CUMULATIVE EXAMINATION IN ANALYTICAL CHEMISTRY

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1. (10 points) The authors have proposed new microfluidic sensors that use anodically-generated chemiluminescence as a “reporter” for the electrode reactions of analytes. Please describe the fundamental bases of these new sensors in terms of the electrochemical reactions and the generation of the luminescence. I am looking for an explanation that would be appropriate for an undergraduate instrumental analysis student.

2. (10 points) On page 314, column 1, the authors state “...we used the well-established anodic ECL (electrochemiluminescence) reaction that involves oxidation of Ru(bpy)$_3^{2+}$ (bpy = bipyridine) and tripropylamine (TPA)...”. Please explain the Ru(bpy)$_3^{2+}$/TPA system as completely as you can. Include answers to such questions as: (1) What is/are the luminescent species? (2) Why does the ECL require an anodic reaction? (3) What is the role of TPA in the process? (4) What is the source of energy for forming the excited state species that luminesces.

3. (10 points) The authors previously described a single-channel system in which both electrodes, the Ru(bpy)$_3^{2+}$/TPA system, and the analyte are present in the same solution in a single channel. The authors state on page 313, column 2, “…A limitation of the previously reported single-channel system is that under certain conditions the detection and reporting reactions interfere with one another because of their close spatial proximity, which can lead to quenching of the ECL reaction and a corresponding loss of reporting fidelity...”. Recall that an electronically excited state is both a better reductant and a better oxidant than the ground state. Explain how the “close spatial proximity” of the ECL system and analyte, say Fe(CN)$_6^{3-}$ might lead to “quenching”.

4. (10 points) In the first paper, the authors propose a two-channel device in which the solutions in the two channels do not mix at the required cross-channel because the flow rates of both channels are carefully balanced and because the flow is laminar.
   (a) Why is the cross-channel necessary?
   (b) Explain how this design eliminates the above limitation of the single-channel device.

5. (10 points) In the view of the Examiner, the truly novel contribution of the papers is the concept of physically separating the electrode reaction of the analyte from the ECL “reporting” system while maintaining (in the two-channel device) a luminescence intensity that is a monotonically increasing function of analyte concentration. Explain as
fully as you can how this was achieved. (Do not be confused, as I was, by the two sets of electrodes shown in Scheme 2, b/b' and a/a'; only one set is used at a time depending on the flow direction).

6. (10 points) Given a flow rate of 1 \( \mu \text{L/minute} \) and the cross-sectional area of the 26 \( \mu \text{m} \) by 200 \( \mu \text{m} \) channel in the vicinity of the electrodes, compute the linear flow rate of the solution.

7. (10 points) The authors demonstrate that, to a first approximation, the response is proportional to the total concentration of analyte in the “detection” channel (Figure 5, page 317). However, at first blush this statement appears to be contradicted by the similar length of the bars for “…1 mM BV\(^{2\text{+}}\) / Ru(NH\(_3\)\(_6\))^{3\text{+}} / \text{Fe(CN)}\(_6\)^{3\text{−}} “ and for “…0.33 mM BV\(^{2\text{+}}\) + Ru(NH\(_3\)\(_6\))^{3\text{+}} + \text{Fe(CN)}\(_6\)^{3\text{−}} “. Please explain.

8. (10 points) In the second paper, the authors introduce a three-channel device (Scheme 1, page 1233).
   (a) This was designed to overcome what limitation of the two-channel sensor?
   (b) Explain why the anode is in contact with both the “ECL Reporting Stream” and the “Analyte Stream”.

9. (10 points) The three-channel sensor is described as an “…Indirect Sensing Approach…” (page 1235, column 1).
   (a) Define as precisely as you can the differences between an indirect detection method and a direct detection method. Please don’t repeat the examples given in the paper. I am interested in the very simple conceptual difference between the two. This question can be answered in one sentence.
   (b) The detection limit is normally described as the concentration that will give a signal (corrected for the background signal) that is three times the standard deviation of the background. From the results shown in Figure 4b (page 1237), estimate whether 10 \( \mu \text{M Fe(CN)}\(_6\)^{3\text{−}} \) is above or below the detection limit. Justify your answer.

10. (10 points) Results for dopamine (Figure 2, page 1236; Figure 5, page 1238) indicate that an analyte with oxidation potential around +0.5 V vs. Ag/AgCl can be successfully analyzed using the three-channel sensor. What is the upper limit for analyte oxidation potential using this sensor? Justify your answer.