

# BRAY-LIEBHAFSKY OSCILLATORY REACTION AS AN EASY AVAILABLE ANALYTICAL TECHNIQUE FOR DETERMINATION OF RESORCINOL CONCENTRATION

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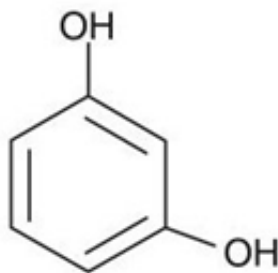
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**Abstract:** The Bray-Liebhafsky (BL) reaction is the oldest known oscillatory reaction. It consists only of three reactants: potassium iodate ( $\text{KIO}_3$ ), sulfuric acid ( $\text{H}_2\text{SO}_4$ ) and hydrogen-peroxide ( $\text{H}_2\text{O}_2$ ) which provides its easy available chemical system. In this work, the resorcinol (1,3-benzenediol) effects on BL reaction dynamics, as well as its unknown concentration determination is investigated. The addition of different resorcinol concentration after fifth oscillation affects the appearance of the sixth oscillation. Consequently, the time between fifth and sixth oscillations vs. resorcinol concentration can be successfully used for analytical curve construction, and further unknown resorcinol concentration determination. This work is an attempt to introduced oscillatory BL reaction for the analytical purpose; so far another oscillatory reaction known as Briggs-Rauscher reaction has been successfully used for these purposes. Regarding very small quantity and resorcinol concentration ( $6.634 \cdot 10^{-5} \text{ mol/dm}^3$ ) which could be detected in BL oscillatory reaction, results obtained can play important role in the forensic analysis (especially for gunshot residual or illegal drugs analysis).

**Keywords:** Bray-Liebhafsky reaction, oscillatory reaction, resorcinol, analytical technique, gunshot residue, illegal drugs

## INTRODUCTION

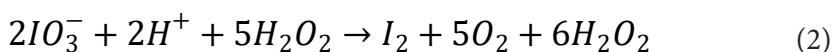
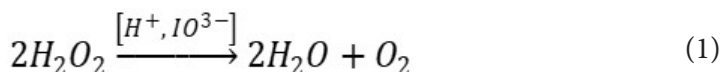
Resorcinol is a white organic crystal with a characteristic aromatic odor. Its structure consists of an aromatic ring with two hydroxyl groups in meta-position (Fig. 1). Because of the position of two hydroxyl groups, resorcinol has high reactivity which is responsible for its wide application.



**Figure 1.** Structure of resorcinol

Resorcinol is primarily used by the rubber industry (Krishan, Venkatesan & Adhinarayanan 2004), as well as in high-quality wood bonding (Gardner 2008). It is also used as an effective chemical intermediate in the production of organic compounds, dyes, in pharmaceutical formulations and as UV absorber in resins (Durairaj 2005). Resorcinol has an important role for medical purposes as an antiseptic and in the treatments of various skin disease (Hampil 1928). The resorcinol with the role of stabilizer is the leading component of Gunshot Residue (GSR) (Benito, Abrego, Sanchez, Unceta, Goicolea & Barrio 2015). GSR analysis answers the bunch of questions on was the weapon used in the criminal act, providing some of the crucial evidence. Additionally, the resorcinol can be an active ingredient (or derivate) some of the most commonly used illegal drugs. (Thorton & Nakamura 1972) It is also established that cannabidiol, an active ingredient in cannabis (one of the commonly used illegal drugs), is resorcinol derivate (Thorton & Nakamura 1972). The concentration of resorcinol and its compounds varies depending on the application, therefore techniques for accurate concentration determination is of great significance.

Bray-Liebhafsky (BL) oscillatory reaction is hydrogen peroxide decomposition reaction catalyzed by iodate and iodine in acidic solutions (Bray & Liebhafsky 1931) in which hydrogen peroxide decomposes on oxygen and water (1). During Bray-Liebhafsky oscillatory reaction, the concentration of reactants and products change stepwise, whereas intermediates experience oscillations of concentration in time. Even though BL reaction is one of the oldest known oscillatory reaction, its detailed mechanism is still unknown. Hydrogen peroxide can reduce iodate to iodine in reaction (2) and oxidize iodine to iodate in reaction (3).

