059}{n_{\text{el}}}$, where n_{el} is the number of electrons (one in the present case), and (iv) the CV peak potentials should not change with increasing ν .

2. SWASV Voltammograms, Linear Calibration Curves, and the Shift of the Analyte's Peak Potential with Increasing Concentration (Three out of Six Repetitions) for All Tested Electrodes

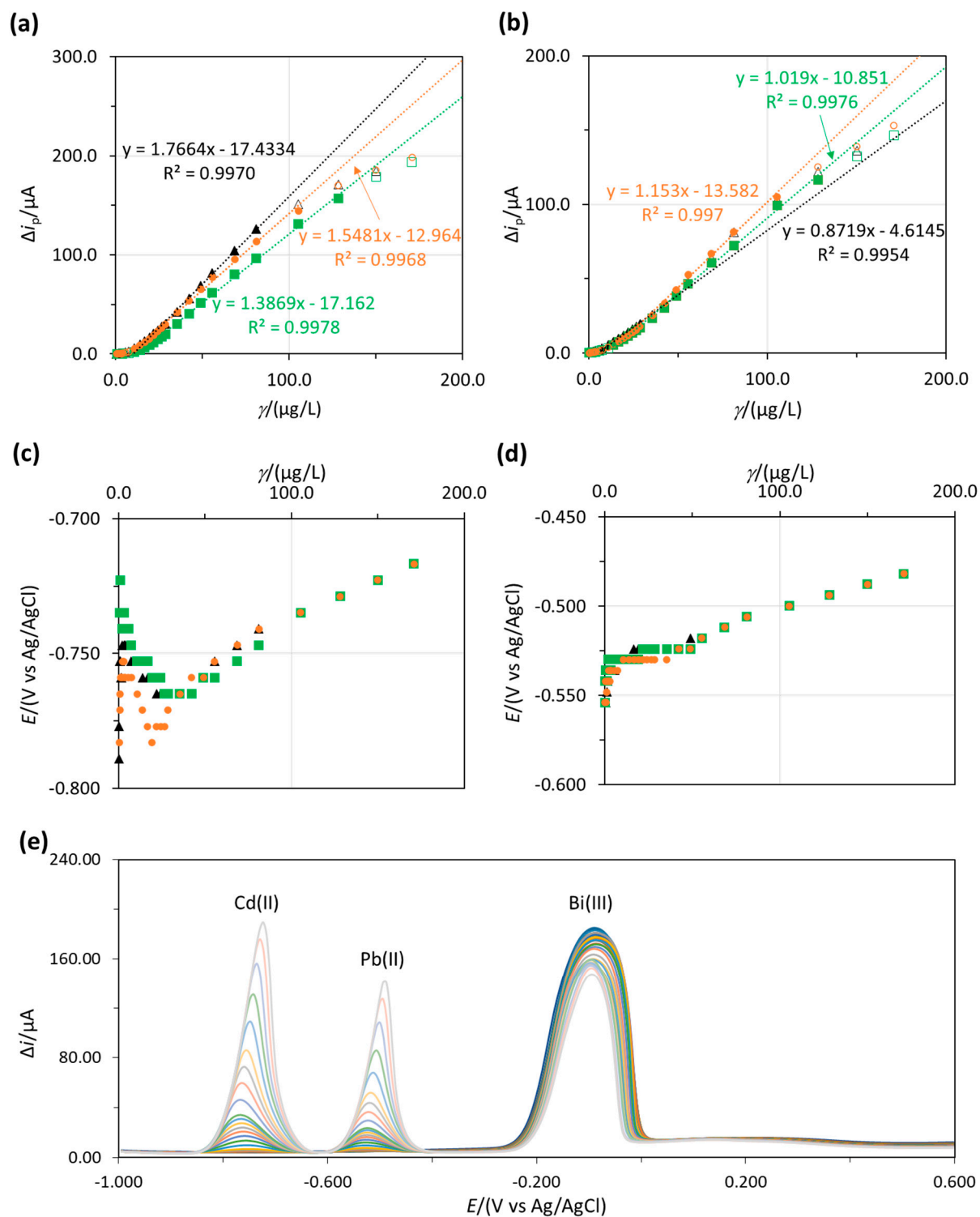


Figure S1. Three repetition measurements for determining the linear concentration ranges for (a) Cd(II) and (b) Pb(II), the stripping peak potentials vs. concentration for (c) Cd(II) and (d) Pb(II), and (e) the corresponding voltammogram (one out of six repetition measurements) using Electrode No. 1 tested in a fractional two-level factorial design in Table 1. The full symbols in (a) and (b) represent the calibration points within the linear concentration range, while the empty symbols represent measurements outside the linear concentration range. Δi_p is the stripping peak height.

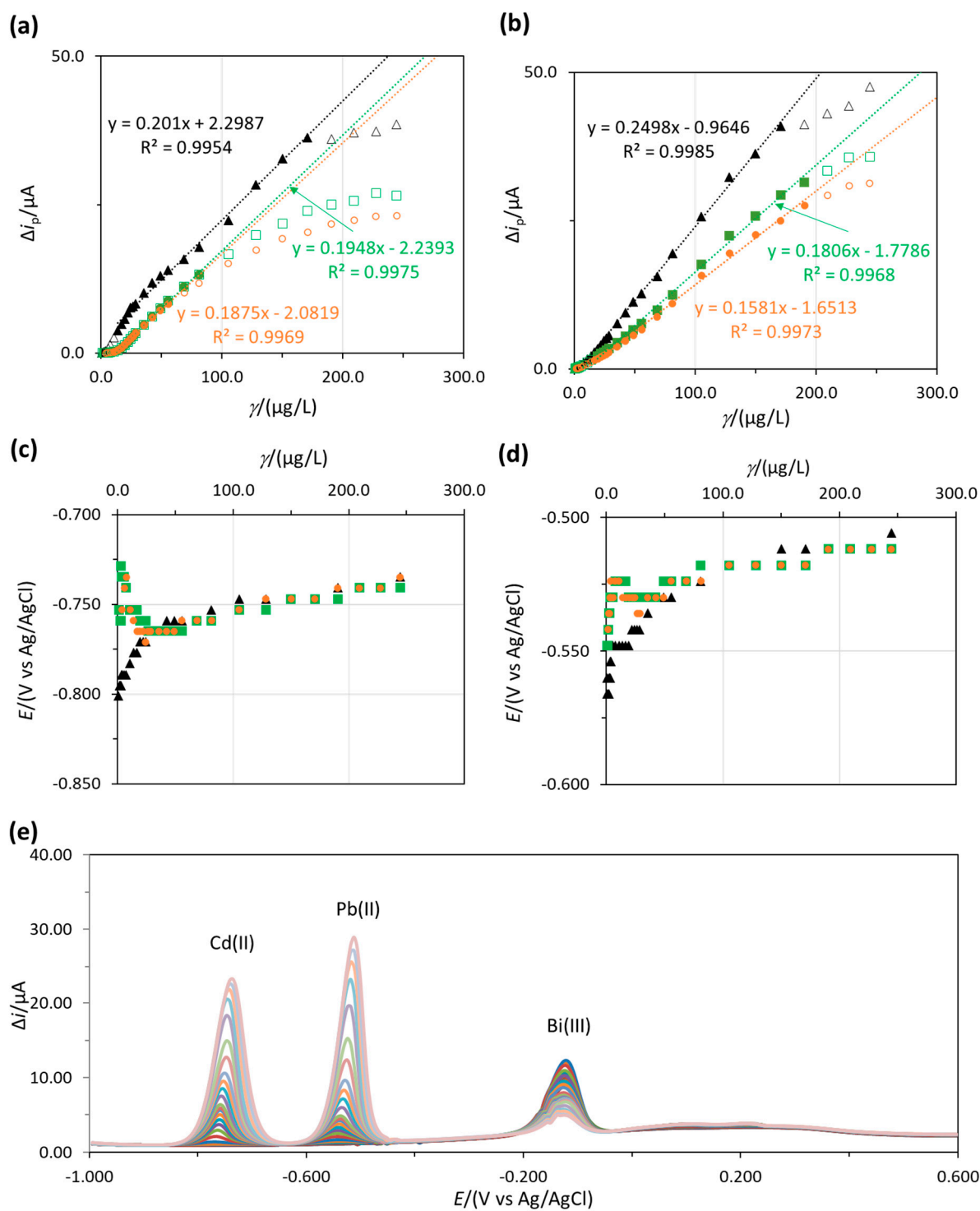


Figure S2. Three repetition measurements for determining the linear concentration ranges for (a) Cd(II) and (b) Pb(II), the stripping peak potentials vs. concentration for (c) Cd(II) and (d) Pb(II), and (e) the corresponding voltammogram (one out of six repetition measurements) using Electrode No. 3 tested in a fractional two-level factorial design in Table 1.

