

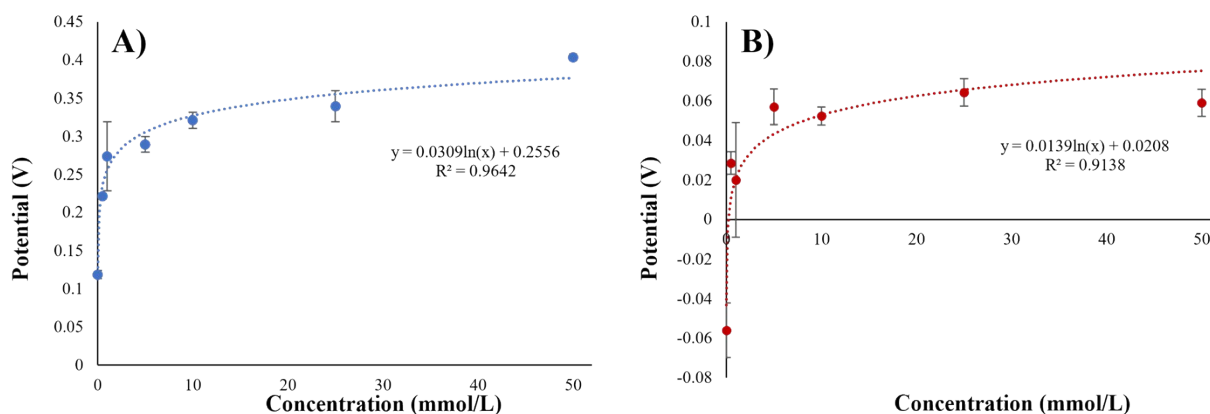
## Strategies for Assessing the Limit of Detection in Electrochemical Voltammetry Methods: Comparison and Evaluation of Approaches

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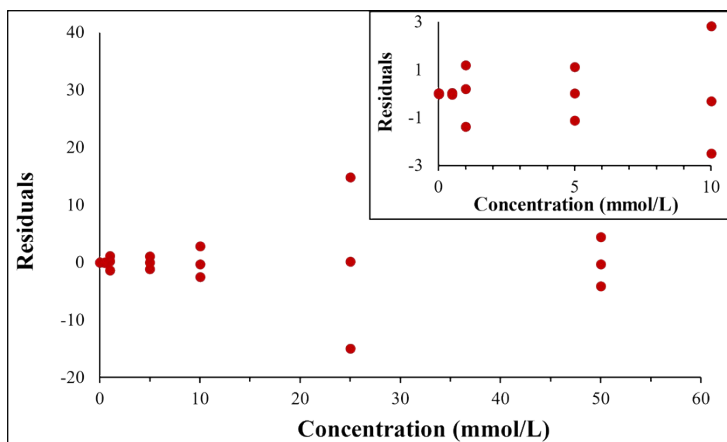
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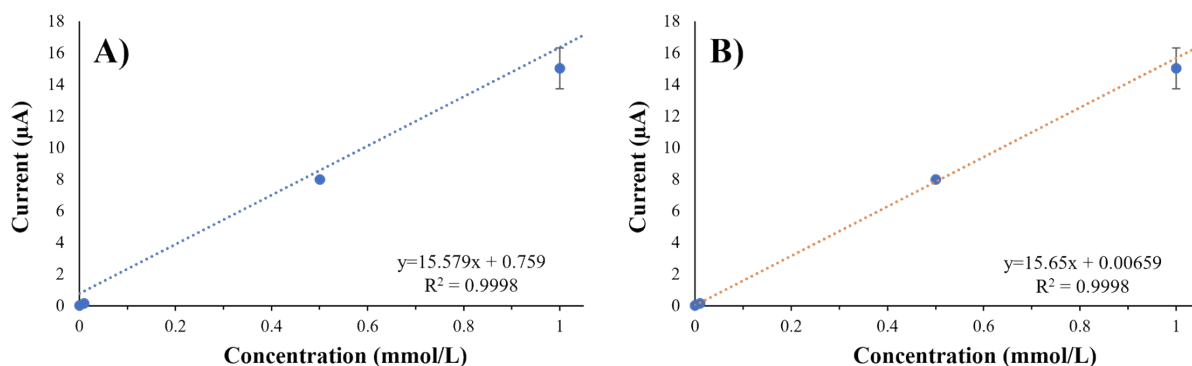
### Supplemental Material



