# **Determination of Morin by Using a Briggs-Rauscher Oscillator**

*Waqar Uddin<sup>1</sup>, Gang Hu<sup>1,\*</sup>, Xuanxuan Sun<sup>1</sup>, Saif Ullah<sup>1</sup>, Saira Sardar<sup>2</sup>, Zhang Wangning<sup>1</sup>, and Muhammad Yasir Nawabi<sup>1</sup>* 

<sup>1</sup> Department of Chemistry, Anhui University, Hefei, 230601, People's Republic of China <sup>2</sup> Institute of Chemical Sciences, University of Peshawar, Pakistan \*E-mail: <u>hugang@ustc.edu</u>

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A suitable and convenient method for the analytical determination of morin was established by using Briggs-Rauscher chemical matrix (BR) in the paper. The macrocyclic Ni-complex [NiL](ClO<sub>4</sub>)<sub>2</sub> was used as catalyst. The ligand L in the complex is 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene. Experimental data has absolutely indicated the inhibitory effect caused by morin on the active BR system. Different concentrations of morin ranging from  $2.44 \times 10^{-6}$  mol/L to  $1.30 \times 10^{-5}$  mol/L have been tested. As a result, oscillating system stopped to oscillate for some instant and then successfully regenerated. Such phenomenon has concentration dependent, meaning as the concentration of morin were increased, the inhibition time (t<sub>in</sub>) of the system were increased and vice versa. Thus, by plotting t<sub>in</sub> against concentrations of morin, a linear regression curve was obtained over a concentration range from  $2.44 \times 10^{-6}$  mol/L to  $1.30 \times 10^{-5}$  mol/L of 0.98. The calculated RSD value is 2.56 %, which was obtained by the 5-measurements of  $1.30 \times 10^{-5}$  mol/L morin. Although the reaction of morin and KIO<sub>3</sub> was confirm through cyclic voltammetry experiment, actually the t<sub>in</sub> was caused due to the reaction of morin with HOO<sup>+</sup> radical (produced during oscillatory reaction).

Keywords: Briggs-Rauscher, Electrochemical Oscillator, Morin, Inhibitory effect

## **1. INTRODUCTION**

Chemical oscillating reaction is well-known example of non-linear chemical dynamics, which shows continuous periodic changes in some intermediates over time [1]. From thousand years, the chemical oscillations exist in nature and, in fact, every living system consists hundreds of oscillations. The thorough investigation of chemical oscillations has a recent interest. Robert Boyle was the first scientist who observed chemical oscillation during his study (flashes of luminescence during the oxidation of phosphorus) [2] at the end of 17<sup>th</sup> century while his hypothesis was accepted in 19<sup>th</sup> century. In 1828 the Fechner discovered the first electrochemical oscillator [3] and thus the

development of the other oscillators [4,5] began. The famous electrochemical oscillators were of beating heart mercury [6] and iron nerve [7]. Various homogenous chemical oscillators were discovered like Bray-Liebhafsky (BL reaction) [8,9], Belousov-Zhabotinsky reaction (BZ-reaction) [10-13] and Briggs-Rauscher reaction (BR reaction) [14,15] etc. The BZ and BR chemical oscillators were extensively studied. On the basis of catalysts, both BZ and BR were classified into two main types i.e. classical and conventional. In the classical BZ, metal ions like Ce<sup>4+,</sup> Mn<sup>2+,</sup> Fe(phen)<sub>3</sub><sup>2+</sup> or Ru(bipy)<sub>3</sub><sup>2+</sup> [16-18] were used as catalyst while in classical BR, free metal catalysts i.e. Ce<sup>4+</sup>, Mn<sup>2+,</sup> were used [14,19]. In the conventional BZ and BR, macrocyclic complexes of Cu and Ni [20] respectively were used as catalysts and were utilized for the determination of various compounds, ions, and species [21-33].