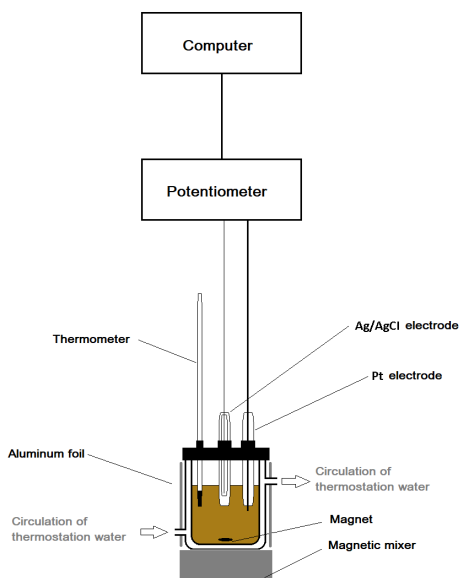


Bray-Liebhafsky reaction, similar to Briggs-Rauscher oscillatory reactions (Briggs & Rauscher 1973), is very sensitive to the concentration of added additives (Pejić, Anić & Kolar-Anić 2012). Since Briggs-Rauscher reaction is already studied as a test for analytical measurements of resorcinol (1,3-dihydroxybenzene) concentration (Cervellati, Höner, Furrow, Neddens & Costa 2001), the possibility of BL system for determination of resorcinol concentration is the main topic of this work. Regarding resorcinol widespread presence especially in GSR and illegal drugs, this work could have significant importance in forensic science analysis in general.

## MAIN PART

### Experimental part

The dynamic states of the BL reaction were recorder potentiometrically, using Pt electrode as a working electrode, and a double junction Ag/AgCl electrode, as a reference. The reaction was carried out in a closed well-stirred system, with a magnetic stirrer at the stirring speed of 900 rpm. The system was thermostated at 62.0 °C and the circulating water bath was used to maintain the temperature of the reaction. The experimental setup is represented in Fig. 2



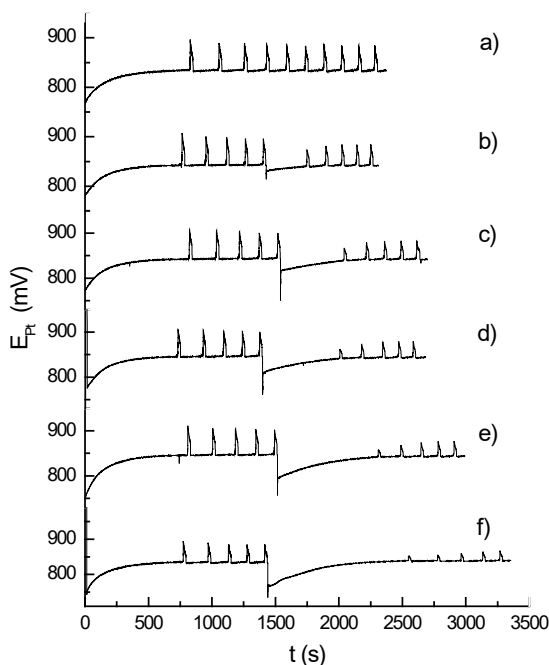
**Figure 2.** Scheme of the experimental setup

The total volume of the reaction cell was 25 ml. The reagents of the BL reaction (sulfuric acid, potassium iodate, and hydrogen peroxide) were prepared using de-

ionized water. Initial concentrations of the solutions were  $[\text{H}_2\text{SO}_4] = 0.048 \text{ mol/dm}^3$ ,  $[\text{KIO}_3]_0 = 0.072 \text{ mol/dm}^3$  and  $[\text{H}_2\text{O}_2]_0 = 0.460 \text{ mol/dm}^3$ . The hydrogen-peroxide was injected last in the system after temperature and Pt-potential were stabilized. This moment is taken as the beginning of the BL reaction and labeled as the zero point of the  $x$ -axis. Resorcinol was added after the fifth oscillation, and the following concentrations were tested  $0.0159 \text{ mol/dm}^3$ ,  $0.0478 \text{ mol/dm}^3$ ,  $0.0796 \text{ mol/dm}^3$  and  $0.1592 \text{ mol/dm}^3$ . The injected volume of tested substance was the same in every experiment ( $100 \mu\text{l}$ ).

