

A novel multicommutation stopped-flow system for the simultaneous determination of sulfamethoxazole (SMX) and trimethoprim (TMP) by differential pulse voltammetry on a boron-doped diamond electrode

Leonardo S. Andrade^{a*} (PQ), Romeu C. Rocha-Filho (PQ), Quézia B. Cass (PQ), Orlando Fatibello-Filho (PQ) *ls_andrade@yahoo.com.br

^a Departamento de Química - Universidade Federal de Goiás, Catalão - GO, Brazil
Departamento de Química - Universidade Federal de São Carlos, São Carlos - SP, Brazil

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Introduction

Due to the importance of sulfonamide drugs in fighting diseases in human and other animals, the interest in the investigation of this class of compounds as well as in the analytical determination of their contents in commercial formulations is always increasing. Multicommutation is one of the most recent flow techniques, based on the use of multiple flow-commutation devices, usually three-way solenoid valves that control the analytical pathway of the solution toward the detector. Thus, the combination of a multicommutation flow system with electrochemical detection for the determination of sulfonamides can be considered an interesting alternative. However, as the corresponding pharmaceutical products consist of both sulfonamide and trimethoprim (a potentiator), their simultaneous determination using a multi-commutated flow system coupled with classical voltammetric techniques is only possible in static systems, i.e. if the flow is interrupted. So, in this work we report on the simultaneous electrochemical determination of SMX and TMP in pharmaceutical products in a multicommutation stopped-flow system coupled with differential pulse voltammetry (DPV) using a HT-BDD electrode (cathodically pre-treated).

Results and Discussion

The multicommutation flow module (Figure 1A) consisted of two solenoid valves (V_1 and V_2) that controlled the injection of the carrier (C) and sample (S) solutions, respectively. The full lines depict the carrier solution pathway toward the electrochemical detector, whereas the dashed lines indicate the solutions pathways when these valves are switched-on. At this condition (switched-on), C is recycling while S moves toward the electrochemical detector. When the flow is interrupted, analyses by voltammetric techniques are initiated and the analytes are determined inside the detector, under static conditions.

Using the DPV optimized conditions¹ and a 500- μ L sample volume, Figure 1B shows the DPV voltammogram series obtained by carrying out triplicate 2-min steps in the optimized multicommutation stopped-flow system using the

HT-BDD electrode at different concentrations of SMX/TMP (from 1.0 to 8.0 mg/L and 0.20 to 1.6 mg/L for SMX and TMP, respectively) in a Britton-Robson buffer solution (pH 7.0).

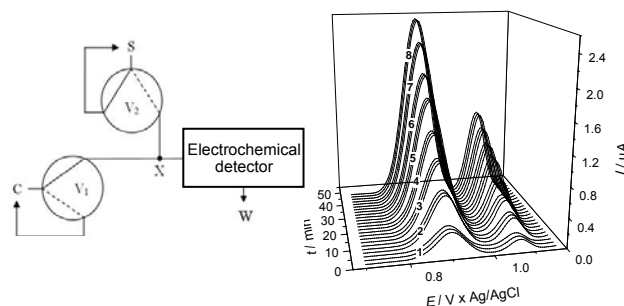


Figure 1 – (A) Diagram of the multicommutation stopped-flow system used. (B) DPV responses on a HT-BDD electrode using the optimized conditions.

As it can be seen in this figure, two well-defined oxidation waves are obtained: the one at $E_p = 0.90$ V corresponds to SMX oxidation and the other at $E_p = 1.07$ V to TMP oxidation. An excellent sample throughput (30 h^{-1}) was achieved, especially if one takes into account that each analysis by the official USP method (HPLC) for the determination of sulfonamides takes about 10 min to be carried out. Therefore, the same analysis could be done five times faster than by the official method.

The analytical curves obtained from the DPV voltammograms are linear in the investigated concentration range ($r^2 = 0.9998$, for both SMX and TMP). The LOD and LOQ values calculated for SMX or TMP were 16.5 $\mu\text{g/L}$ and 55.1 $\mu\text{g/L}$ or 18.3 $\mu\text{g/L}$ and 61.1 $\mu\text{g/L}$, respectively. The results obtained employing the proposed method for two commercial formulations were in satisfactory agreement with the ones obtained with the USP method.

Conclusions

The obtained results clearly indicate that quite low concentrations of SMX and TMP can be detected on the HT-BDD electrode using the proposed method. Besides, the mode of analysis allows total automation of the system as well as a significant increase in the analytical frequency.

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