In this article, the determination of morin was carried out by its perturbation effects on a Ni-Complex [NiL](ClO<sub>4</sub>)<sub>2</sub> catalyzed BR chemical oscillator. The ligand L in the complex is 5,7,7,12,14,14-hexamethyl-1,4,8,11- tetra-aza- cyclotetradeca-4,11-diene. The addition of morin into the active BR-system could temporarily stop oscillation for some instant. Such temporary cease in oscillation was given the name as inhibition time (t<sub>in</sub>) which was found directly proportional to the concentration of morin. Increase in the concentrations of morin led to increase the t<sub>in</sub> of the system and vice versa. Although the redox reaction between morin and KIO<sub>3</sub> was confirmed through cyclic voltammetry (CV), t<sub>in</sub> was actually caused by the reaction between morin and intermediate radical (HOO'). The detail explanations about this were discussed in the mechanism section.

#### 2. EXPERIMENTAL

#### 2.1. Reagents

All the analytical grade reagents, malonic acid (MA) (Sinopharm chemical reagent, China),  $H_2SO_4$  (Aldrich, 98%), KIO<sub>3</sub> (Sinopharm chemical reagent, China) and  $H_2O_2$  (Sinopharm chemical reagent, China), and morin (alddin) were commercially purchased and were used directly without further analysis. The Ni-complex catalyst, [NiL](ClO<sub>4</sub>)<sub>2</sub>, was prepared as reported [34,35] and was identified by instrumental technique (IR spectrum) and elementary analysis. Scheme 1 shows the structure of [NiL](ClO<sub>4</sub>)<sub>2</sub>. The solution of  $2.50 \times 10^{-2}$  mol/L  $H_2SO_4$  was prepared. Using such solution of  $2.50 \times 10^{-2}$  mol/L  $H_2SO_4$  as a solvent in the preparation of other solutions like  $1.40 \times 10^{-1}$  mol/L KIO<sub>3</sub>,  $1.73 \times 10^{-2}$  mol/L [NiL](ClO<sub>4</sub>)<sub>2</sub>, 2.00 mol/L malonic acid and 4.00 mol/L of  $H_2O_2$ . Ethyl alcohol was used as solvent in the preparation of morin solutions.



Scheme 1. Structure of [NiL](ClO<sub>4</sub>)<sub>2</sub>

#### 2.2. Apparatus

The BR apparatus and its setting are highly simple. In 50 ml batch reactor, 40 ml of oscillating solutions was poured and was continuously stirred through magnetic bar (Jiangsu, China) at 750 rpm. In the solution of batch reactor, the two electrodes (platinum (Pt) and saturated calomel electrode (SCE)) were dipped. The nature of both the electrodes was quite different. A Pt-electrode (model 213 Shanghai, China) was served as a working electrode while SCE (Model 217 Shanghai, China) was used as a reference electrode. Electrodes were connected to PC through amplifier (Vernier Software Technology, USA) and GO!Link sensor interface (Vernier Software Technology, USA). The Logger Lite data-acquisition software was used to record the potential *vs.* time in PC. The temperature of the system was kept at 4.50 °C.

## 2.3. Procedure

The order of putting the reagents into batch reactor was kept as follows, 14.50 ml of  $0.025 \text{ mol/L H}_2\text{SO}_4$  solution, 6.50 ml of 0.14 mol/L KIO<sub>3</sub> solution, 2.00 ml of 0.0173 mol/L [NiL](ClO<sub>4</sub>)<sub>2</sub> solution, 3.00 ml of 2.00 mol/L MA solution , 14.00 ml of 4.00 mol/L H<sub>2</sub>O<sub>2</sub> solution. The batch reactor was kept in the ice bath and the reaction temperature was maintained at 4.50 °C. The electrodes were immersed into the solutions and potential *vs*. time was recorded in PC through amplifier and the GO!Link sensor interface. Different concentrations of morin were injected into the BR reactor at the end of 4<sup>th</sup> cycle and the variations in inhibition time (t<sub>in</sub>) were observed.