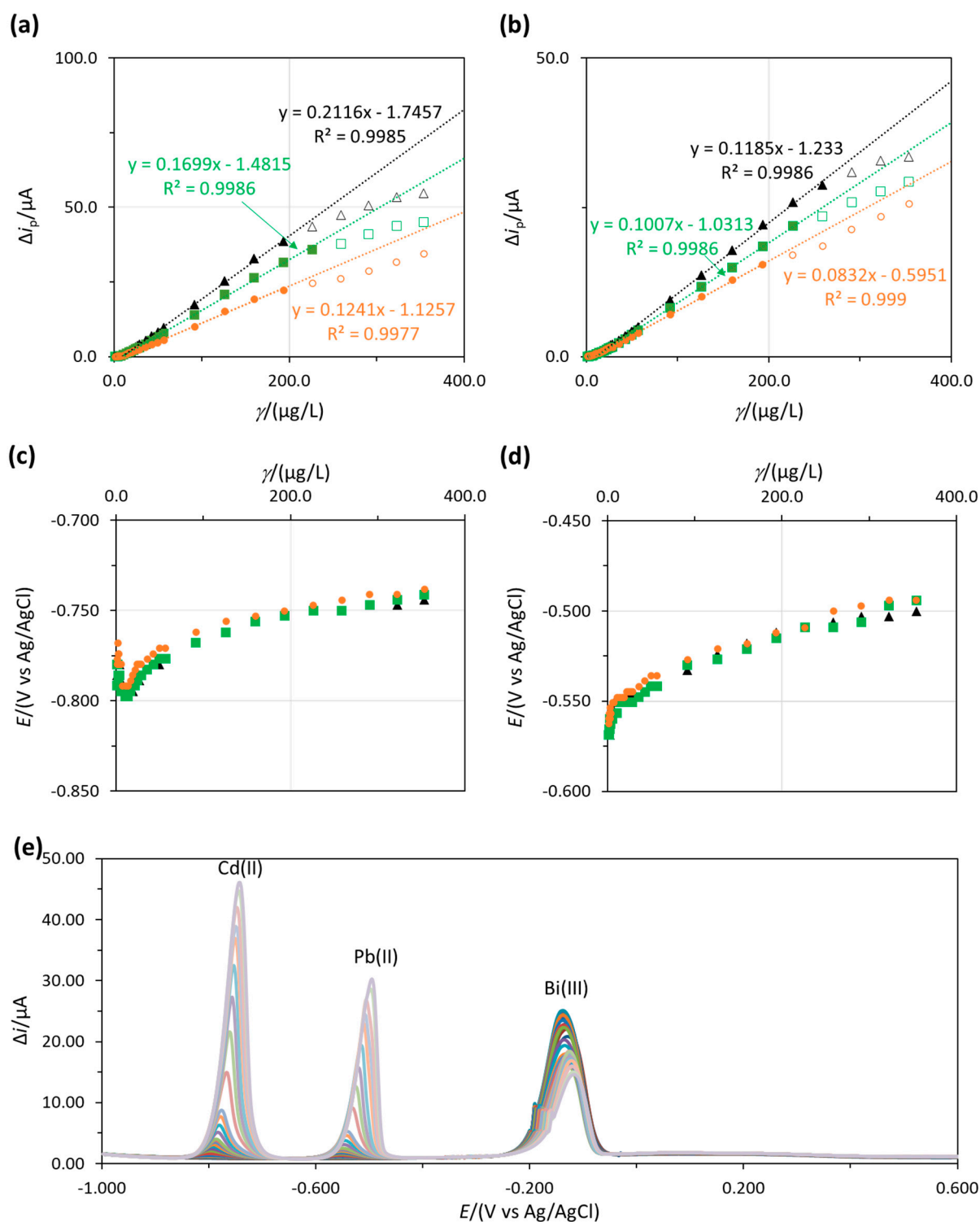


Figure S3. Three repetition measurements for determining the linear concentration ranges for (a) Cd(II) and (b) Pb(II), the stripping peak potentials vs. concentration for (c) Cd(II) and (d) Pb(II), and (e) the corresponding voltammogram (one out of six repetition measurements) using Electrode No. 4 tested in a fractional two-level factorial design in Table 1.

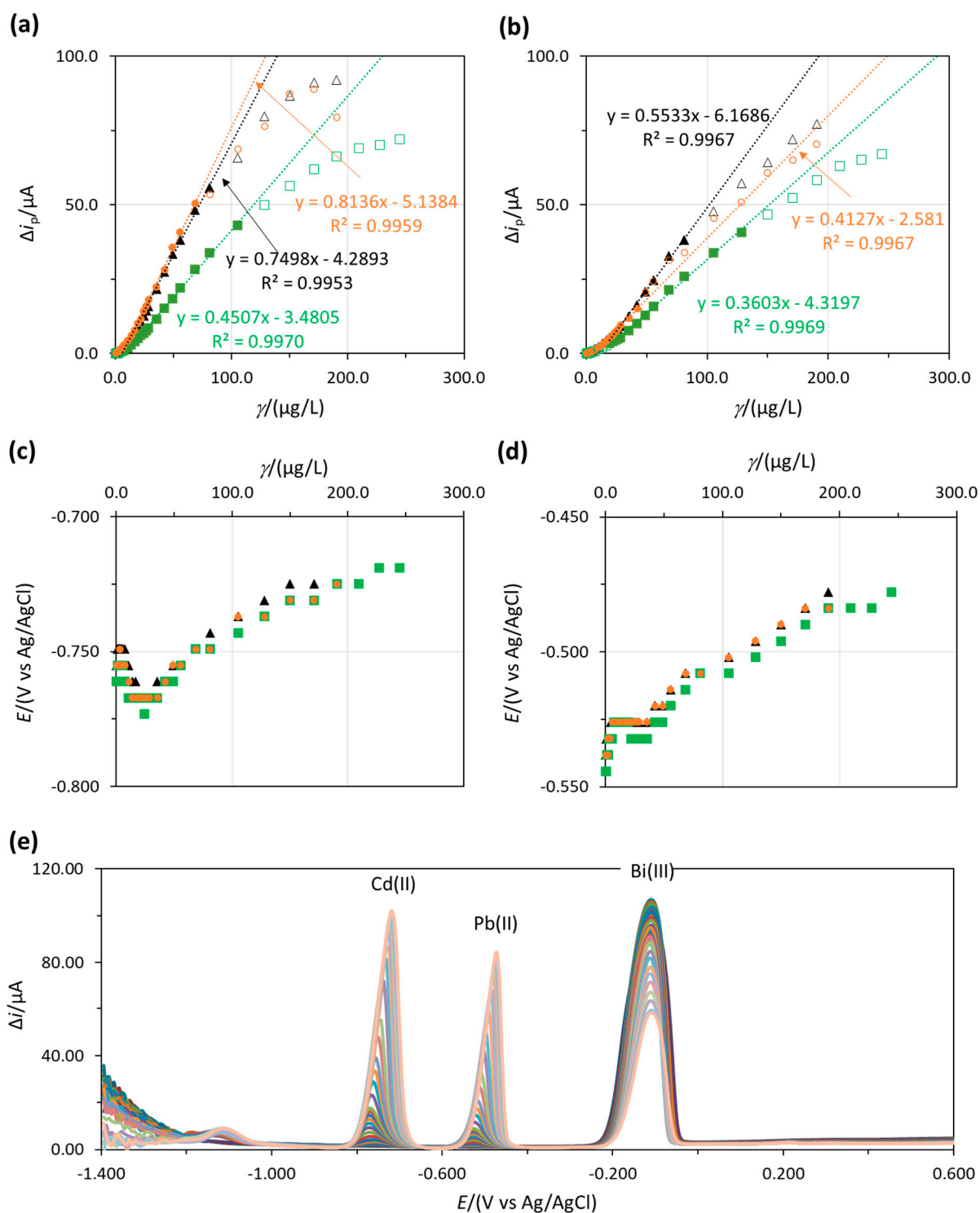


Figure S4: Three repetition measurements for determining the linear concentration ranges for (a) Cd(II) and (b) Pb(II), the stripping peak potentials vs. concentration for (c) Cd(II) and (d) Pb(II), and (e) the corresponding voltammogram (one out of six repetition measurements) using Electrode No. 5 tested in a fractional two-level factorial design in Table 1.

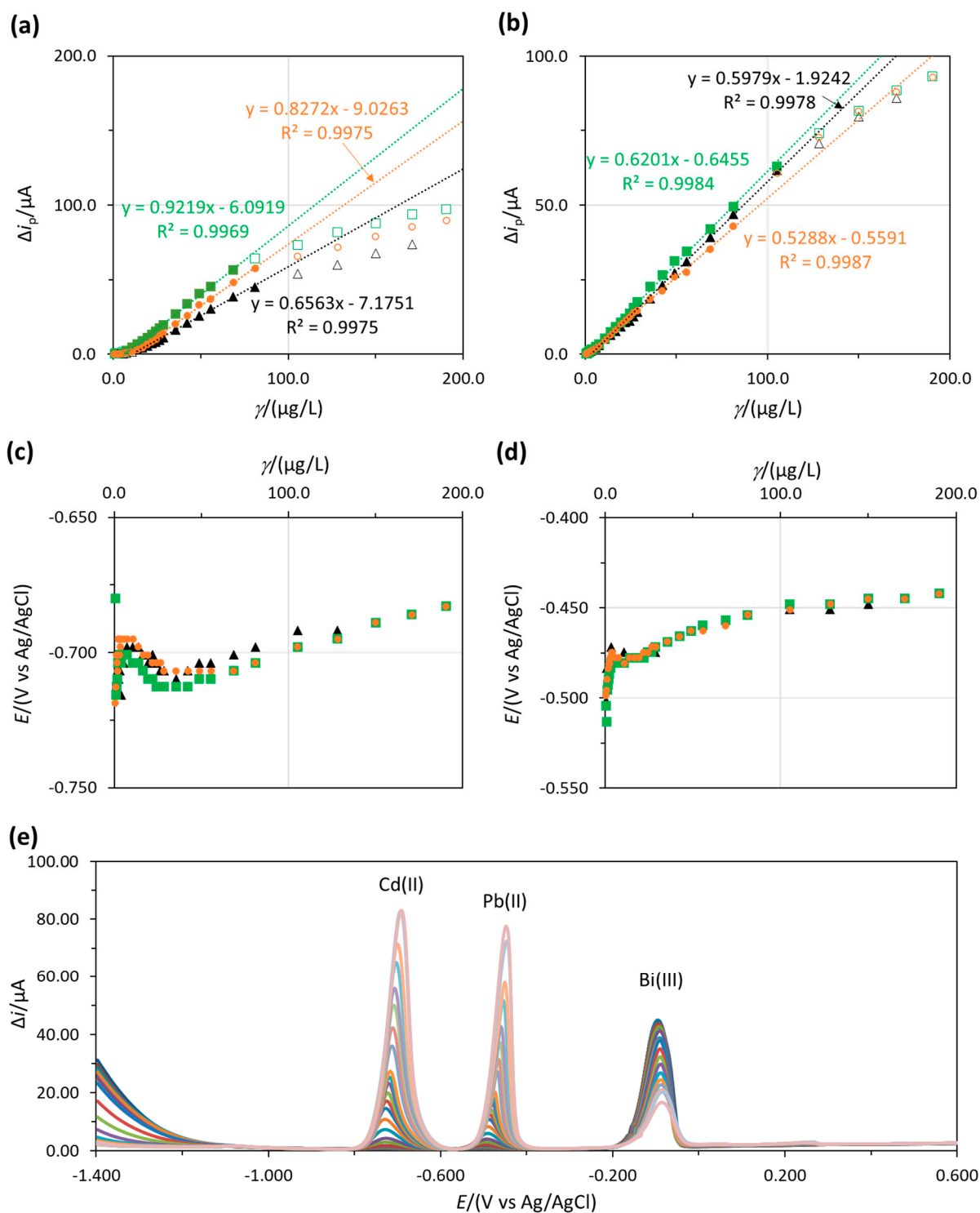


Figure S5: Three repetition measurements for determining the linear concentration ranges for (a) Cd(II) and (b) Pb(II), the stripping peak potentials vs. concentration for (c) Cd(II) and (d) Pb(II), and (e) the corresponding voltammogram (one out of six repetition measurements) using Electrode No. 6 tested in a fractional two-level factorial design in Table 1.