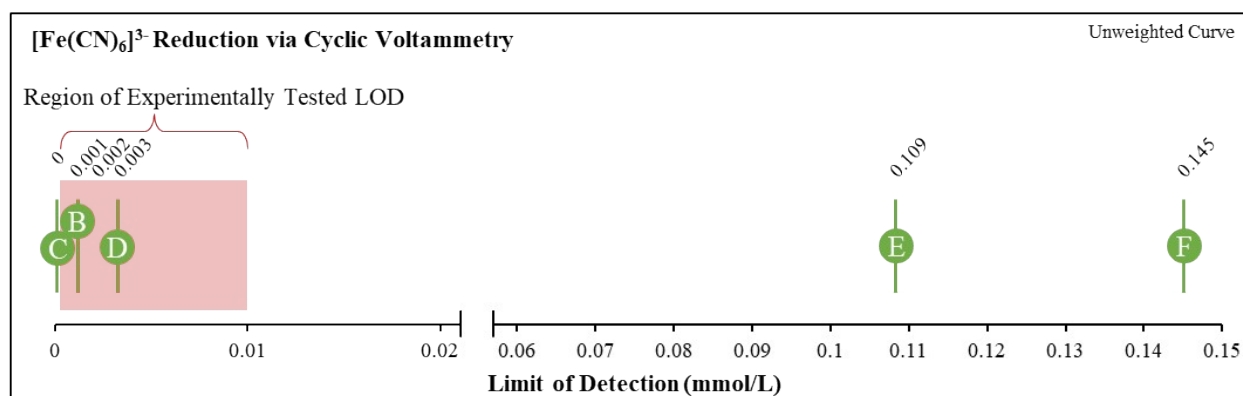
**Supplemental Figure S1.** Potential shift of A) the oxidation peak and B) the reduction peak for the analysis of the redox couple  $[\text{Fe}(\text{CN})_6]^{4-} \rightleftharpoons \text{Fe}[(\text{CN})_6]^{3-}$  via cyclic voltammetry. Error bars represent the standard deviation.



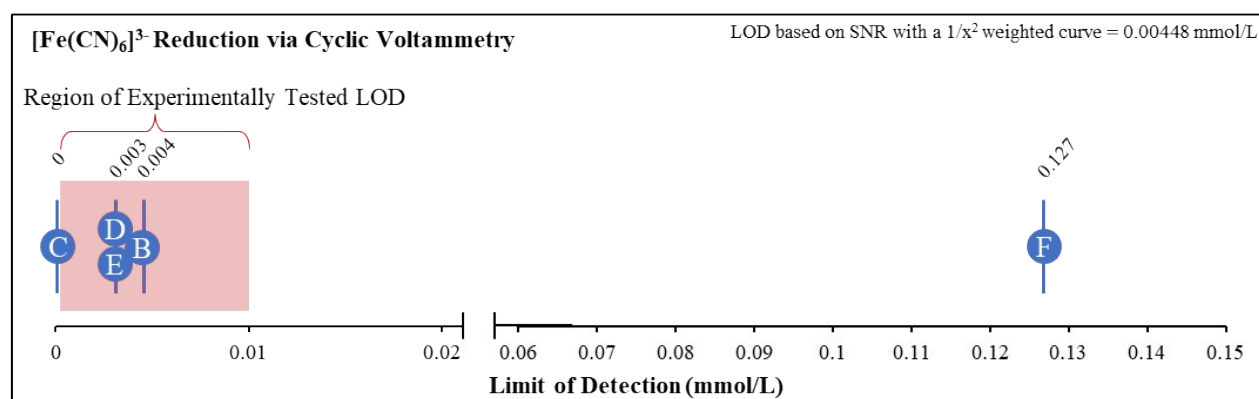
**Supplemental Figure S2.** Residual plots for the oxidation peak for the redox couple  $[\text{Fe}(\text{CN})_6]^{4-} \rightleftharpoons \text{Fe}[(\text{CN})_6]^{3-}$  demonstrating the heteroscedasticity of the residuals across the calibration range.



**Supplemental Figure S3.** Comparison between the A) unweighted linear regression and B)  $1/x$  weighted linear regression for the redox couple  $[\text{Fe}(\text{CN})_6]^{4-} \rightleftharpoons \text{Fe}[\text{CN}]_6]^{3-}$  showing the improvement in the low concentration region for the weighted curve of the oxidation peak. Error bars represent the standard deviation.