#### **3. RESULTS AND DISCUSSION**

## 3.1. Typical Oscillation

The Figure 1(a) shows the typical oscillation of BR, which was taken from the BR mixture on the abovementioned order. In oscillation systems usually the color of the solution was continuously interchanging. In  $Mn^{2+}$ -catalyzed BR reaction, the color continuously changes from colorless to yellow to blue [36], whereas in our proposed method (Ni-Complex catalyzed BR reaction) the color of solution was continuously interconverted into yellow and brown [37], The color changes in the solution represented the exchange of single electron between [NiL]<sup>2+</sup> and [NiL]<sup>3+</sup> as mention below.

 $[NiL]^{2+}(yellow) \Leftrightarrow [NiL]^{3+}(green)$ 

In BR oscillation, the color appearance of  $[NiL]^{3+}$  was supposed to be green but experimentally the solution was observed brown. It was because the production of I<sub>2</sub> within oscillatory reactions and was dissolved in oscillating mixture, that is why the color of the solution was observed brown instead of green.

In comparison with the  $Ce^{3+}$  /  $Mn^{2+}$  catalyzed BR oscillator, the oscillation features of the current oscillation (Ni-complex catalyzed BR) were quite different both in duration of oscillation and in number of oscillation cycle [30, 38-40]. For example, the current typical oscillation obtained

through Ni-complex catalyzed BR oscillator has an oscillation duration of 1400 seconds with 41 cycles. However, the reported typical oscillation recorded through  $Mn^{2+}$  catalyzed BR oscillator has a duration of 240 seconds with only 22 oscillation cycles [30].

#### 3.2. Perturbation of BR oscillator

The Figure 2(b) shows the perturbation of active BR profile by adding  $1.30 \times 10^{-5}$  mol/L of morin, resulting in the temporary delay of oscillations. The concentration range of morin was tested from  $2.44 \times 10^{-6}$  to  $1.30 \times 10^{-5}$  mol/L. As experimentally it were noticed that as the concentrations of morin were increased into the system the t<sub>in</sub> was increased and vice versa.

In contrast, perturbation effects on the Ni-complex catalyzed BR oscillator may be reflected in producing inhibition time or without producing inhibition time if other kind of additives were injected into the system. According to our pervious publication, the injecting of ethyl vanillin [41] and the two positional isomers of vanillin (ortho and para) [42] into the active BR could cause the t<sub>in</sub>. However, the addition of 2-hydroxy benzoic acid into the BR oscillator could result in decrease in potential (amplitude), increase in the period of oscillation and a decrease in the number of the oscillation cycle but without producing inhibition time [43].



Figure 1. The oscillation profile for the proposed BR oscillator in the absence and presence of morin perturbation using Pt vs SCE electrodes. a): [Morin] = 0 mol/L; b): [Morin] =  $1.30 \times 10^{-5}$  mol/L; Common condition: [H<sub>2</sub>SO<sub>4</sub>] =  $2.50 \times 10^{-2}$  mol/L; [KIO<sub>3</sub>] =  $2.275 \times 10^{-2}$  mol/L; [[NiL](ClO<sub>4</sub>)<sub>2</sub>] =  $8.65 \times 10^{-4}$  mol/L; [MA] =  $1.25 \times 10^{-1}$  mol/L; [H<sub>2</sub>O<sub>2</sub>] = 1.40 mol/L; t =  $4.50 \times 10^{-5}$  C.

## 3.3. Influences of Experimental variables

BR chemical reaction is highly sensitive. Therefore, in order to select the suitable concentrations of the reagents for the accurate and precision observation on the determination of morin, the influences of variables concentration have been tested by keeping the concentration of one reagent variable while the concentrations of other reagents were kept fixed [29,41]. In Such observation, the concentration of the morin was kept constant ( $5.60 \times 10^{-6}$  mol/L).