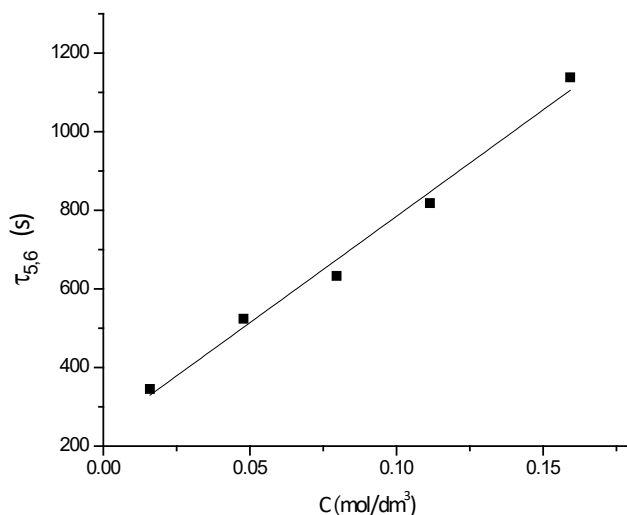
## Results and discussion

Experimentally obtained effects of the different resorcinol concentrations on the oscillatory evolution of the BL reaction, along with the basic oscillogram to compare, are shown in Fig. 3.



**Figure 3.** BL oscillograms obtained by the Pt electrode: a) basic BL oscillogram without the addition of resorcinol; oscillograms obtained with the addition of resorcinol: b)  $0.0159 \text{ mol/dm}^3$ ; c)  $0.0478 \text{ mol/dm}^3$ ; d)  $0.0796 \text{ mol/dm}^3$ ; e)  $0.1114 \text{ mol/dm}^3$ ; f)  $0.1592 \text{ mol/dm}^3$

In all experiments only first ten oscillations were recorded, in order to compare BL oscillograms before and after the addition of resorcinol. It can be seen from Fig. 3 that all of six particular experiments had the same induction period (750 s), in the range of error ( $\pm 120$  s). Different concentrations of resorcinol were added at the root of the fifth oscillation observed by the initial decline of the Pt-potential. As evidenced on Fig. 3, even the addition of small concentration of resorcinol (100  $\mu\text{l}$  of 0.0159 mol/dm<sup>3</sup> added in 25 ml reaction system) caused the widening of the inter-oscillatory period between the fifth and sixth oscillation ( $\tau_{5,6}$ ) and decrease of the first amplitude after the resorcinol addition (sixth amplitude). By increasing the concentration of added resorcinol, the gap between fifth and sixth oscillation becomes wider. The duration of the inter-oscillatory period between the fifth and sixth oscillation shows a linear dependence of the added concentration of resorcinol (Fig. 4). Therefore, the obtained linear dependence ( $\tau_{5,6} = 5500 \cdot c_{\text{resorcinol}} + 250$ ) can be used to determinate the unknown concentration of resorcinol.



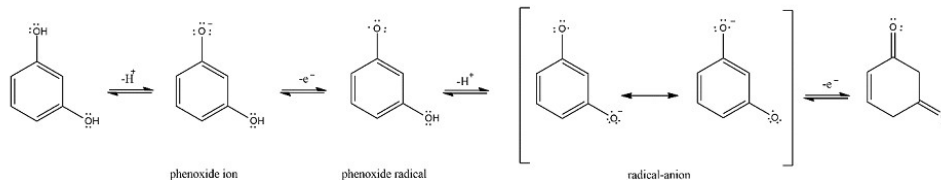
**Figure 4.** Dependence of an inter-oscillatory period between the fifth and sixth oscillation on the added concentration of resorcinol

Regarding very small quantity and resorcinol concentration (100  $\mu\text{l}$  of 0.0159 mol/dm<sup>3</sup>) which could be detected in BL oscillatory reaction, results obtained can play important role in the forensic analysis (especially for previously mentioned GSR or illegal drugs analysis). Namely, the addition of 100  $\mu\text{l}$  aliquot of 0.0159 mol/dm<sup>3</sup> resorcinol means the resorcinol concentration of  $6.634 \cdot 10^{-5}$  mol/dm<sup>3</sup> in 25 ml reaction system. It is evident that such small resorcinol concentration does not affect the concentration of reactants (order of magnitude  $10^{-2}$  mol/dm<sup>3</sup>