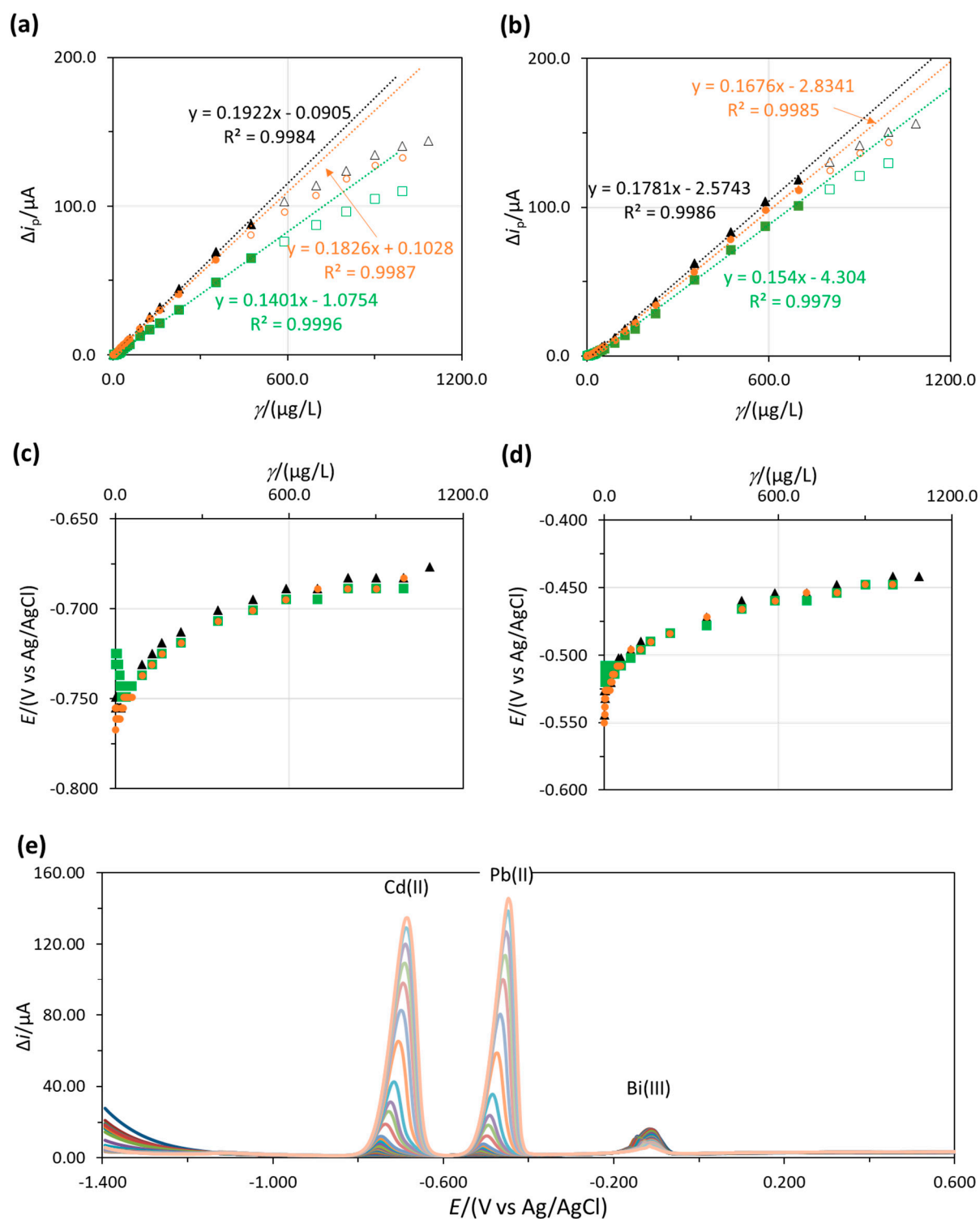


Figure S6: Three repetition measurements for determining the linear concentration ranges for (a) Cd(II) and (b) Pb(II), the stripping peak potentials vs. concentration for (c) Cd(II) and (d) Pb(II), and (e) the corresponding voltammogram (one out of six repetition measurements) using Electrode No. 7 tested in a fractional two-level factorial design in Table

1.

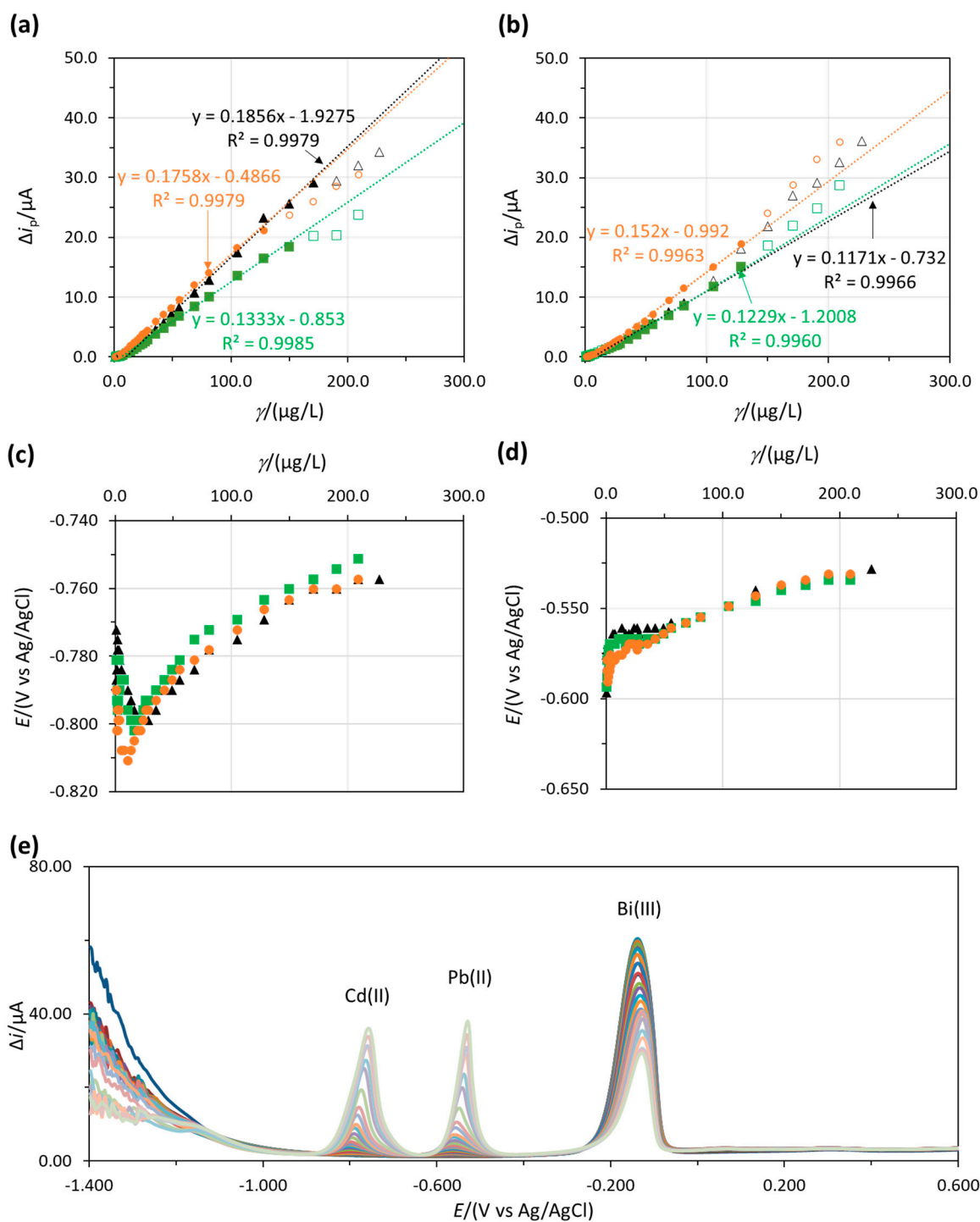


Figure S7: Three repetition measurements for determining the linear concentration ranges for (a) Cd(II) and (b) Pb(II), the stripping peak potentials vs. concentration for (c) Cd(II) and (d) Pb(II), and (e) the corresponding voltammogram (one out of six repetition measurements) using Electrode No. 8 tested in a fractional two-level factorial design in Table 1.

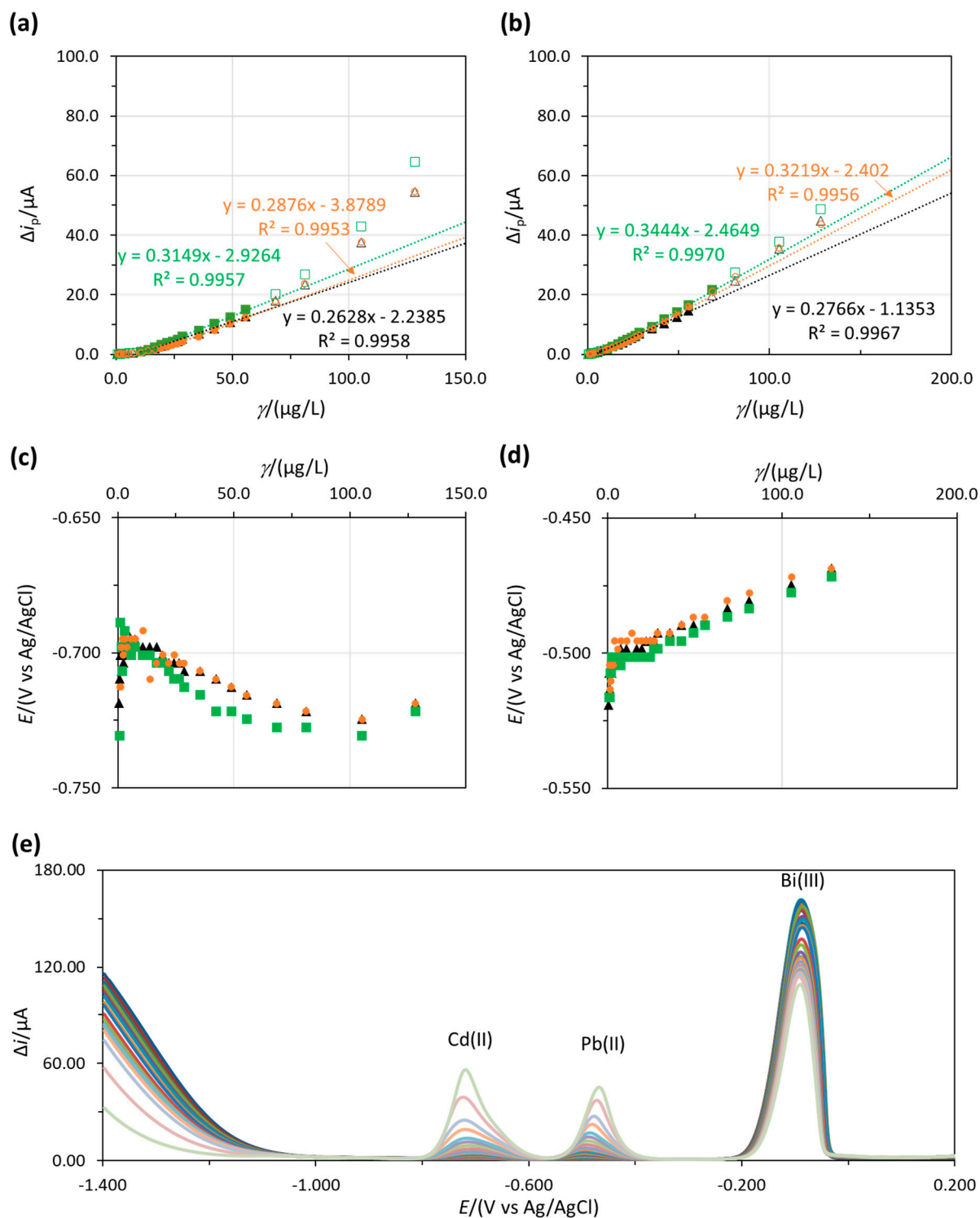


Figure S8: Three repetition measurements for determining the linear concentration ranges for (a) Cd(II) and (b) Pb(II), the stripping peak potentials vs. concentration for (c) Cd(II) and (d) Pb(II), and (e) the corresponding voltammogram (one out of six repetition measurements) using Electrode B1_{prod} tested in a simplex optimization procedure in Table 4.