The sulfuric acid is the main solvent in the BR system, and its concentration range was tested from  $1.25 \times 10^{-2}$  to  $5.00 \times 10^{-2}$  mol/L. The decrease in the t<sub>in</sub> was recorded with increase in the concentration of sulfuric acid as shown in Figure 2(a). Such phenomenon indicated that the relationship between the t<sub>in</sub> and sulfuric acid has the similar tendency to that in determination of eugenol and ethyl vanillin as reported in the articles [29,41]. For the exact determination of morin, the concentration of  $2.50 \times 10^{-2}$  mol/L of sulfuric acid was selected as optimal because at this concentration the BR-system was quite steady.

The influence of KIO<sub>3</sub> concentration was found similar with that of sulfuric acid. The increased concentration of KIO<sub>3</sub> reduced  $t_{in}$  of the system as indicated in Figure 2(b). This occurrence is closely similar to our pervious reported works [29,41]. The concentration range of KIO<sub>3</sub> was studied from 1.50  $\times 10^{-2}$  to 2.90  $\times 10^{-2}$  mol/L. Thus for working condition 2.20  $\times 10^{-2}$  mol/L KIO<sub>3</sub> was selected as optimum because at this point the system was uniform.

The effect of [NiL](ClO<sub>4</sub>)<sub>2</sub> resembles the influences of sulfuric acid and KIO<sub>3</sub>. The t<sub>in</sub> of the system decreased as the concentration of [NiL](ClO<sub>4</sub>)<sub>2</sub> increased as shown in Figure 2(c). The obtained result is identical as the literatures [29,41]. The variations of catalyst concentration were examined in the range of  $7.40 \times 10^{-4}$  mol/L to  $1.08 \times 10^{-3}$  mol/L, from which  $8.50 \times 10^{-4}$  mol/L [NiL](ClO<sub>4</sub>)<sub>2</sub> was selected as optimal concentration because at this concentration the system is well-behaved.

The disparities of malonic acid concentration were observed quite different as compared with the influences of other reagents. Increasing amount of malonic acid into the system yields in increase  $t_{in}$  as displayed in Figure 2(d). Such spectacle is agreement with one of our publication [21] but quite different from another work [41]. The reported work [41] described different relationship between the  $t_{in}$  and malonic acid concentration while determining ethyl vanillin: the  $t_{in}$  increased first but then decreased with further increasing concentration of malonic acid. The concentration of malonic acid was verified over concentration range of  $5.00 \times 10^{-2}$  to  $2.25 \times 10^{-1}$  mol/L from which  $1.25 \times 10^{-1}$  mol/L MA was nominated as optimal concentration.

A dramatic phenomenon was noticed while analyzing the influences of  $H_2O_2$  concentration. Concentration range of  $H_2O_2$  was studied from 1.25 to 1.6 mol/L. The t<sub>in</sub> was first increased when the concentration of  $H_2O_2$  was increased from 1.25 to 1.4 and then t<sub>in</sub> was decreased with decrease concentration of  $H_2O_2$  from 1.40 to 1.60 mol/L as shown in Figure 2(e). This influence is alike with our recent publication [41] but dissimilar to that in determination of eugenol in our alternate work [21], in which the increase concentration of  $H_2O_2$  led to decrease t<sub>in</sub> of the system. Thus the top middle point was selected for working condition because at this concentration of  $H_2O_2$ , the oscillation was quite normal and suitable.

The temperature has a remarkable influence on the Ni-complex catalyzed BR system. The increases or decreases temperature could easily change the behavior or parameter of oscillations i.e. (inhibition time, amplitude, duration of oscillation etc.). Therefore, the BR system was run at various temperatures (2 to 7  $^{\circ}$ C) and was found the best optimal temperature for working condition is 4.50  $^{\circ}$ C.

Besides the influences of the reagents concentrations and temperature variation, the Nicomplex catalyzed BR system has greatly been affected by the interference of foreign species. The value of interference producing inaccuracy below 5 % in the determination of  $1.00 \times 10^{-5}$  mol/L morin was considered as tolerance range.