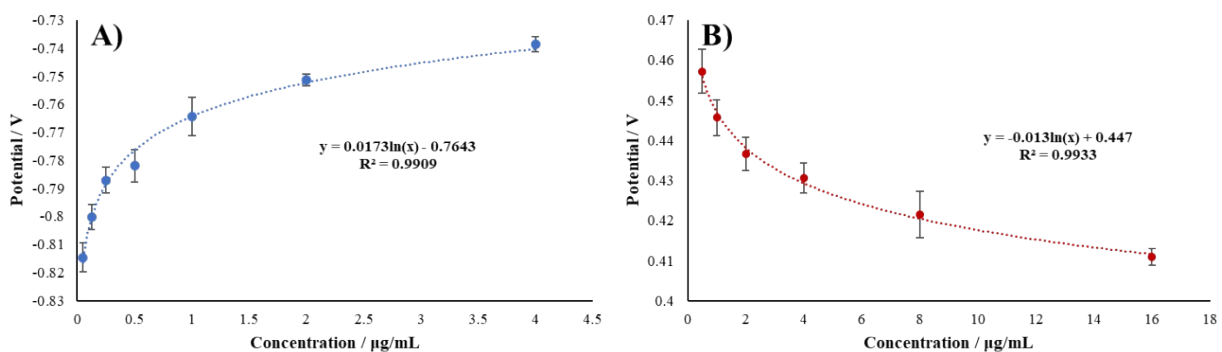
**Supplemental Figure S4.** Graphical comparison of the LOD values for the reduction peak of the redox couple  $[\text{Fe}(\text{CN})_6]^{4-} \rightleftharpoons \text{Fe}[\text{CN}]_6]^{3-}$  in relationship to the experimentally tested LOD value for the unweighted curve.



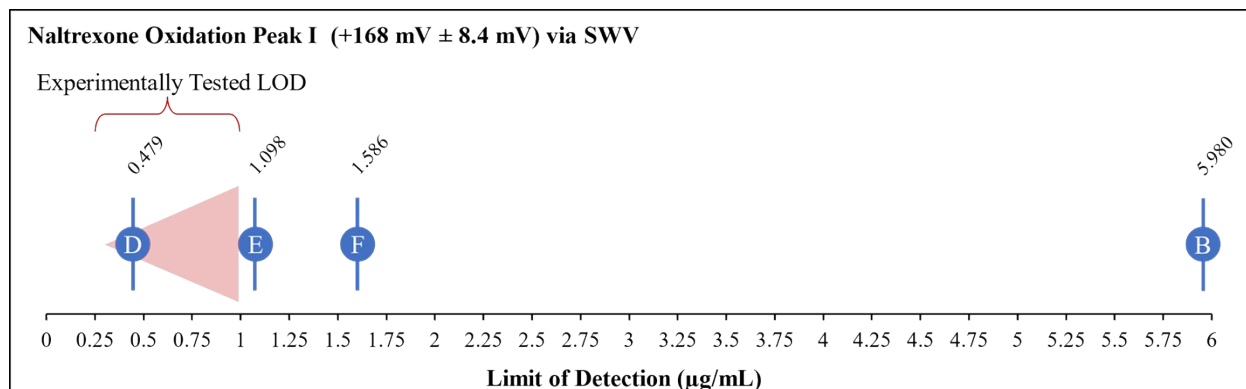
**Supplemental Figure S5.** Graphical comparison of the LOD values for the reduction peak of the redox couple  $[\text{Fe}(\text{CN})_6]^{4-} \rightleftharpoons \text{Fe}[\text{CN}]_6]^{3-}$  in relationship to the experimentally tested LOD value for the weighted ( $1/x^2$ ) curve.

**Supplemental Table S1.** Assessment and comparison of the LOD, in mmol/L, for ferricyanide via cyclic voltammetry using the various reported methods in the literature for the reduction peak compared between the weighted and unweighted linear curves. Method A contains units of  $\mu\text{A}$  for the signal domain as measured by the height of the noise peak.