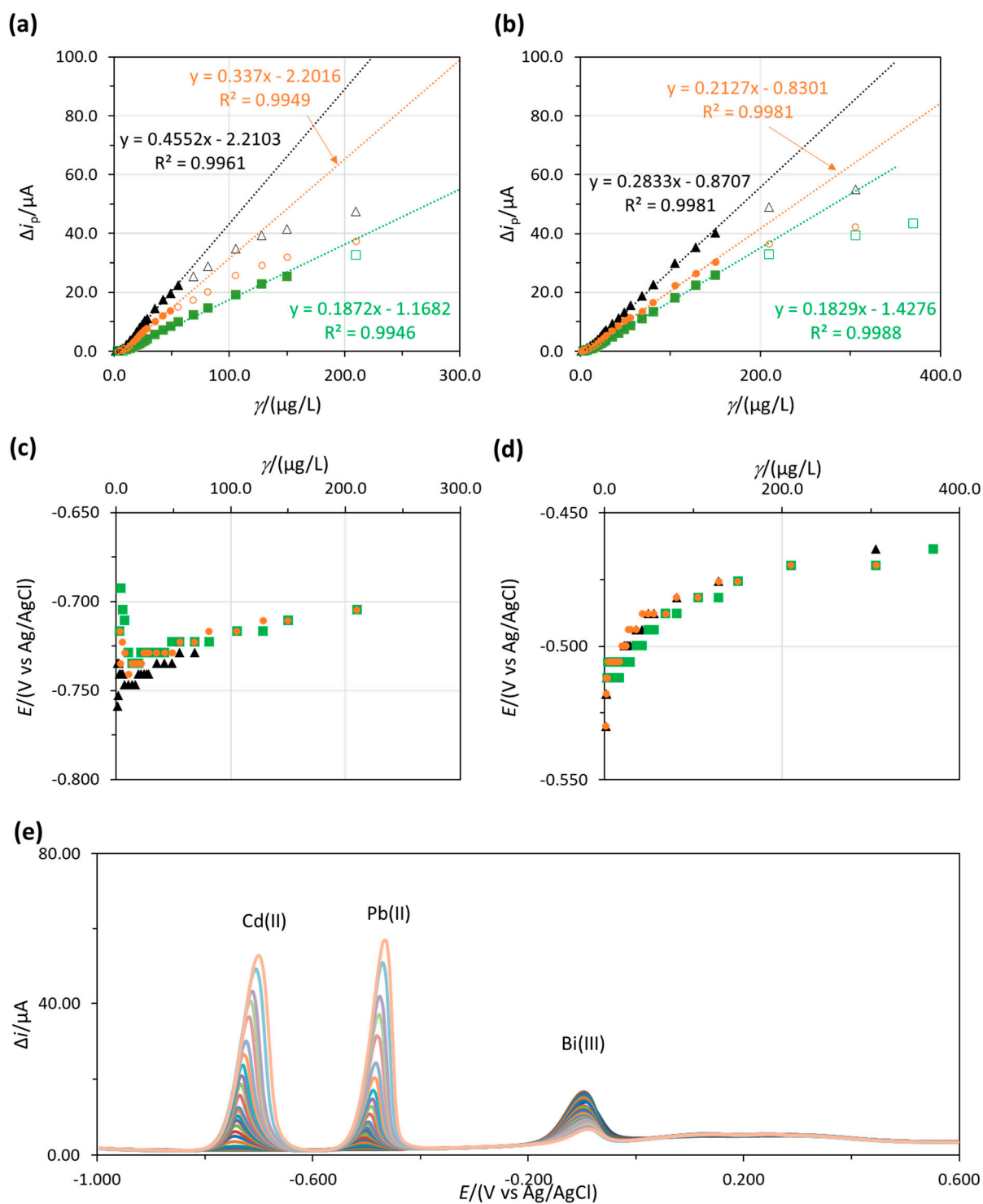


Figure S9: Three repetition measurements for determining the linear concentration ranges for (a) Cd(II) and (b) Pb(II), the stripping peak potentials vs. concentration for (c) Cd(II) and (d) Pb(II), and (e) the corresponding voltammogram (one out of six repetition measurements) using Electrode B2_{prod} tested in a simplex optimization procedure in Table 4.

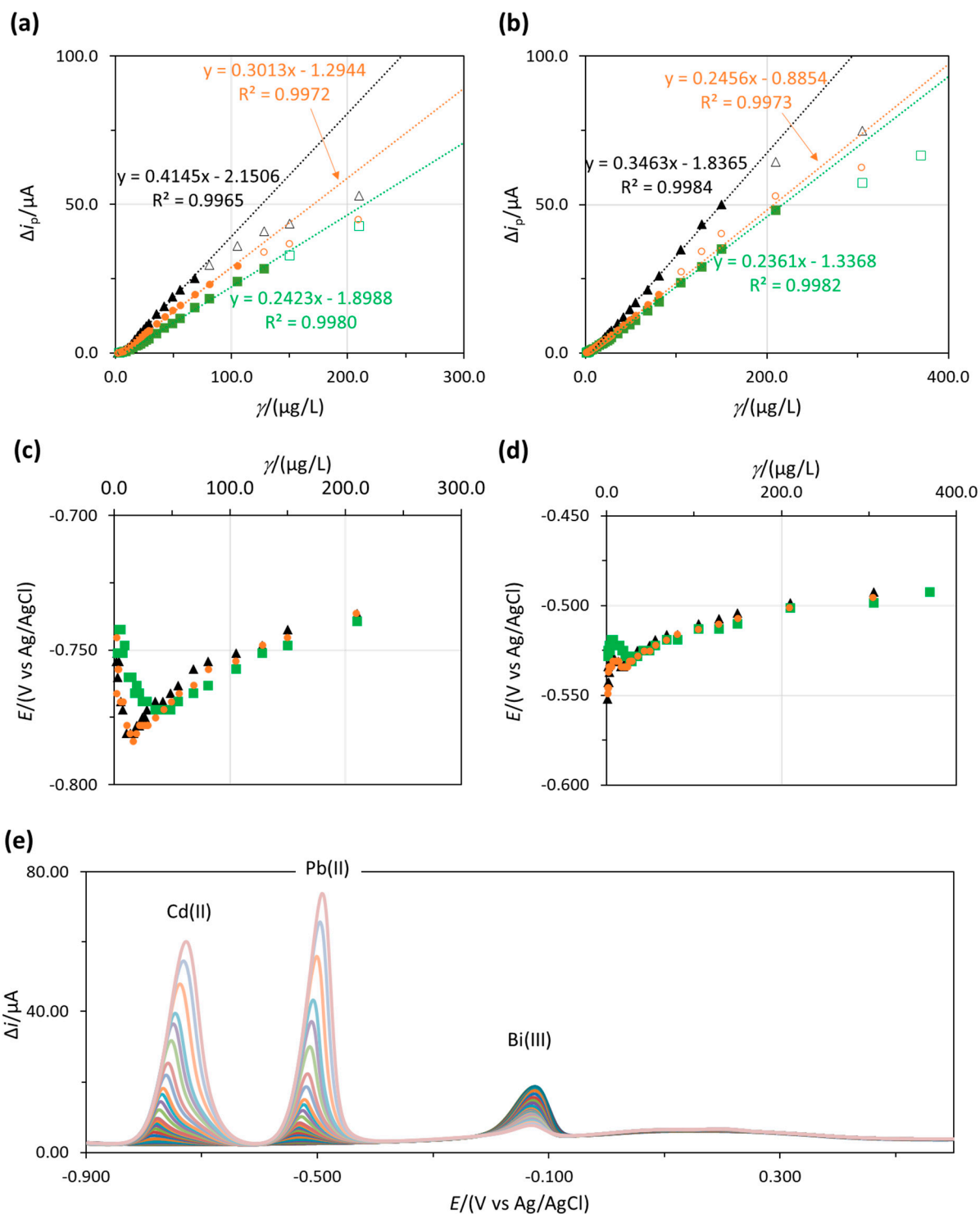


Figure S10: Three repetition measurements for determining the linear concentration ranges for (a) Cd(II) and (b) Pb(II), the stripping peak potentials vs. concentration for (c) Cd(II) and (d) Pb(II), and (e) the corresponding voltammogram (one out of six repetition measurements) using Electrode B3_{prod} tested in a simplex optimization procedure in Table 4.

