Indirect detection of thiosulfate with a dual barrier carbon microelectrode

Paula C. Falcoswki[1], Douglas P.M. Saraiva[1], Nicolas A. Ishiki[2], Edson A. Ticianelli[2], Mauro Bertotti[1]

[1], Institute of Chemistry, University of São Paulo-USP, São Paulo, Brazil

[2] São Carlos Institute of Chemistry, University of São Paulo-USP, São Carlos, São Paulo, Brazil

**e-mail: paula.calli@usp.br*

Some analytes can be detected indirectly using electrochemical sensors, with the aid of intermediate species [1]. One such approach involves generator-collector systems, where the reaction between the analyte and an electrochemically generated species affects the collection efficiency. In this work, a dual carbon fiber microelectrode was fabricated using theta borosilicate capillaries pulled with a laser-based puller (P-2000, Sutter Instrument). The resulting microdisks were separated by a thin glass wall of approximately 1–2 μm, allowing operation in a generator-collector configuration. The electrochemical performance was first evaluated in a 5 mM $[Ru(NH_3)_6]Cl_3$ solution prepared in 0.5 M KCl, resulting in a collection efficiency of 0.24 ± 0.04. For thiosulfate detection, the electrode was immersed in a solution containing 2 mM KI, pH 5.2. A linear sweep voltammetry from 0 to 1.0 V (vs Ag/AgCl) was applied to the generator electrode (WE1), while the collector electrode (WE2) was held at 0 V. In these conditions, iodide is oxidized to iodine at WE1, which diffuses to WE2 and is reduced back to iodide. When thiosulfate is added to the solution, it reacts with the generated iodine, decreasing the amount of iodine reaching WE2 and thereby reducing the collector current. A calibration curve was obtained, showing a linear response between 20 and 200 μM, with a detection limit of 6 μM, calculated using the 3σ/s method (where σ is the standard deviation of the intercept and s is the slope).

Acknowledgments:

The authors would like to thank FAPESP (grants 2019/22183-6, 2022/03665-2, 2023/00246-1, and 2024/07124-1), CNPq, (grant 140813/2021-7), and CAPES for the generous funding. The authors also acknowledge Dr. Alex Lima Silva for the initial contributions.

References:

[1] Heineman, W. R., et al., Journal of Electrochemical Society, v.168, 2021