Foreign ion and species	Tolerated ratio
Br , I	0.2:1
$Ag^+, Fe^{2+}, Cl^-$	2:1
F	10:1
$H_2PO_4$ , $Co^{2+}$	200:1
Ni <sup>2+</sup> , Li <sup>+</sup>	1000:1
$Na^{+}, K^{+}, Al^{3+}, Zn^{2+}$	2000:1

**Table 1.** Influence of foreign ions and species on the determination of  $5.70 \times 10^{-6}$  mol/L Morin\*

\* Common condition:  $[H_2SO_4] = 2.50 \times 10^{-2} \text{ mol/L}; [KIO_3] = 2.275 \times 10^{-2} \text{ mol/L}; [[NiL](CIO_4)_2] = 8.65 \times 10^{-4} \text{ mol/L}; [MA] = 1.25 \times 10^{-1} \text{ mol/L}; [H_2O_2] = 1.40 \text{ mol/L}; t = 4.5 ^{\circ}C.$ 



Figure 2. Influence of the concentrations of reactants on the inhibition time: (a) H<sub>2</sub>SO<sub>4</sub>; conditions; [KIO<sub>3</sub>] = 2.275 × 10<sup>-2</sup> mol/L; [[NiL](ClO<sub>4</sub>)<sub>2</sub>] = 8.65 × 10<sup>-4</sup> mol/L; [MA] = 1.25 × 10<sup>-1</sup> mol/L; [H<sub>2</sub>O<sub>2</sub>] = 1.40 mol/L; t = 4.50 °C. [Morin] =  $5.70 \times 10^{-6}$  mol/L. (b) KIO<sub>3</sub>; conditions: [H<sub>2</sub>SO<sub>4</sub>] = 2.50 × 10<sup>-2</sup> mol/L; [[NiL](ClO<sub>4</sub>)<sub>2</sub>] = 8.65 × 10<sup>-4</sup> mol/L; [MA] =  $1.25 \times 10^{-1}$  mol/L; [H<sub>2</sub>O<sub>2</sub>] = 1.40 mol/L; t = 4.50 °C. [Morin] =  $5.70 \times 10^{-6}$  mol/L. (c) [NiL](ClO<sub>4</sub>)<sub>2</sub>; conditions: [H<sub>2</sub>SO<sub>4</sub>] = 2.50 × 10<sup>-2</sup> mol/L; [KIO<sub>3</sub>] =  $2.275 \times 10^{-2}$  mol/L; [MA] =  $1.25 \times 10^{-1}$  mol/L; [H<sub>2</sub>O<sub>2</sub>] = 1.40 mol/L; t = 4.50 °C. [Morin] =  $5.70 \times 10^{-6}$  mol/L. (d) H<sub>2</sub>O<sub>2</sub>; conditions: [H<sub>2</sub>SO<sub>4</sub>] =  $2.50 \times 10^{-2}$ mol/L; [KIO<sub>3</sub>] =  $2.275 \times 10^{-2}$  mol/L; [[NiL](ClO<sub>4</sub>)<sub>2</sub>] =  $8.65 \times 10^{-4}$  mol/L; [MA] =  $1.25 \times 10^{-1}$ mol/L; [KIO<sub>3</sub>] =  $2.275 \times 10^{-2}$  mol/L; [[NiL](ClO<sub>4</sub>)<sub>2</sub>] =  $8.65 \times 10^{-4}$  mol/L; [MA] =  $1.25 \times 10^{-1}$ mol/L; [KIO<sub>3</sub>] =  $2.275 \times 10^{-2}$  mol/L; [[NiL](ClO<sub>4</sub>)<sub>2</sub>] =  $8.65 \times 10^{-4}$  mol/L; [MA] =  $1.25 \times 10^{-1}$ mol/L; [KIO<sub>3</sub>] =  $2.275 \times 10^{-2}$  mol/L; [[NiL](ClO<sub>4</sub>)<sub>2</sub>] =  $8.65 \times 10^{-4}$  mol/L; [H<sub>2</sub>O<sub>2</sub>] = 1.40 mol/L; t = 4.50 °C. [Morin] =  $5.70 \times 10^{-6}$  mol/L. (e) MA, conditions: [H<sub>2</sub>SO<sub>4</sub>] =  $2.50 \times 10^{-2}$ mol/L; [KIO<sub>3</sub>] =  $2.275 \times 10^{-2}$  mol/L; [[NiL](ClO<sub>4</sub>)<sub>2</sub>] =  $8.65 \times 10^{-4}$  mol/L; [H<sub>2</sub>O<sub>2</sub>] = 1.40 mol/L; t = 4.50 °C. [Morin] =  $5.70 \times 10^{-6}$  mol/L. (e) MA, conditions: [H<sub>2</sub>SO<sub>4</sub>] =  $2.50 \times 10^{-2}$ mol/L; [KIO<sub>3</sub>] =  $2.275 \times 10^{-2}$  mol/L; [[NiL](ClO<sub>4</sub>)<sub>2</sub>] =  $8.65 \times 10^{-4}$  mol/L; [H<sub>2</sub>O<sub>2</sub>] = 1.40 mol/L; t = 4.50 °C. [Morin] =  $5.70 \times 10^{-6}$  mol/L.