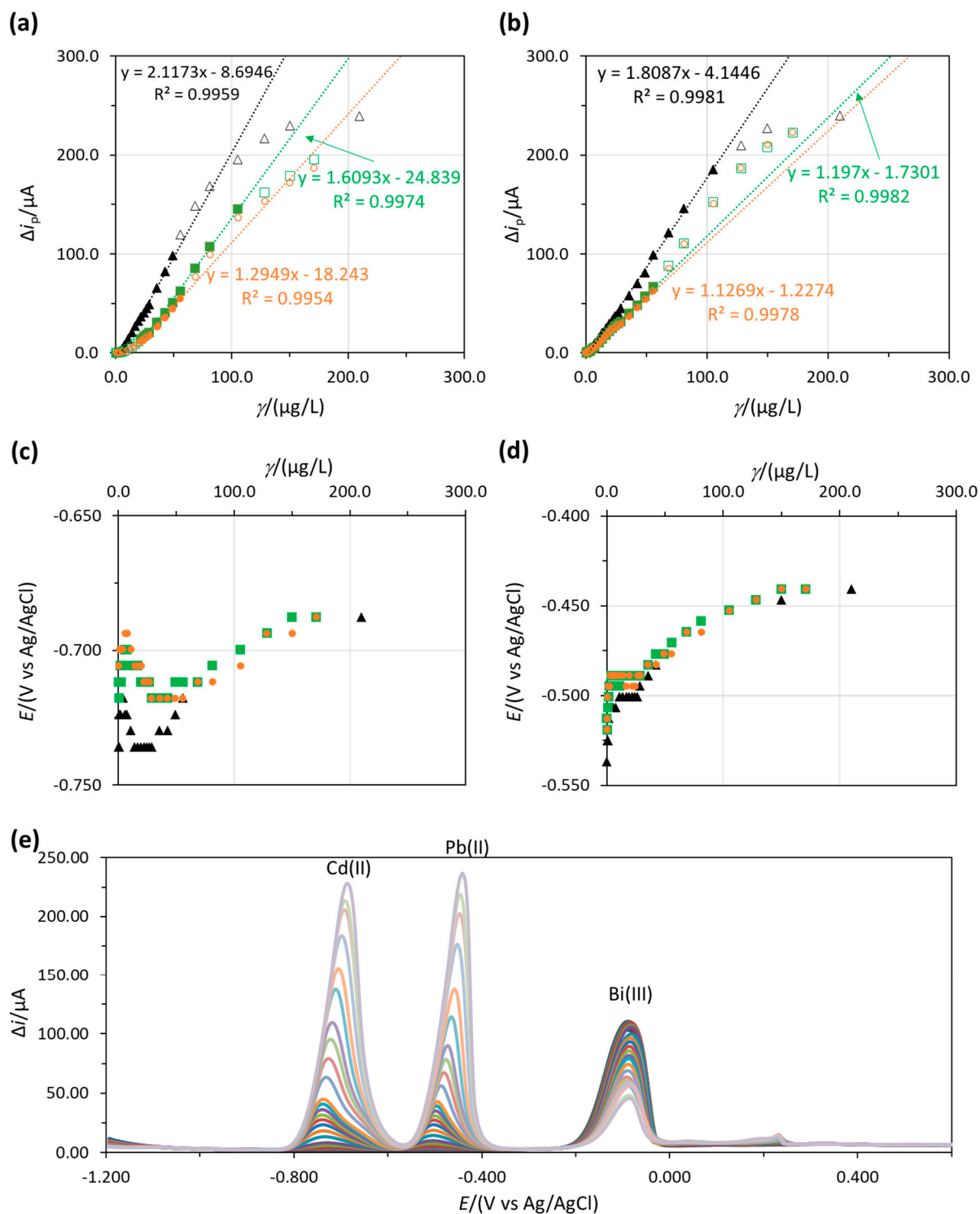


Figure S11: Three repetition measurements for determining the linear concentration ranges for (a) Cd(II) and (b) Pb(II), the stripping peak potentials vs. concentration for (c) Cd(II) and (d) Pb(II), and (e) the corresponding voltammogram (one out of six repetition measurements) using Electrode B4_{prod} tested in a simplex optimization procedure in Table 4.

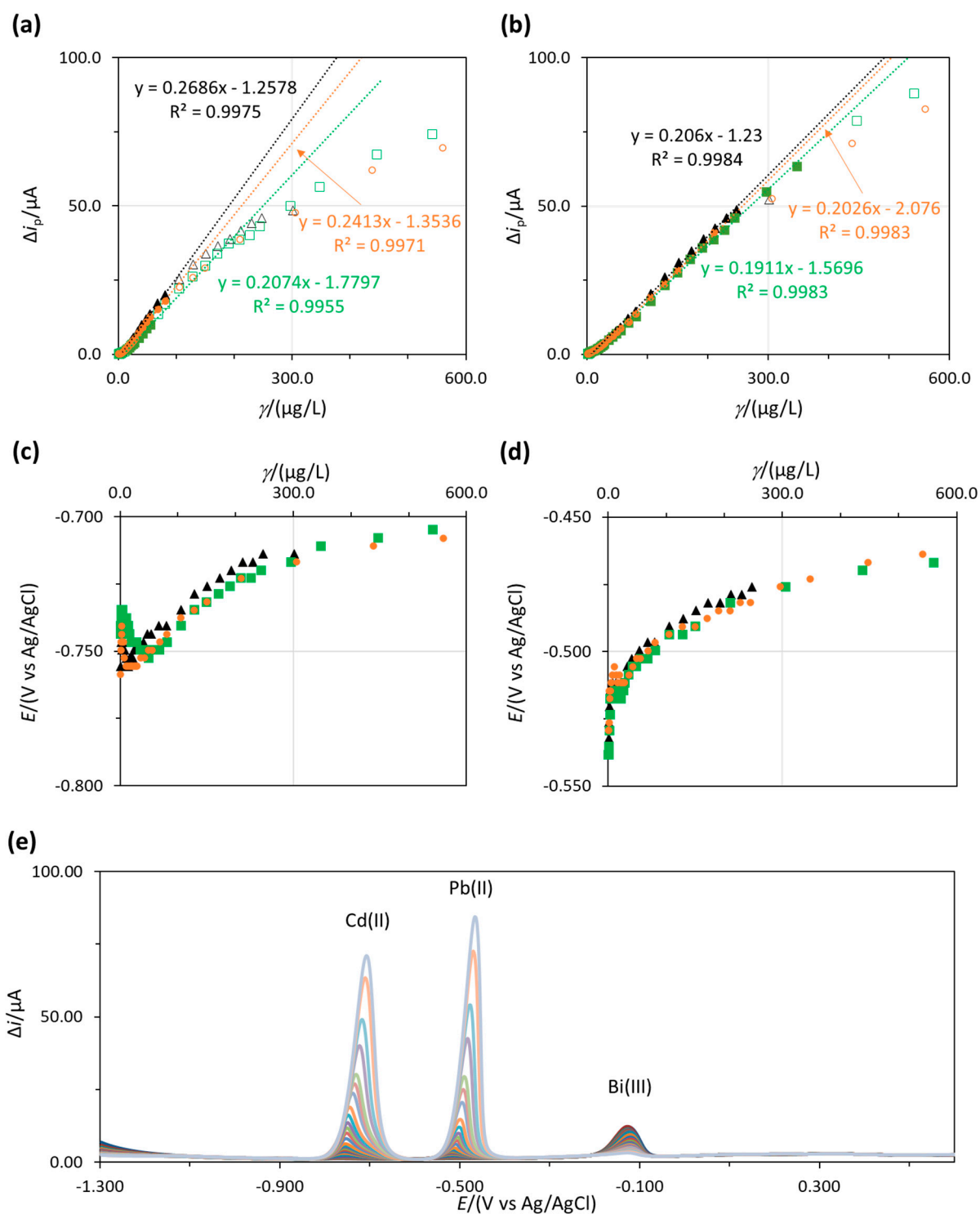


Figure S12: Three repetition measurements for determining the linear concentration ranges for (a) Cd(II) and (b) Pb(II), the stripping peak potentials vs. concentration for (c) Cd(II) and (d) Pb(II), and (e) the corresponding voltammogram (one out of six repetition measurements) using Electrode B5_{prod} tested in a simplex optimization procedure in Table 4.

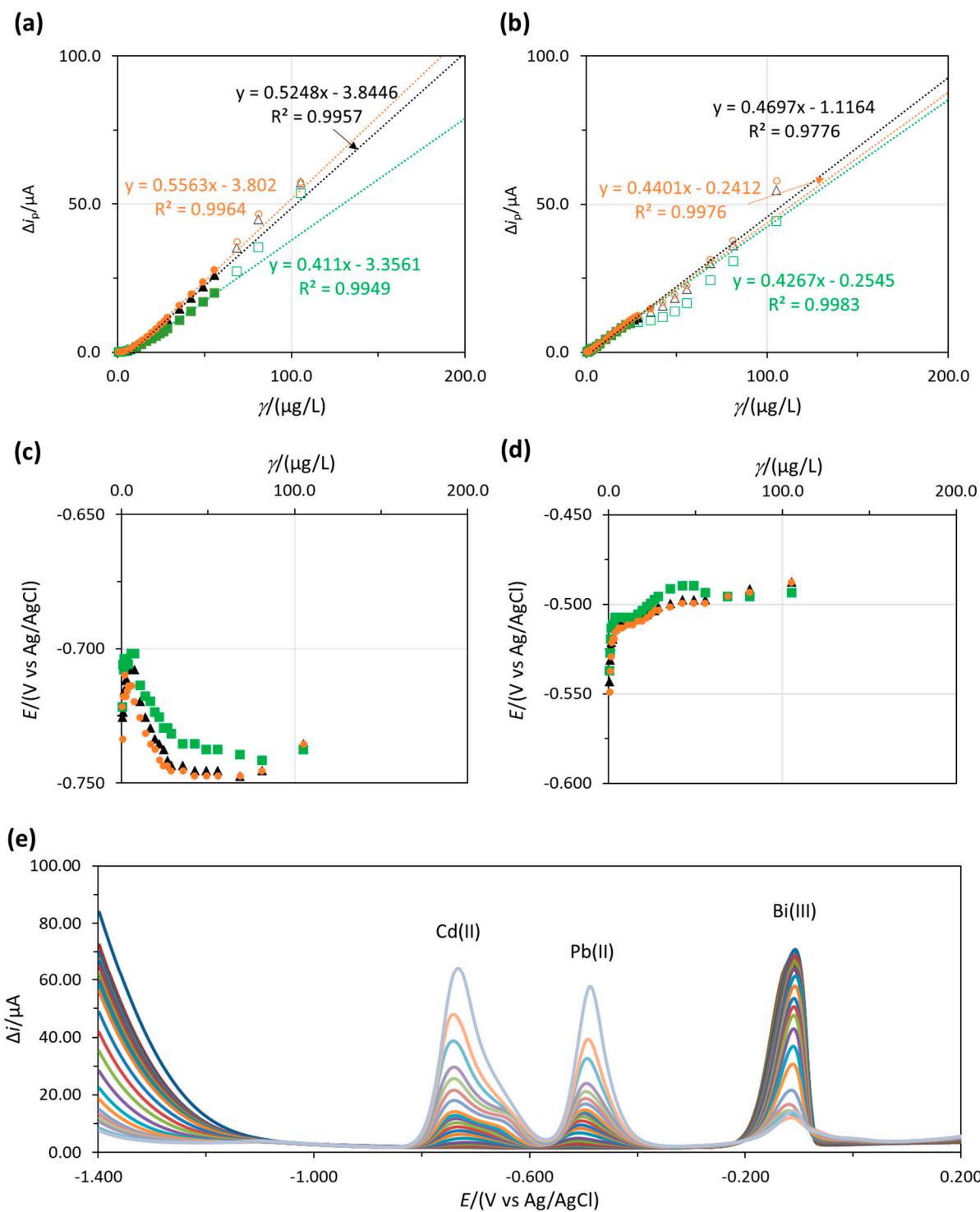


Figure S13: Three repetition measurements for determining the linear concentration ranges for (a) Cd(II) and (b) Pb(II), the stripping peak potentials vs. concentration for (c) Cd(II) and (d) Pb(II), and (e) the corresponding voltammogram (one out of six repetition measurements) using Electrode B6_{prod} tested in a simplex optimization procedure in Table 4.

