

Electronic Supporting Information (ESI)

**Quantitative Analysis of Trace Palladium Contamination in Solution using
Electrochemical X-Ray Fluorescence (EC-XRF)**

Zoe J. Ayres,^a Mark E. Newton^b and Julie V. Macpherson^{a*}

^aDepartment of Chemistry, University of Warwick, Coventry, CV4 7AL, UK and

^bDepartment of Physics, University of Warwick, Coventry, CV4 7AL, UK

*Email: j.macpherson@warwick.ac.uk

S1. EC-XRF electrochemical cell characterisation

S2. Anodic Stripping Voltammetry (ASV) of Pd²⁺

S3. Cyclic voltammetry (CV) of Pd²⁺

S4. Screening calibration plot

S5. Electrochemical response of the electroactive molecules (1) L-ascorbic acid; (2) caffeine
and (3) riboflavin

S6. Ultra CarryTM XRF response

S1. EC-XRF electrochemical cell characterisation

The electrochemical response of the BDD disc (1.4 cm diameter in the RDE setup) was investigated. Figure S1 shows the CV of 1 mM $\text{Ru}(\text{NH}_3)_6^{3+}$ ($E_{1/2} = -0.11$ V versus SCE) in 0.1 M KNO_3 at a scan rate of 0.1 V s^{-1} (black) under stationary (black) and forced convection (red) conditions. In stationary solution, near reversible electron transfer kinetics were observed (peak-to-peak - ΔE_p - separation of 65 mV) indicative of highly doped diamond material. This value also indicates that ohmic drop is minimal and there is a good electrical connection to the BDD. Furthermore, the observed peak current (i_p) of 0.40 mA, is close to that predicted by Randles Sevcik theory¹ of 0.39 mA, described in equation S1, assuming room temperature = 298 K:

$$i_p = 268600 n^{\frac{3}{2}} A D^{\frac{1}{2}} C^* v^{\frac{1}{2}} \quad [1]$$

n is the number of electrons transferred per redox event ($n = 1$); A is the electrode area (1.54 cm^2); D is the diffusion coefficient for $\text{Ru}(\text{NH}_3)_6^{3+}$ ($8.65 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$); v is the scan rate (0.1 V s^{-1}) and C^* is the concentration of the analyte (1 mM).

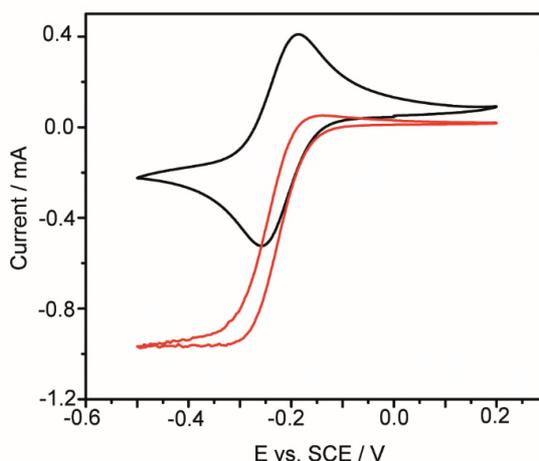


Figure S1. CV response for the reduction of 1 mM $\text{Ru}(\text{NH}_3)_6^{3+}$ in 0.1 M KNO_3 at a scan rate of 0.1 V s^{-1} , in stationary (black) solution and with the electrode rotated at 20 Hz (red).

To ensure rapid analysis times, forced convection was implemented to increase mass transport to the electrode surface, with steady state currents (i_{lim}) obtained at 20 Hz (red) of 0.97 mA, similar to those as predicted by Levich theory¹ (0.95 mA), calculated as shown in Equation S2:

$$i_{lim} = 1.544 n F A D^{\frac{2}{3}} f^{\frac{1}{2}} \nu^{-\frac{1}{6}} C^* \quad [2]$$

F is the Faraday constant (96486 C mol^{-1}), ν is the kinematic viscosity of water ($0.001004 \text{ cm}^2 \text{ s}^{-1}$) and f is the rotation frequency (Hz).

