On Limit of Detection: Why Is the Theoretical Value So Different from the Empirical in Electroanalytical Techniques?

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The limit of detection (LOD) is one of the most critical parameters in analytical chemistry, directly impacting the applicability and reliability of any analytical method. In electroanalytical techniques, which are often chosen for their low cost, simplicity, and portability, the pursuit of lower LOD values is a constant goal. However, a recurring issue in the literature is the significant discrepancy between theoretically calculated LOD values and those experimentally observed [1,2]. This work aims to critically discuss the origin of these differences by evaluating various theoretical approaches to LOD calculation—including methods based on blank signal standard deviation, propagation of errors, sample standard deviation, and graphical approaches—and comparing them with empirical results obtained from square wave voltammetry (SWV) using graphite sheet electrodes. Experimental results demonstrate that, while certain theoretical equations suggest extremely low LOD values (down to 0.03 μmol L^{-1}), these values are often unattainable in practice. In contrast, the lowest empirically detectable concentration was found to be approximately 1.95 μmol L^{-1} under the tested conditions. This discrepancy arises from multiple factors inherent to real-world measurements. The findings highlight the necessity of distinguishing between LOD as a statistical estimation and the lowest quantifiable concentration (LQ) that can be reliably detected in practical applications. This work proposes an alternative empirical strategy for LOD determination based on systematically lowering analyte concentration until the signal is no longer distinguishable from the noise. This approach provides a more realistic assessment of method sensitivity and avoids the misleading optimism often associated with purely theoretical LOD calculations.

References: (1) Currie, L. A. *Analytica Chimica Acta*. 1999, pp 127–134. (2) Currie, L. A.. *Pure Appl. Chem.* **1995**, *67* (10), 1699–1723.