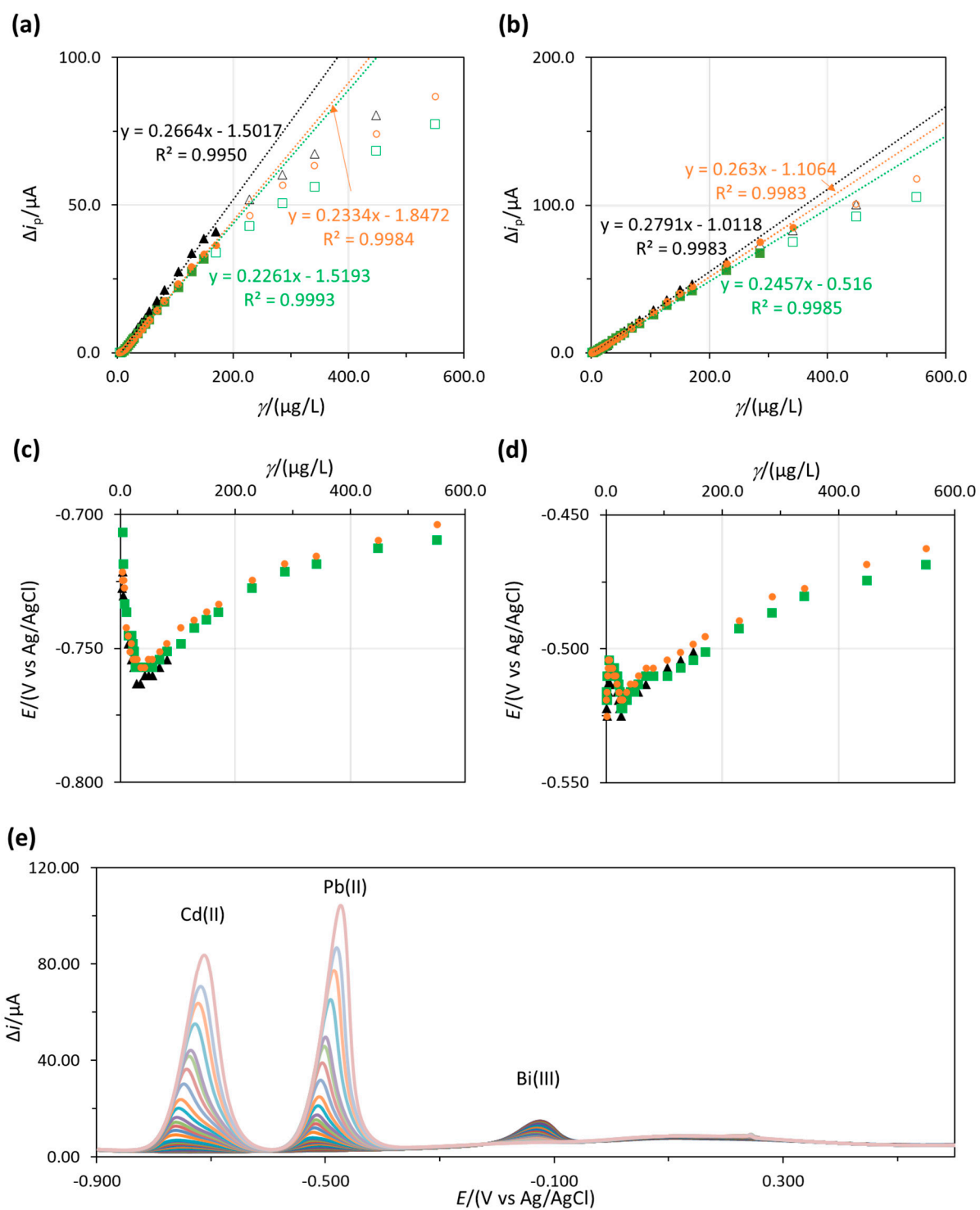


Figure S14: Three repetition measurements for determining the linear concentration ranges for (a) Cd(II) and (b) Pb(II), the stripping peak potentials vs. concentration for (c) Cd(II) and (d) Pb(II), and (e) the corresponding voltammogram (one out of six repetition measurements) using Electrode B1_{sum} tested in a simplex optimization procedure in Table 5.

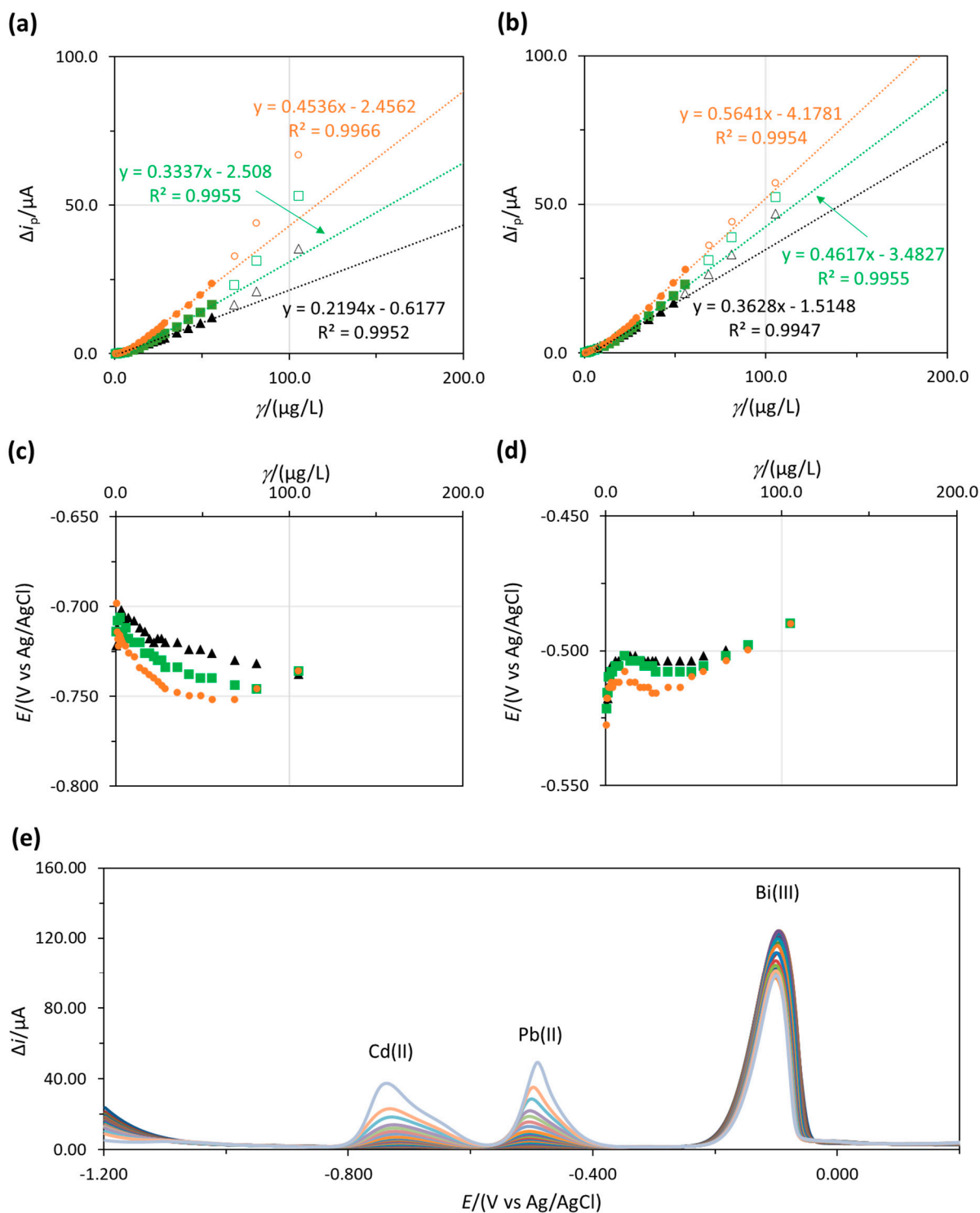


Figure S15: Three repetition measurements for determining the linear concentration ranges for (a) Cd(II) and (b) Pb(II), the stripping peak potentials vs. concentration for (c) Cd(II) and (d) Pb(II), and (e) the corresponding voltammogram (one out of six repetition measurements) using Electrode B2_{sum} tested in a simplex optimization procedure in Table 5.

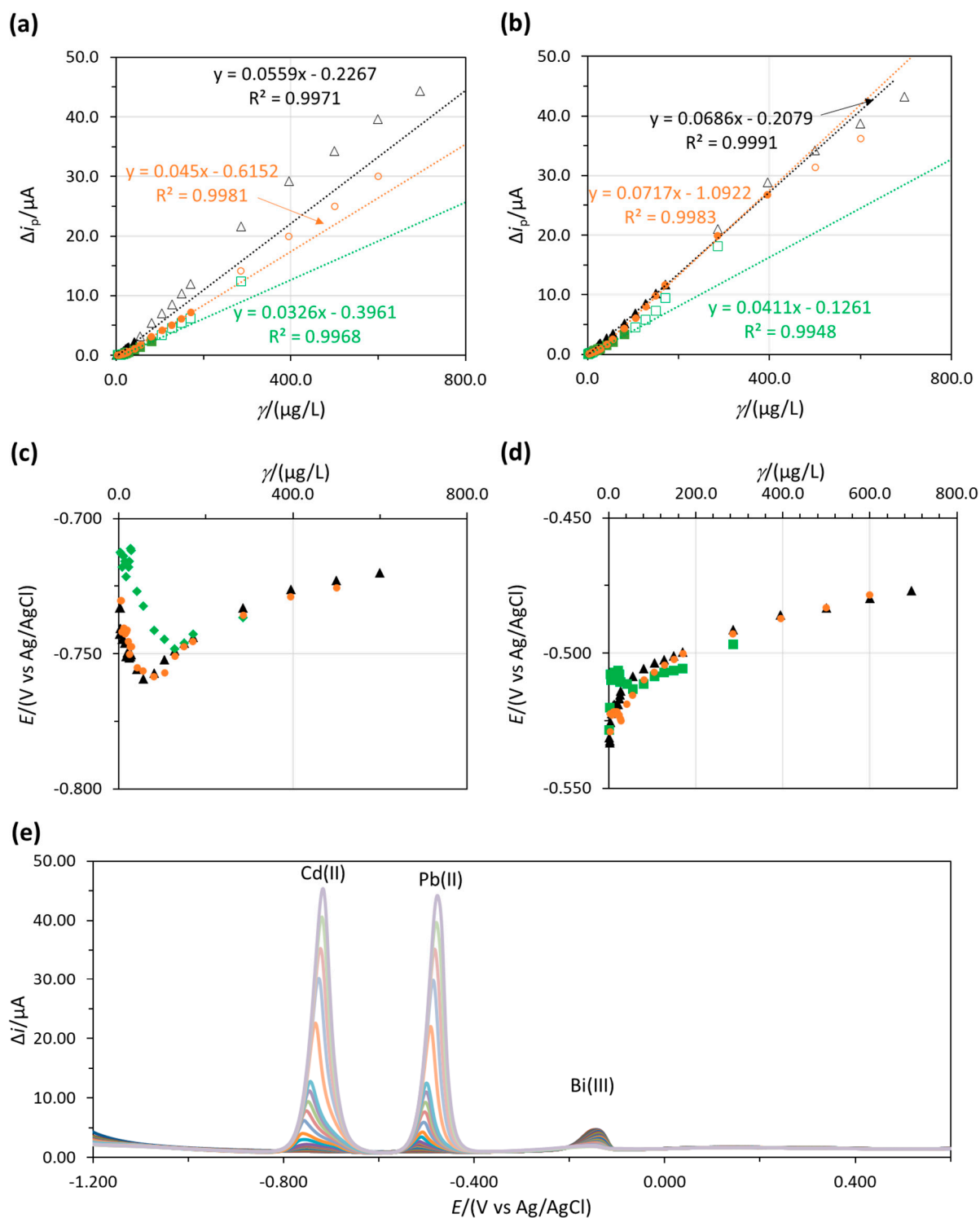


Figure S16: Three repetition measurements for determining the linear concentration ranges for (a) Cd(II) and (b) Pb(II), the stripping peak potentials vs. concentration for (c) Cd(II) and (d) Pb(II), and (e) the corresponding voltammogram (one out of six repetition measurements) using Electrode B3_{sum} tested in a simplex optimization procedure in Table 5.