S2. Anodic Stripping Voltammetry (ASV) of Pd/Pd²⁺

A 1 mm BDD electrode,² was held at -1.5 V for 300 s in 1.1 μM Pd²⁺ (palladium (II) chloride (PdCl₂: 99.0 %, Sigma Aldrich) in 0.2 M KNO₃ (pH 3), under stationary conditions, then subsequently stripped from the surface by scanning from 0 V to 0.65 V, at a scan rate of 0.1 V s⁻¹ in 0.2 M KNO₃ solution. The ASV is shown in Figure S2. A Pd²⁺ stripping peak is observed at 0.56 V vs. SCE.

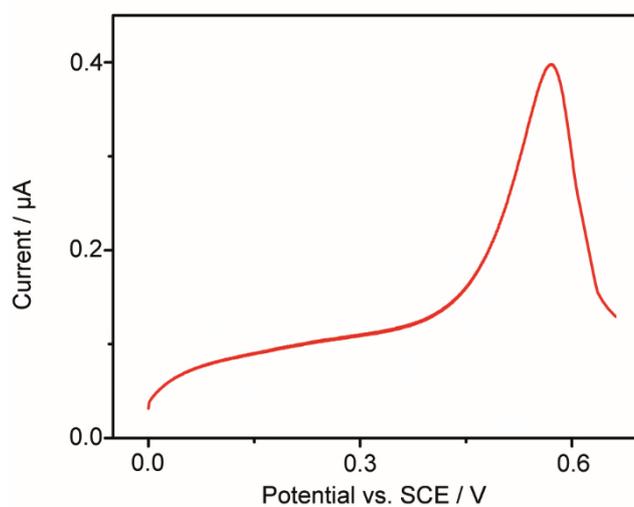


Figure S2. ASV of 1.1 μM Pd²⁺ in 0.2 M KNO₃ (pH 3), at a scan rate of 0.1 V s⁻¹ after deposition for 300 s at -1.5 V, swept from 0 V to +0.65 V.

S3. Cyclic voltammetry (CV) of Pd²⁺

The CV characteristics for Pd²⁺ electrodeposition on the BDD EC-XRF electrode (diameter = 1.4 cm), were recorded at 0.1 V s⁻¹ in a stationary solution containing 1.1 μM Pd²⁺ (palladium (II) chloride (PdCl₂: 99.0 %, Sigma Aldrich), as depicted in Figure S3. The CV shows the reduction currents associated with Pd electrodeposition on the surface of the BDD, along with hydrogen adsorption and desorption peaks.³ From Figure S3 the half wave reduction potential (vs. SCE) for Pd²⁺ was determined to be + 0.16 V.

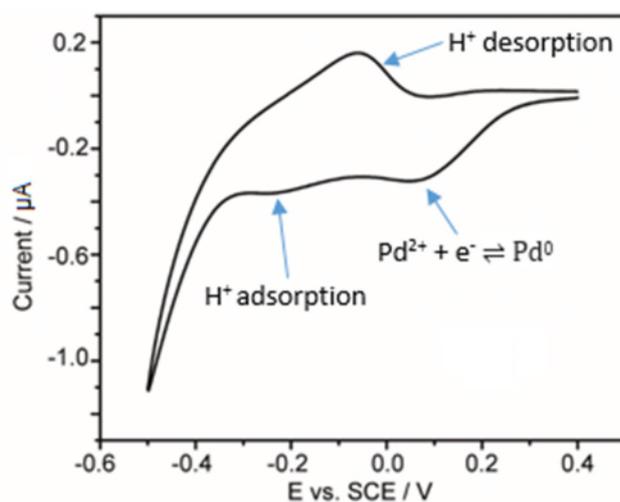


Figure S3. CV of 1.1 μM Pd²⁺ in 0.2 M KNO₃ (pH 3) under stationary conditions, using the EC-XRF BDD electrode at a scan rate of 0.1 V s⁻¹.

S4. Screening calibration plot

Pd screening to positively discriminate between samples containing safe and toxic Pd²⁺ levels in the presence of ACM (12 g/L) was investigated at $t_{\text{dep}} = 325$ s and $E_{\text{dep}} = -1.5$ V. XRF_{max} was plotted with respect to [Pd²⁺] (Figure S4) to determine the linearity of the XRF_{max} versus [Pd²⁺] response. As shown, a high correlation R² value of 0.999 is obtained.

