Direct Identification and Analysis of Heavy Metals in Solution (Hg, Cu, Pb, Zn, Ni) using In-Situ Electrochemical X-Ray Fluorescence

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Electronic supporting Information

S1. Optimization of Electrode Deposition Parameters for Pb^{2+}

In order to maximize sensitivity and to achieve the lowest detection limits, the deposition parameters were optimized using Pb^{2+} as a model system. Figure S1a shows the results of the Pb^{2+} E_{dep} optimization experiments. Pb^{2+} depositions were carried out in 100 μM Pb^{2+}, with \( V_f = 7.0 \text{ cm}^{-3} \text{ min}^{-1} \) and \( t_{dep} = 900 \text{ s} \). Figure S1a shows a significant increase in XRF signal as \( E_{dep} \) is increased, which agrees with our previous findings for Pb^{2+} deposition using an ex-situ approach in combination with a rotating disk electrode.\(^1\) \( E_{dep} = -1.5 \text{ V} \) was chosen as the deposition potential which maximized XRF signal whilst providing minimal deviation between replicate experiments.

To optimize \( V_f \) similar experiments were carried out but with \( E_{dep} = -1.5 \text{ V} \) and \( t_{dep} = 1800 \text{ s} \). Flow rates were selected based on the results in Figure 2b, where mass transport could be described using wall-jet theory (\( i.e. \ V_f > 10 \text{ mL min}^{-1} \)). A significant increase in the Pb_{La} intensity is observed between 10 – 14 mL min^{-1}, while a decrease is observed after 14 mL...
The decrease is attributed to electrodeposited Pb being removed from the surface due to the velocity of the impinging jet. For all experiments $V_f = 14 \text{ ml min}^{-1}$ was employed.

**Figure S1**: Characterization of deposition parameters for Pb$^{2+}$ in 0.2 M KNO$_3$. (a) Dependence of $E_{dep}$ on XRF signal intensity; Pb$^{2+} = 100 \mu$M; $t_{dep} = 900$ s, $V_f = 7$ mL min$^{-1}$. Inset shows XRF spectra for Pb$_{L\alpha}$ at $E_{dep} = -0.5$ V (black line); -1.0 V (red line); -1.5 V (blue line); -1.75 V (green line). (b) Dependence of $V_f$ on XRF signal intensity; Pb$^{2+} = 10 \mu$M; $E_{dep} = -1.5$ V versus Ag/AgCl, $t_{dep} = 1800$ s.

**S2. The effect of the rate of spectral acquisition on XRF response**

In order to quantitatively determine the best operation conditions for in situ XRF measurements, analysis of background signals was made for different collection times. In these experiments, the signal of the Pb$_{L\alpha}$ peak was recorded at four different collection time intervals in 0.2 M KNO$_3$ solution. Spectra were collected for a total time of 60 minutes. Note that during spectra acquisition, the sample was illuminated for the entire measurement time, however the detector collects the fluorescence emission for the specified time (1, 10, 30 or 50 seconds).

In order to generate the histogram shown in Figure S2, the intensity of the Pb$_{L\alpha}$ peak was integrated using identical parameters for Figures 3, 4 and 5 in the main text. The integration results were plotted as a normalized histogram in order to visualize the variation in the datasets. From the results plotted in Figure S2 it is clear that the noise decreases
significantly with increasing collection time, as expected. As discussed in the main text, a collection time of 50 seconds was used in order to provide high signal to noise, while still retaining high temporal resolution.

![Graph showing normalized counts vs. peak area/keV cps mA⁻¹ for different collection times (1s, 10s, 30s, 50s).](image)

**Figure S2:** Histograms comparing the average noise for the Pb_Lα line of blank samples.

**S3. Interpretation of the square wave-anodic stripping (SW-ASV) response of an aqueous solution containing six dissolved metals, Zn^{2+}, Pb^{2+}, Ni^{2+}, Cu^{2+}, Hg^{2+} and Fe^{3+}**

Six individual solutions were prepared containing Zn^{2+}, Pb^{2+}, Ni^{2+}, Cu^{2+}, Hg^{2+} and Fe^{3+} all at a concentration of 10 µM in 0.2 M KNO₃. Deposition was carried out using a 1 mm diameter BDD macroelectrode with $E_{dep}$ = -1.5 V versus Ag/AgCl and $t_{dep} = 5$ mins (black line), under stirred conditions (magnetic flea). Only in the case of Ni^{2+} was a $t_{dep}$ time of 10 mins (red line) employed to emphasize the stripping peak position(s). Square wave anodic stripping voltammetry (SW-ASV) was carried out (4 mV steps, 10 mV amplitude, 25 Hz) under stirred conditions for each metal, as shown in Figure S3. The response for Fe^{3+} is not shown as no peak could be identified in the SW-ASV response. The central plot (in grey) shows the SW-ASV response recorded in one solution containing 10 µM of each of the six metals.
metals, Zn$^{2+}$, Pb$^{2+}$, Ni$^{2+}$, Cu$^{2+}$, Hg$^{2+}$ and Fe$^{3+}$, and 0.2 M KNO$_3$ (Figure 5a from the main text). SW-ASV of the individual metals enables the peaks labelled (i) to (v) to be correlated with (i) Zn$^{2+}$; (ii) Pb$^{2+}$ with a small contribution from Ni$^{2+}$; (iii) Cu$^{2+}$; (iv) Hg$^{2+}$ and (v) Ni$^{2+}$.

Figure S3: SW-ASV recorded for 10 μM individual metal solutions of the metal ions, Zn$^{2+}$, Pb$^{2+}$, Ni$^{2+}$, Cu$^{2+}$, Hg$^{2+}$ and Fe$^{3+}$ (Fe$^{3+}$ is not shown as no peak response could be observed), in 0.2 M KNO$_3$, for $E_{\text{dep}} = -1.5$ V and $t_{\text{dep}} = 5$ mins (black line) and 10 mins (red line), under stirred conditions. Central image (grey): SW-ASV response for a solution containing all six metals at 10 μM concentration each in 0.2 M KNO$_3$ for $E_{\text{dep}} = -1.5$ V and $t_{\text{dep}} = 5$ mins (black line) and 10 mins (red line), under stirred conditions.

References