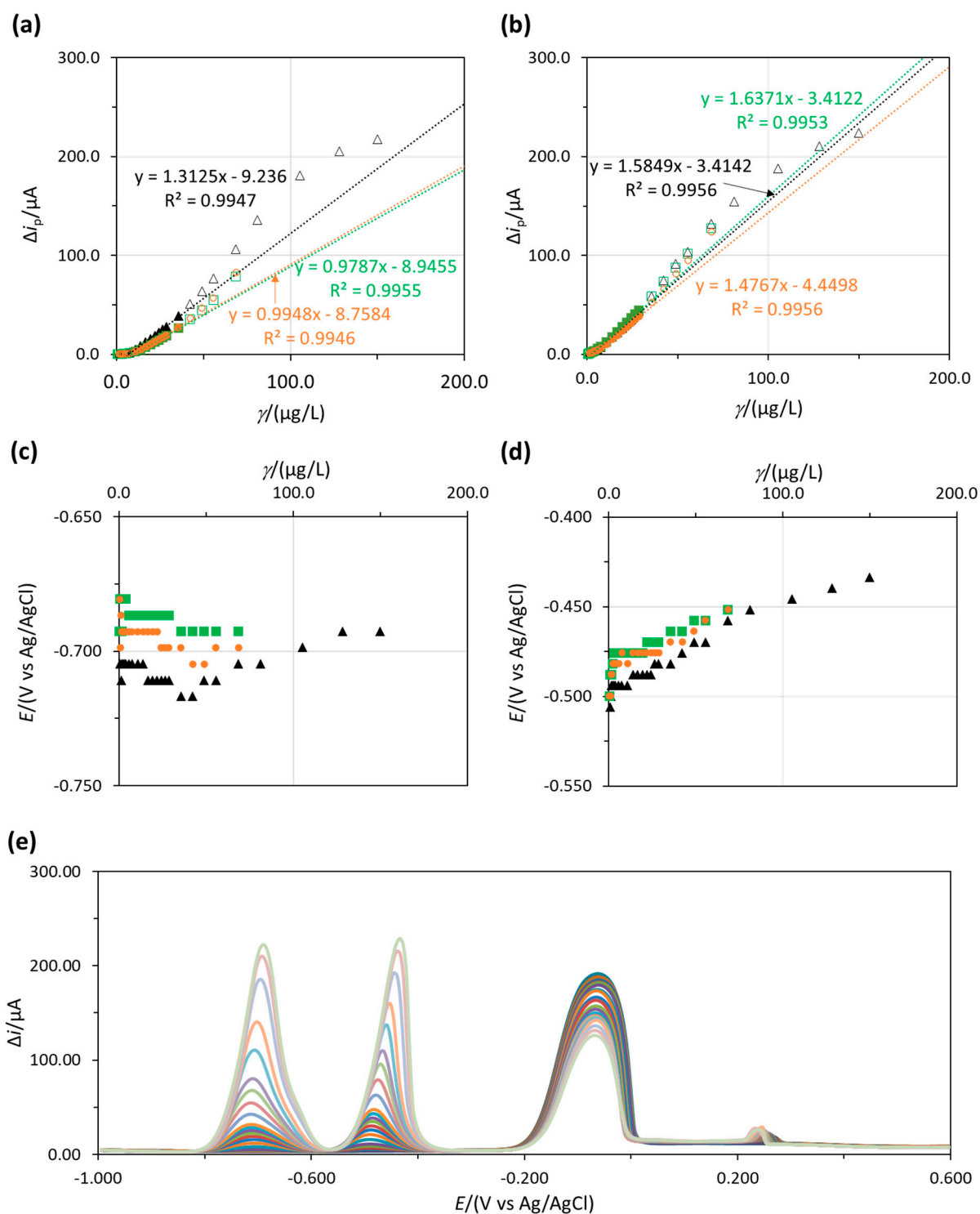


Figure S17: Three repetition measurements for determining the linear concentration ranges for (a) Cd(II) and (b) Pb(II), the stripping peak potentials vs. concentration for (c) Cd(II) and (d) Pb(II), and (e) the corresponding voltammogram (one out of six repetition measurements) using Electrode B4_{sum} tested in a simplex optimization procedure in Table 5.

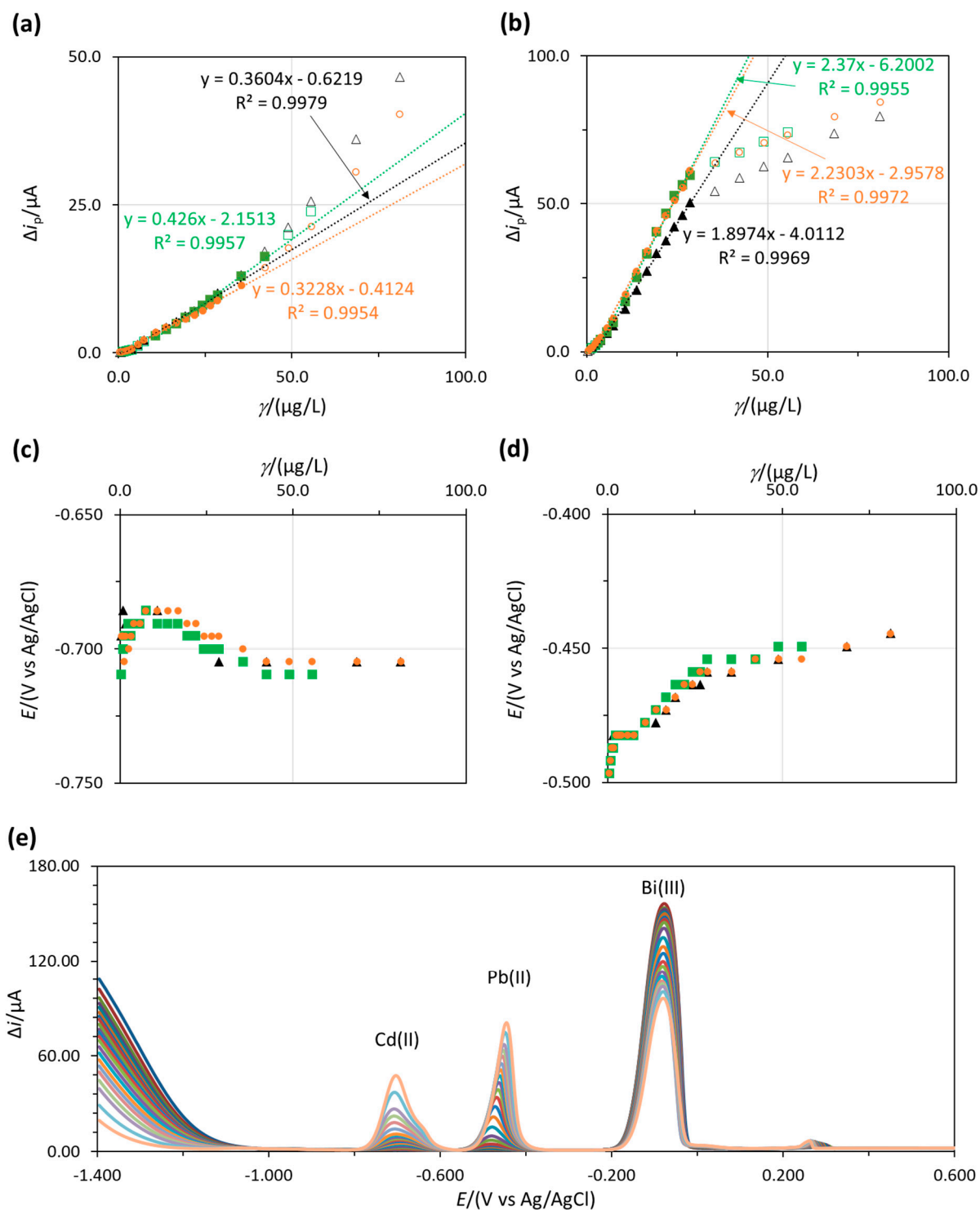


Figure S18: Three repetition measurements for determining the linear concentration ranges for (a) Cd(II) and (b) Pb(II), the stripping peak potentials vs. concentration for (c) Cd(II) and (d) Pb(II), and (e) the corresponding voltammogram (one out of six repetition measurements) using Electrode B5_{sum} tested in a simplex optimization procedure in Table 5.