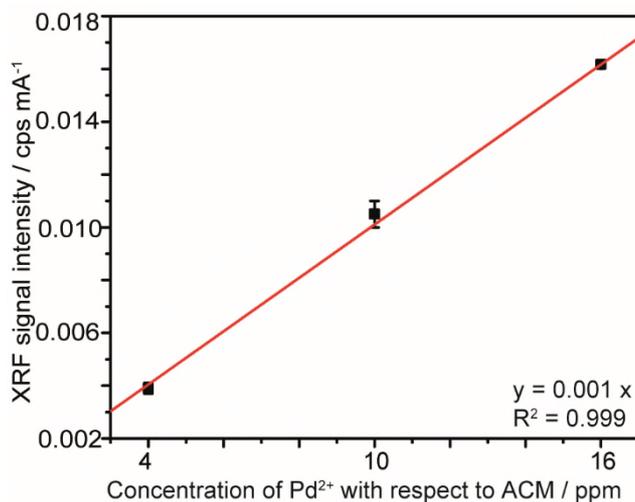


Figure S4. Plot of EC-XRF_{max} versus [Pd²⁺] concentration at an $E_{\text{dep}} = -1.5$ V and t_{dep} of 325 s in 0.2 M KNO₃ (pH 3, rotated at 20 Hz).

S5. Electrochemical response of the electroactive molecules (1) L-ascorbic acid; (2) caffeine and (3) riboflavin

Individual CVs of 10 mM L-ascorbic acid, caffeine and riboflavin in 0.2 M KNO₃, acidified to pH 3 with HCl, were run in stationary solution, at a scan rate of 0.1 V s⁻¹, using a 1 mm diameter glass sealed BDD macroelectrode, as shown in Figures S5, S6 and S7 respectively. For all molecules the potential was scanned first from 0 V in the negative direction. It was found for both L-ascorbic acid and caffeine that minimal reductive signatures were observed during the first scan. For riboflavin, a reductive signal was observed (-0.6 V vs. SCE). For both L-ascorbic acid and riboflavin, electrode fouling is likely occurring due to oxidation (L-ascorbic acid) and reduction (riboflavin).

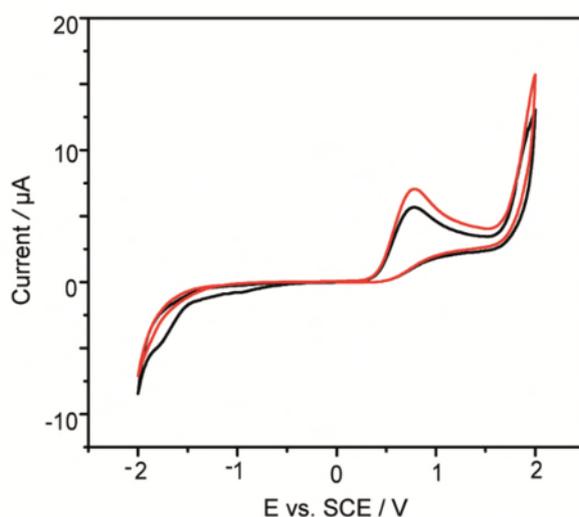


Figure S5. CV of 10 mM L-ascorbic acid in 0.2 M KNO₃ (pH 3) using a 1 mm BDD electrode in stationary solution, at 0.1 V s⁻¹; first scan (red) and second scan (black).

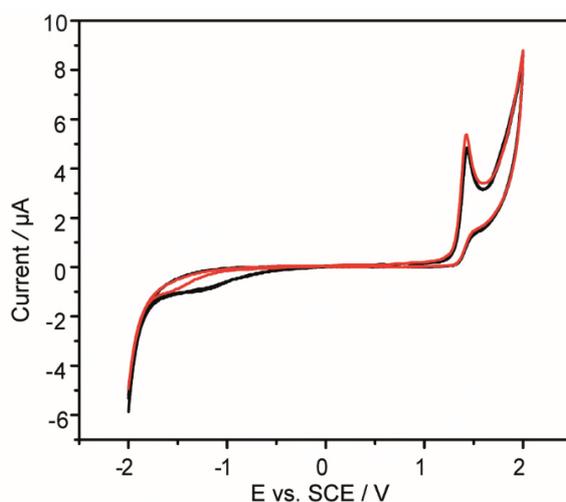


Figure S6. CV of 10 mM caffeine in 0.2 M KNO₃ (pH 3) using a 1 mm BDD electrode in stationary solution, at 0.1 V s⁻¹; first scan (red) and second scan (black).