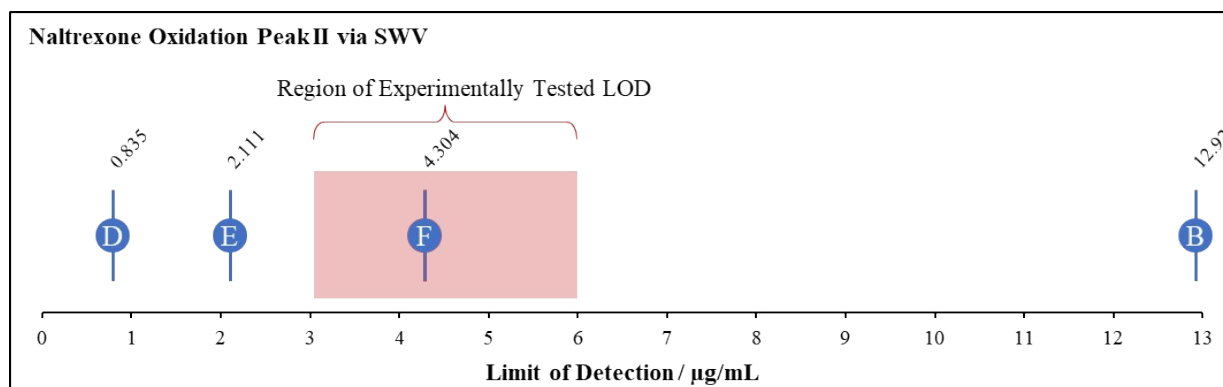
Method		Unweighted	$1/x^2$ Weighted
A	$3 * \text{Noise}$		0.009 $\mu\text{A}$
B	$\bar{X}_B + 3.3 * s_B$	0.00109	0.00378
C	$(3.3 * \sigma_B)/m$	N/A	N/A
D	$(3.3 * \sigma_{L1})/m$	0.00319	0.00305
E	$(3.3 * \sigma_y)/m$	0.10874	0.00348
F	99 % C.L.	0.14476	0.12652
Experimental	Serial Dilution	0.001 < LOD < 0.01	



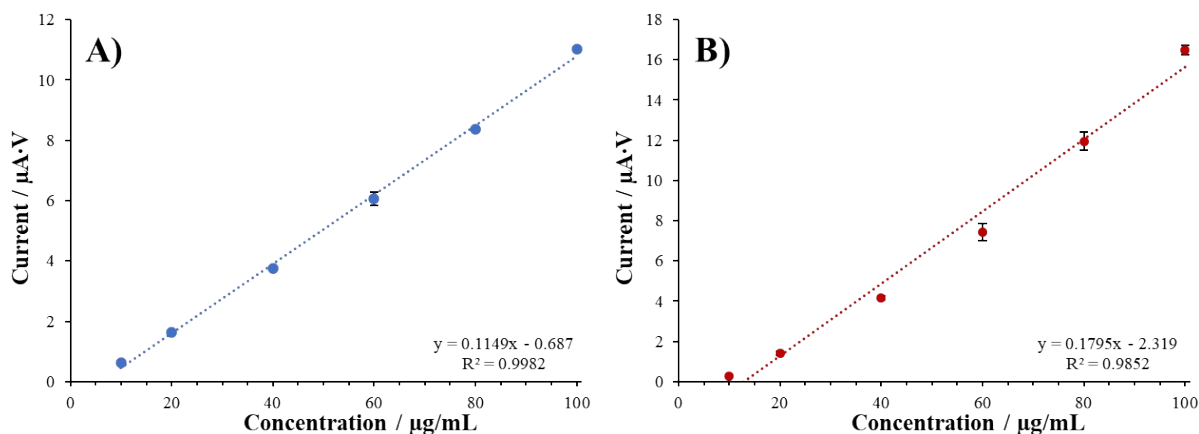
**Supplemental Figure S6.** Potential shift for the A) Pb oxidation peak and B) DPA oxidation peak,  $n=10$ . Error bars represent the standard deviation.



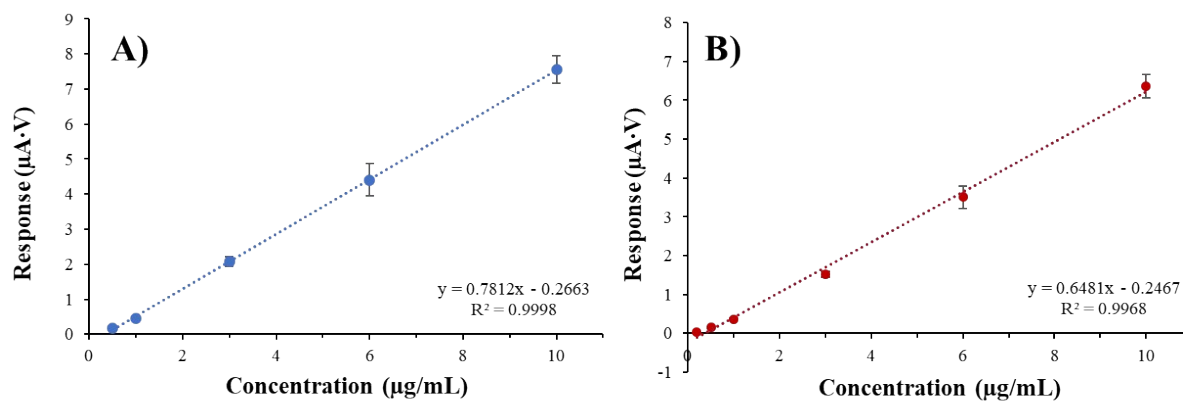
**Supplemental Figure S7.** Graphical comparison of the LOD values for oxidation Peak I (+168 mV) of Naltrexone in relationship to the experimentally tested LOD value.



