

Investigation of Briggs-Rauscher Oscillograms via Peak Area Integration

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Abstract: The Briggs-Rauscher (BR) oscillatory reaction is a chemical reaction that exhibits oscillations in the concentration of intermediate species. It is well known that oscillograms with the same number of oscillations and duration time could visually drastically distinguish. Therefore, to analyze the oscillograms from the BR reaction, peak area integration becomes a promising tool. The main idea of this work was to integrate the areas under the peak/oscillations of three BR oscillograms obtained under identical experimental conditions, using suitable computer program. In this work, the total peak area was calculated with a 95% confidence interval for the mean of three measurements is 3430 ± 130 for applied experimental conditions. The peak area integration is a promising tool to gain insights into the total quantity during the oscillation dynamics. Results obtained will be a good starting point for further analysis of the influence of different analytes on the BR reaction dynamics.

Keywords: Briggs-Rauscher reaction, oscillatory reaction, peak area integration, Python script

1. Introduction

The Briggs-Rauscher (BR) reaction is one of the classic examples of oscillating reactions, created by high school chemical teachers Thomas Briggs and Warren Rauscher in 1973 [1]. The BR reaction contains the following components: hydrogen peroxide (H_2O_2) and iodate ions (IO_3^-), involved in the reduction-oxidation processes, manganese ions (Mn^{2+}) as catalyst, malonic acid ($\text{C}_3\text{H}_4\text{O}_4$) as the organic substrate for the reaction,

which oxidases during reaction course [2]. The BR reaction proceeds through complex mechanism, which is still unknown. However, the oscillations arise from the feedback loops and/or autocatalytic steps in the reaction pathways [3]. Due to the complexity of all process, every new information connected to reaction dynamics and oscillograms (measuring output of the reaction dynamics) is highly important.

Basic oscillogram parameters are amplitudes, number of oscillations, oscillatory period and/or frequency, oscillatory time and induction period (if exists). It is well known that oscillograms with the same number of oscillations and duration time could visually drastically distinguish [4]. Therefore, the main idea of this paper is to introduce the peak area integration using adequate computer program (a program is also written for these purposes), as one of parameter which could be considered among basic one, to obtain insights into the total quantity during the oscillation dynamics.

2. Experimental

2.1 Briggs-Rauscher reaction experimental setup

The experiments were conducted in a closed, well-stirred batch reactor (stirring rate $\sigma = 900$ rpm) maintained at a constant temperature of (36.7 ± 0.1) °C. The initial concentrations of the reactants were as follows: $[\text{C}_3\text{H}_4\text{O}_4]_0 = 0.0789$ M, $[\text{MnSO}_4]_0 = 0.0075$ M, $[\text{HClO}_4]_0 = 0.0300$ M, $[\text{KIO}_3]_0 = 0.0752$ M, and $[\text{H}_2\text{O}_2]_0 = 1.2690$ M. All reagents were of analytical grade and used as received, without further purification. Each reaction was performed in a total volume of 25 ml. Once the system reached thermal and electrochemical stability, 3 ml of H_2O_2 was added, marking the official start of the reaction. The Briggs-Rauscher oscillatory reaction was monitored over time using potentiometric methods. A PC-Multilab EH4 electrochemistry analyzer with 16-bit analog-to-digital conversion was directly connected to the reactor. Measurements were taken using a platinum working electrode paired with a double-junction Ag/AgCl reference electrode to continuously record the potential changes at the Pt electrode.

2.2 Peak Area Calculations

To calculate the area between a electrode potential vs time graph (in our case oscillogram), we can interpret the area as the integral of the potential function over time. The general process involves integrating the potential function $V(t)$ with respect to time t :

$$\text{Area} = \int_{t_1}^{t_2} V(t) dt \quad (1)$$

where, $V(t)$ is the potential as a function of time experimentally obtained, and t_1 and t_2 are the limits of time (start and end times). In this work is arbitrary used $t_1 = 0$ s (when hydrogen-peroxide is added and BR reaction starts), and $t_2 = 100$ s (it approximately time when BR reaction is ended). Therefore, a time-series dataset containing time (t) and

signal amplitude (V) was imported using Python script. The data were filtered for the interval $0 \leq t \leq 100$. Local minima in the signal were identified using the `argrelextrema` function from the `scipy.signal` module. A lower envelope was generated by linear interpolation between these minima. The area where the signal lay above this envelope was calculated using the trapezoidal rule. All steps, including preprocessing, local minima detection, envelope interpolation, and area integration, were visualized using `matplotlib`.

3. Results and Discussion

The results of the peak area calculations for three BR oscillograms obtained under identical experimental conditions (see Experimental Section) are given in Table 1 (together with basic oscillatory parameters), and shown in Figure 1.

Table 1. Characteristic parameters obtained from BR oscillogram (τ_{osc} - oscillatory time, n - number of oscillations, ν - frequency of oscillation)

Experiment	τ_{osc} / s	n	ν / s^{-1}	Peak Area Calculation
1.	104.64	42	0.40	3368
2.	104.60	42	0.40	3462
3.	105.12	42	0.40	3440

The Student's t coefficient with 95% confidence and 3 measurements is 4.303. Total surface area calculated with the 95% confidence interval for the mean of our three measurements is 3430 ± 130 . This result gives us control parameter for future measurements.

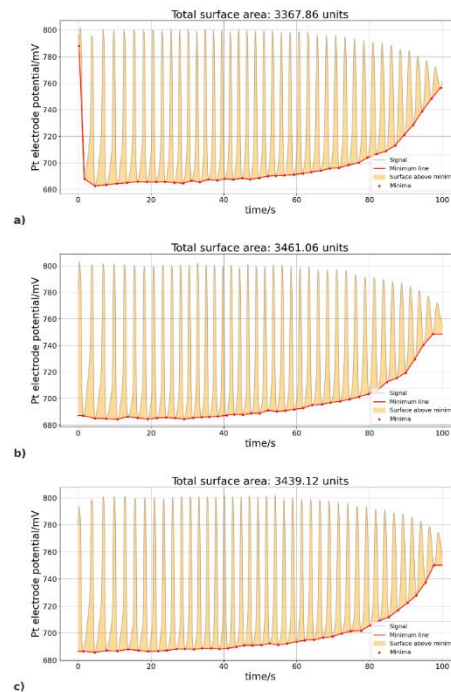


Figure 1. The results of peak area integration for three BR oscillograms obtained under same experimental conditions

As it can be seen, the three BR oscillograms obtained under same experimental conditions, have practically identical basic oscillatory parameters (see Table 1), but total surface areas are slightly differed (within confidence interval). This means that peak area integration is sensitive control parameter. The calculating total surface area opens up possibilities for better quantitative oscillogram investigation, as well as the kinetical examination of particular intermediates, and it is making a good starting point for quantifying different analyte influence on BR oscillatory dynamics [5].

4. Conclusions

The areas under the peaks of the three BR oscillograms obtained under identical experimental conditions, are integrated using adequate computer program. The total area calculated with a 95% confidence interval for the mean of our three measurements is 3430 ± 130 for the applied experimental conditions. This result gives us control parameter for future measurements. Peak area integration is a promising tool to gain insights into the total quantity during the oscillation dynamics and to analyze the BR oscillograms. The results obtained will be the starting point for further analysis of the influence of different analytes on the BR reaction dynamics.

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