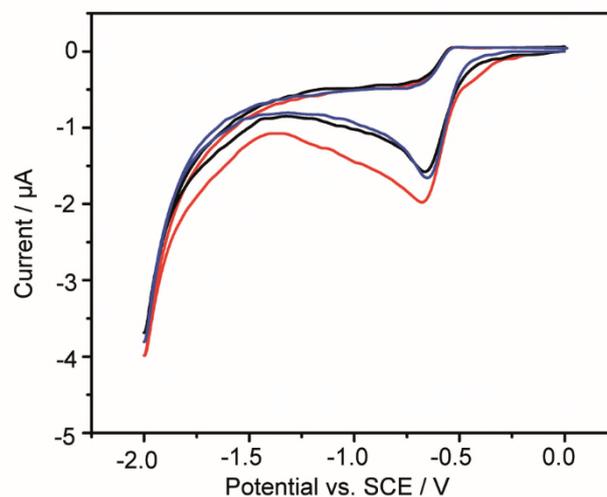


Figure S7. CV of 10 mM riboflavin in 0.2 M KNO₃ (pH 3) using a 1 mm BDD electrode in stationary solution, at 0.1 V s⁻¹; first scan (red) and second scan (black). Blue scan recorded immediately after holding the electrode at -1.5 V for 325 s in 10 mM riboflavin in 0.2 M KNO₃ (pH 3).

S6. Ultra Carry™ energy-dispersive XRF response

The Rigaku patented solution evaporation methodology for analyte pre-concentration (Ultra Carry™) in combination with energy dispersive-XRF, was utilised. 200 μL of the multi-metal solution containing 1.1 μM Pd^{2+} , Pb^{2+} , Cu^{2+} , Cd^{2+} , Fe^{3+} , Zn^{2+} was pipetted onto the hydrophilic region of the absorbent pad. The Ultra Carry™ plate was then heated on a hot plate (IKA RCT Basic) at 45°C for ca. 60 minutes, until all solution had evaporated. The XRF signal intensities obtained (using both the Mo and Al_2O_3 secondary targets to optimise the XRF signals), are shown in Figure S8. The XRF signals are significantly lower than using the EC-XRF technique alone, and indistinguishable from the background signals (as evidenced by the fact the peak maxima do not correlate with the position of the transmission lines on the energy scale).

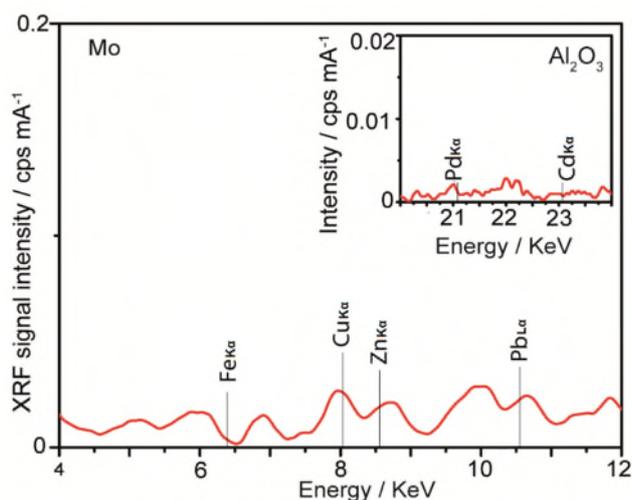


Figure S8. XRF signal intensities for 1.1 μM Fe^{3+} , Cu^{2+} , Zn^{2+} , Pb^{2+} , Pd^{2+} and Cd^{2+} , evaporatively pre-concentrated onto the Ultra Carry™ for ca. 1 hour. Note, lines indicate energy of most intense X-ray transmissions.

References

1. A. J. Bard and L. R. Faulkner, *Electrochemical methods: fundamentals and applications*, Wiley New York, 1980.
2. L. Hutton, M. E. Newton, P. R. Unwin and J. V. Macpherson, *Anal. Chem.*, 2009, **81**, 1023-1032.
3. C. Batchelor-McAuley, C. E. Banks, A. O. Simm, T. G. J. Jones and R. G. Compton, *ChemPhysChem*, 2006, **7**, 1081-1085.