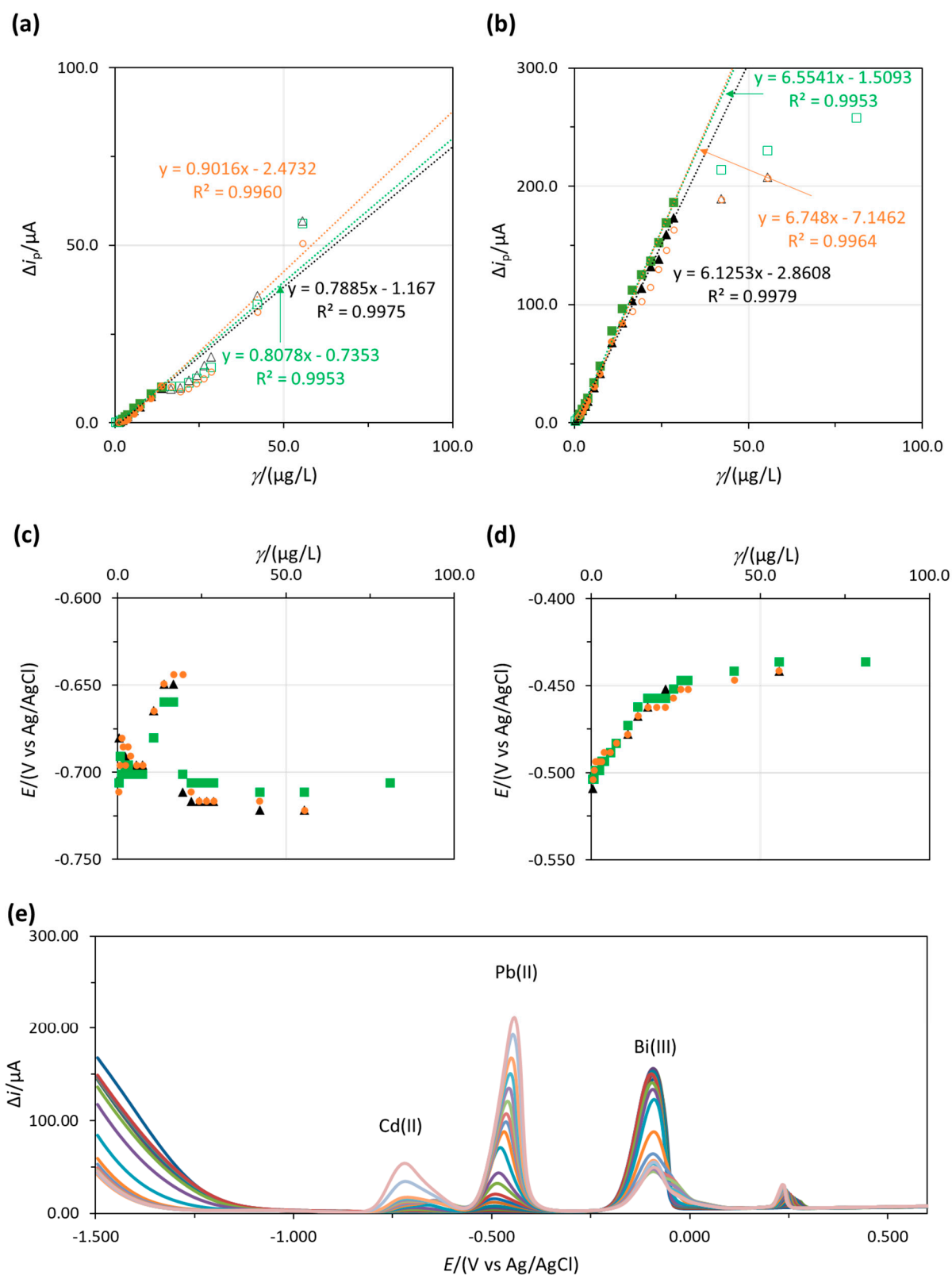


Figure S19: Three repetition measurements for determining the linear concentration ranges for (a) Cd(II) and (b) Pb(II), the stripping peak potentials vs. concentration for (c) Cd(II) and (d) Pb(II), and (e) the corresponding voltammogram (one out of six repetition measurements) using Electrode B6_{sum} tested in a simplex optimization procedure in Table 5.

3. Interferences

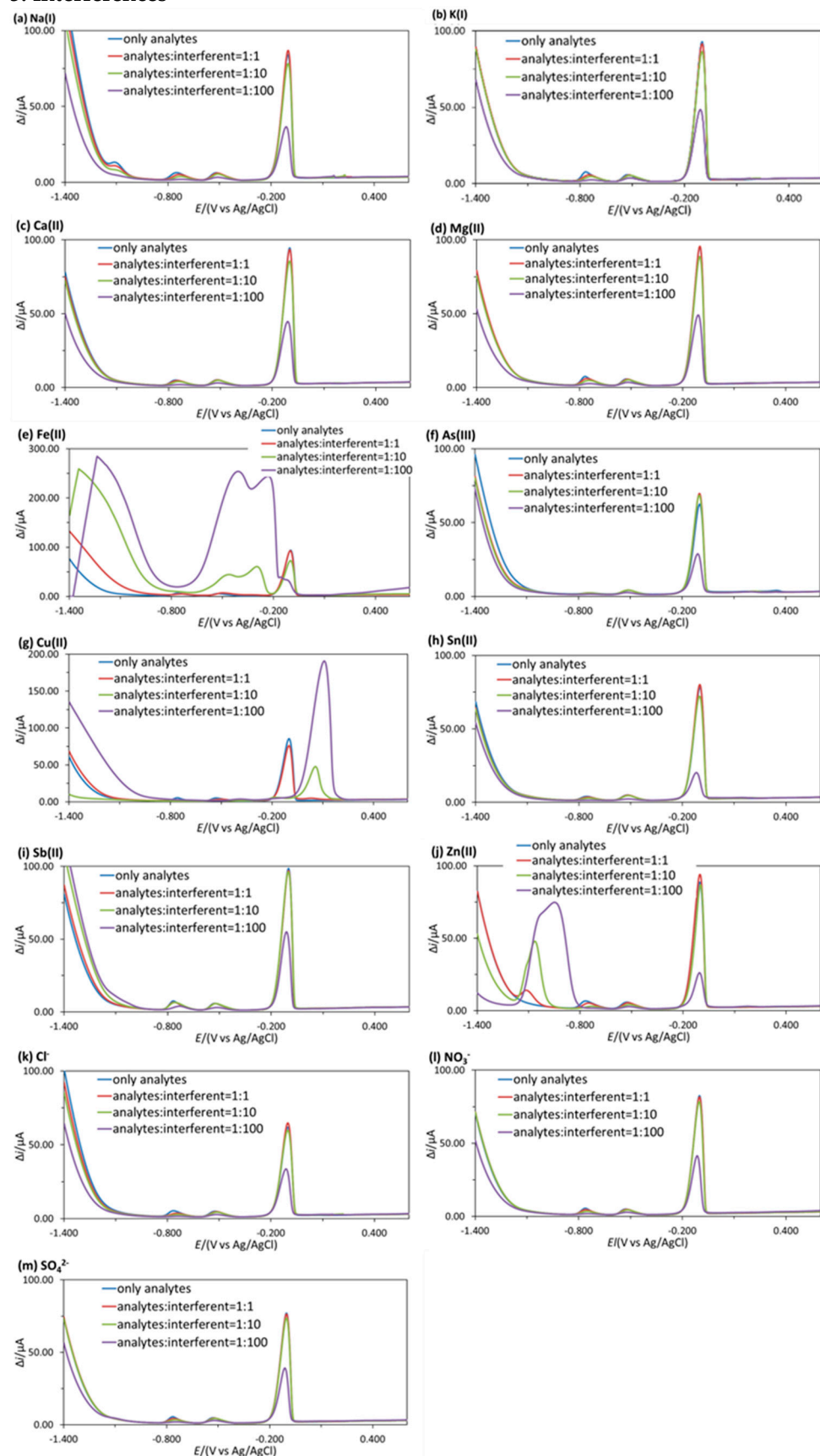


Figure S20. SWASV measurements in 0.1 M acetate buffer solution with and without possible interferents present at a mass concentration ratio of 1:1, 1:10, and 1:100; (a) Na(I), (b) K(I), (c) Ca(II), (d) Mg(II), (e) Fe(II), (f) As(III), (g) Cu(II), (h) Sn(II), (i) Sb(III), (j) Zn(II), (k) Cl⁻, (l) NO₃⁻, and (m) SO₄²⁻ using Electrode B6_{prod.}

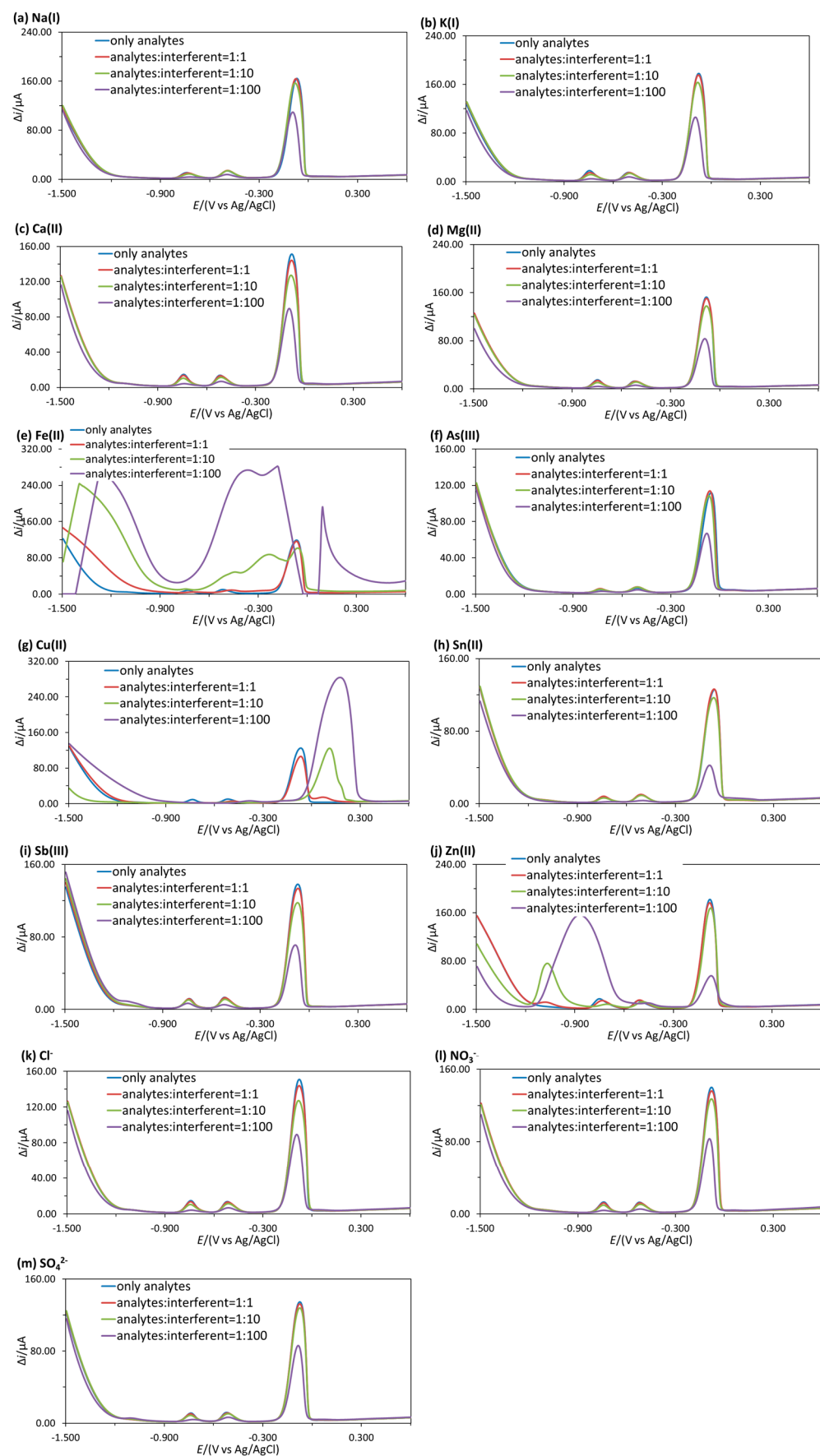


Figure S21. SWASV measurements in 0.1 M acetate buffer solution with and without possible interferents present at a mass concentration ratio of 1:1, 1:10, and 1:100; (a) Na(I), (b) K(I), (c) Ca(II), (d) Mg(II), (e) Fe(II), (f) As(III), (g) Cu(II), (h) Sn(II), (i) Sb(III), (j) Zn(II), (k) Cl⁻, (l) NO₃⁻, and (m) SO₄²⁻ using Electrode B6_{sum}.