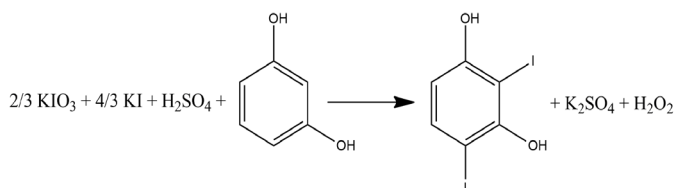
or higher) in direct resorcinol-reactant chemical reactions and on that way effect BL oscillatory dynamics. Thus, obtained effects of resorcinol addition in BL reaction can only be a consequence of:

- i) resorcinol reaction (or reactions) with some key intermediate in BL reaction
- ii) resorcinol reaction(s) with reactant(s) producing further BL “active” organic compound(s).
- iii) both i) and ii)

Thus, the presumed mechanism of resorcinol effects on the oscillating BL reaction is primarily due to the oxidation of benzene hydroxyl groups (Fig. 5) or iodination of the benzene ring (Fig. 6). The oxidation process of phenols starts with two releases of protons from the hydroxyl group leading to the formation of semiquinone radical anion (Vollhardt & Schore 2003). This mechanism is presented in Fig.5.



**Figure 5.** Mechanism of the oxidation process of phenols



**Figure 6.** The iodination reaction of the benzene ring

As previously known, semiquinones are very unstable and highly reactive substances, especially with oxygen molecular forms. (Munday 2004). As it is assumed, an oxidative form of resorcinol can react with intermediate(s) formed in BL reaction and accordingly be responsible for obtained behavior. On the other hand, it is well-known the application of the  $\text{KIO}_3/\text{KI}/\text{H}^+$  system for iodination of the resorcinol (Frederick 1976), producing in rapid reactions two products,

2,4-diiodoresorcinol (Fig. 6) and 2,4,6-triiodoresorcinol. These organic products can be further active and react with BL intermediates generating obtained effects in BL system.

With this acknowledgment and in line with what's stated above, it can be presumed that cannabis (active component cannabidiol) and other organic derivatives of resorcinol would potentially have a similar mechanism of reaction in BL system as the pure resorcinol. In support of this assumption is that one of the usually used tests for detection of cannabis - Duquenois-Levin test (Kelly, Addanki & Bagasra 2012) gives false-positive results in the presence of resorcinol due to the similar mechanism of resorcinol and cannabidiol action. Consequently, here proposed BL technique could also be potentially used for the determination of cannabidiol concentration, as an active ingredient of cannabis. To investigate the usage of the proposed technique for the determination of cannabis requires further examinations and it will be conducted in the future.

## CONCLUSION

In this work, the Bray-Liebhafsky oscillatory reaction, as an easily available analytical system is used for determination of resorcinol concentration. The different resorcinol concentrations were added after the fifth oscillations and the time between fifth and sixth oscillation were measured. The duration of the inter-oscillatory period shows a linear dependence of the added concentration of resorcinol and the obtained linear dependence can be satisfactorily used for determination of unknown resorcinol concentration. This linear dependence could potentially indicate the new, certain and easy technique for organic GSR analysis for resorcinol as a common stabilizer and possibly other organic compounds that can be found in smokeless powders. The potential mechanisms of resorcinol acting in BL system were also proposed. The similar structure of resorcinol and cannabidiol, and thus their oxidation process, leads to the belief that these two compounds have a similar mechanism of action in the BL system. The proposed BL technique could also be potentially used in the determination of cannabidiol concentration, as an active ingredient of illegal drug - cannabis. To investigate the usage of the proposed technique for determination of cannabis requires further examinations and will be conducted in the future. However, results obtained in this work indicate that Bray-Liebhafsky oscillatory reaction as an easy available chemical system for detection of resorcinol could have significant importance in forensic science analysis in general.

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