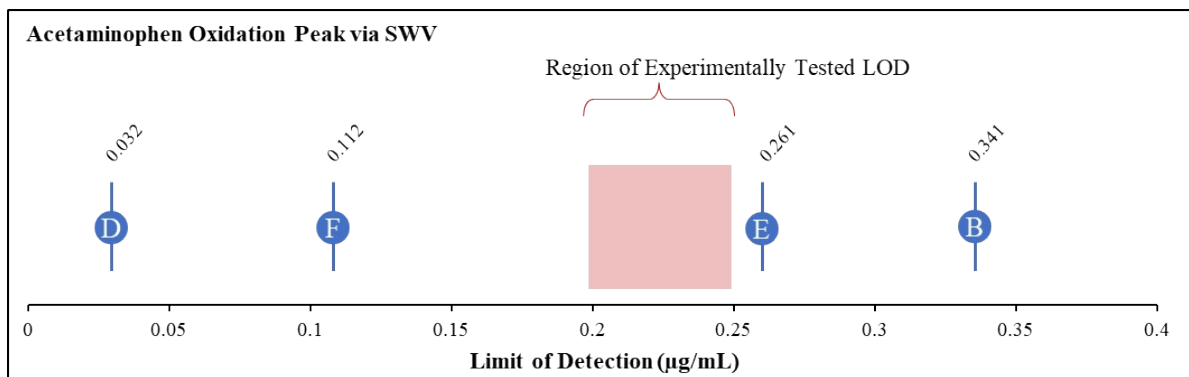
**Supplemental Figure S8.** Graphical comparison of the LOD values for oxidation Peak II (+752 mV) of Naltrexone in relationship to the experimentally tested LOD value.



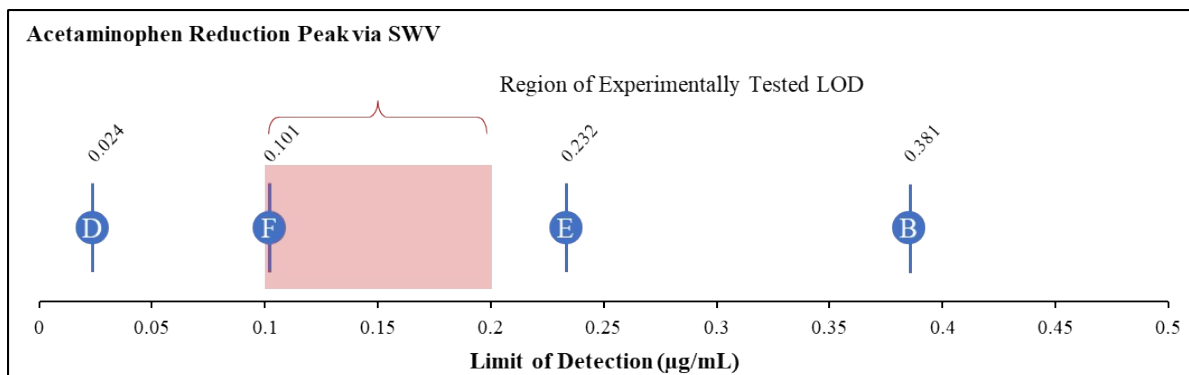
**Supplemental Figure S9.** Calibration curves for Naltrexone for A) Oxidation Peak I (+168 mV) and B) Oxidation Peak II (+752 mV). Error bars represent the standard deviation.



**Supplemental Figure S10.** Calibration curves for Acetaminophen for the A) oxidation peak between 0.5  $\mu\text{g/mL}$  and 10  $\mu\text{g/mL}$  and B) reduction peak between 0.2  $\mu\text{g/mL}$  and 10  $\mu\text{g/mL}$ . Error bars represent the standard deviation.



**Supplemental Figure S11.** Graphical comparison of the LOD values for the oxidation peak of Acetaminophen in relationship to the experimentally tested LOD value.



**Supplemental Figure S12.** Graphical comparison of the LOD values for the reduction peak of Acetaminophen in relationship to the experimentally tested LOD value.

**Disclaimer:**

Certain commercial products are identified in order to adequately specify the procedure; this does not imply endorsement or recommendation by the National Institute of Standards and Technology (NIST), nor does it imply that such products are necessarily the best available for the purpose.