A dual barrel carbon fiber microelectrode for SECM generator collector experiments

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Generator-collector systems are widely explored in the literature for various applications in electrochemistry, such as elucidating electrochemical reaction mechanisms, determining kinetic constants and diffusion coefficients of the involved species, and indirect detection of non-electroactive species, among others [1]. These electrodes can have various geometries, one of which is the microdisk configuration, where the device can be fabricated within a theta capillary body. In this way, each microdisk is electrically isolated, allowing the fabrication of two electrodes placed extremely close to each other within the same glass body, where one acts as a generator electrode and the other as a collector electrode. In this work, a dual carbon fiber electrode was constructed, inserting the fibers into the orifices of a theta capillary, which was pulled using a Flaming/Brown Micropipette Puller (P-97). The fabricated electrodes were tested in $[Ru(NH_3)_6]Cl_3$ 5 mM + KCl 0.5 M solution and the obtained collection factor was 0.24 ± 0.05. We also evaluated the behavior of the collection factor as a function of the distance between a double electrode and an insulating surface (Fig. 1). In such an experiment, an increase in the collection factor for the Ru^{3+}/Ru^{2+} system was noticed and explained by the confinement of the species produced in the generator electrode. Such confinement hinders the species diffusion to the bulk, causing them to remain surrounding the collector electrode. On the other hand, when this distance becomes too small, the diffusion layer is compressed between the electrode and the substrate. As a result, the transport of the generated species to the collector electrode is hindered, reducing the collection factor. The fabricated sensor was applied to the indirect quantification of thiosulfate using the iodine/iodide system in a generator/collector configuration. In such a system, thiosulfate chemically consumes electrogenerated iodine, and the increase in thiosulfate concentration is responsible for the decrease in the collection factor, enabling its quantification with a dynamic linear range from 1 to 200 µM in experiments carried out at 80 µm above the substrate. Furthermore, the calibration curves obtained for the iodine/iodide and thiosulfate system also showed a signal increase (enhancement of the collection factor) as the electrode was brought closer to the surface (3.5 µm).

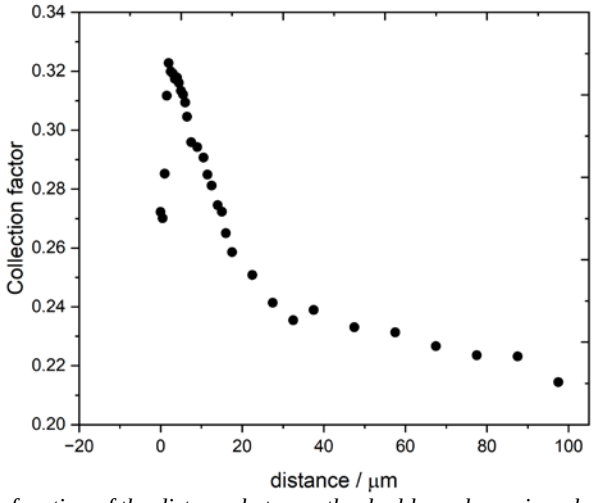

Fig. 1 – Collection factor as function of the distance between the double carbon microelectrode and an insulating silicon substrate in a 5 mM $[Ru(NH_3)_6]Cl_3$ + 0.5 M KCl solution. $E_{generator}$ = -0.300 V ; $E_{collector}$ = 0.200 V

[1] Barnes, E. O., Lewis, G. E. M., Dale, S. E. C., Marken, F., & Compton, R. G. (2012). Generator-collector double electrode systems: A review. In Analyst (Vol. 137, Issue 5, pp. 1068–1081). Royal Society of Chemistry. https://doi.org/10.1039/c2an16174e