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The Use of Multivariate Analysis in the Control of the Morphological Period of (Electro)Chemical Oscillators

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Abstract
This study employ a multivariate statistical analysis in chemical and electrochemical oscillators to determine accurately the effect of experimental parameters on the oscillation frequency. This work has been published in Physical Chemistry Chemical Physics (PCCP) and highlighted as an outside front cover.

Key words:
Multivariate analysis, nonlinear oscillators, frequency

Introduction

The effect of experimental parameters on the frequency of chemical oscillators has been systematically studied since the first observations of clock reactions. The approach is mainly based on univariate changes in one specific parameter while others are kept constant. The frequency is then monitored, and the effect of each parameter is discussed separately. This type of analysis, however, does not take into account the multiple interactions among the controllable parameters and the synergic responses on the oscillation frequency.

This work has the objective of performing a multivariate analysis of the chemical (BZ-ferroin) and electrochemical (Cu/Cu_2O cathodic deposition) oscillators to obtain a parametric relation between frequency and experimental parameters. It has been published in Physical Chemistry Chemical Physics (PCCP) and highlighted as an outside front cover[1].

Results and Discussion

The results obtained from the chemical and electrochemical system allowed us to obtain a response surface, where Figure 1 demonstrates the frequency changes with the variation of the experimental parameters.

In the Figure 2a it is observed that the BZ reaction presented a strong dependence on the initial concentration of sodium bromate and temperature, resulting in a frequency increase. The concentration of malonic acid, the organic substrate, affects the system but with lower intensity compared with the combination of sodium bromate and temperature.

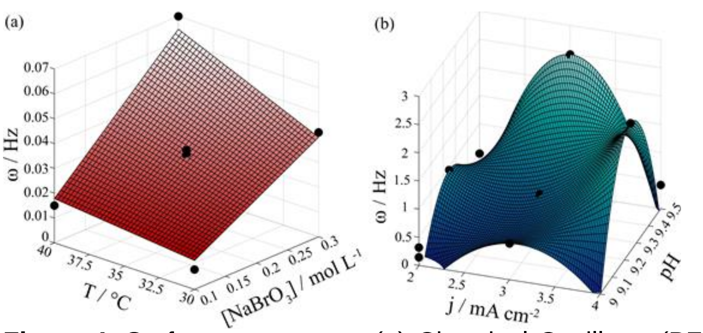

Figure 1. Surfaces responses (a) Chemical Oscillator (BZ reaction) and (b) Electrochemical Oscillator (Cu/Cu_2O - Cathodic Deposition).

On the other hand, the Cu/Cu_2O electrochemical oscillator showed to be less sensitive to changes in the temperature, as shown in the Figure 2b. The applied current density and pH were the two parameters which most perturbed the system. Interestingly, the frequency behaved nonmonotonically with a quadratic dependence. The multivariate analysis of both oscillators exhibited significant differences - while the homogenous oscillator displayed a linear dependence with the factors, the heterogeneous one revealed a more complex dependence with quadratic terms.

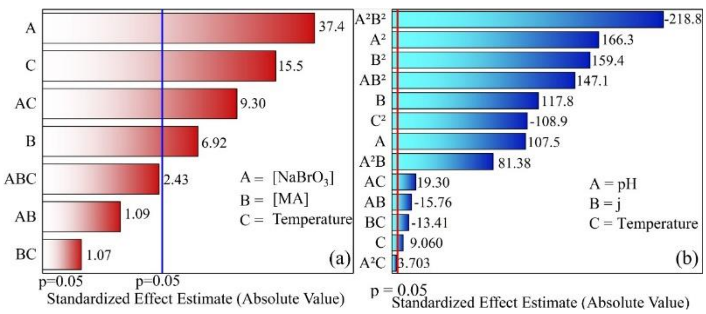

Figure 2. Pareto chart representing the significance of the Effects with confidence level of 95 % ($p = 0.05$) for (a) BZ reaction and (b) Electrochemical Oscillator (Cu/Cu_2O - Cathodic Deposition).

Conclusions

The multivariate statistical analysis allowed to study the effect of experimental parameters on the frequency of chemical (BZ-ferroin catalyzed reaction) and electrochemical (Cu/Cu_2O cathodic deposition) oscillators. This approach provides an accurate model for a frequency selection which is of utmost importance in the development of biomimetic or self-organized smart materials.

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[1] B.T. Kitagaki, M.R. Pinto, A.C. Queiroz, M.C. Breitkreitz, F. Rossi, R. Nagao, Phys. Chem. Chem. Phys., 2019. DOI: 10.1039/C9CP01998G