We examined the effect of various species on the system (as indicated in Table 1), we found that only  $\Gamma$  and Br<sup>-</sup> could cause the great effect on the oscillation while other ions like Na<sup>+</sup> did not have any effect on system.

#### 3.4. Determination of Morin



Figure 3. (a). The Linear regression curve between  $t_{in}$  and concentration of Morin in the range of 2.44  $\times 10^{-6}$  to  $1.30 \times 10^{-5}$  mol/L; (b).  $t_{in}$  vs. scheduled time commencing perturbation performance (N: ordinal number of cycle for the oscillations) in the presence of  $5.70 \times 10^{-6}$  mol/L Morin. Common condition: [H<sub>2</sub>SO<sub>4</sub>] =  $2.50 \times 10^{-2}$  mol/L; [KIO<sub>3</sub>] =  $2.275 \times 10^{-2}$  mol/L; [[NiL](ClO<sub>4</sub>)<sub>2</sub>] =  $8.65 \times 10^{-4}$  mol/L; [MA] =  $1.25 \times 10^{-1}$  mol/L; [H<sub>2</sub>O<sub>2</sub>] = 1.40 mol/L; t = 4.50 °C.

Table 2. D	etermination	results	and	recovery	for	Morin*
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Sample	Known concentration / 10 <sup>-5</sup> mol/L	Added concentration/10 <sup>-5</sup> mol/L	Found concentration/10 <sup>-5</sup> mol/L	Recovery %
1	0.87	0.10	0.91	94.00
2	0.94	0.10	0.94	91.00
3	0.10	0.10	1.01	92.00
4	1.06	0.10	1.09	94.20
5	1.13	0.10	1.14	93.00
6	1.19	0.10	1.19	92.00
7	1.25	0.10	1.23	96.10
8	1.31	0.10	1.33	95.20

\* **Common condition:**  $[H_2SO_4] = 2.50 \times 10^{-2} \text{ mol/L}; [KIO_3] = 2.275 \times 10^{-2} \text{ mol/L}; [[NiL](ClO_4)_2] = 8.65 \times 10^{-4} \text{ mol/L}; [MA] = 1.25 \times 10^{-1} \text{ mol/L}; [H_2O_2] = 1.40 \text{ mol/L}; t = 4.5 ^{O}C.$ 

Under the optimal conditions, the perturbation experiments were formed by putting different concentrations of morin at the bottom of the  $4^{th}$  cycle and a series of  $t_{in}$  values were recorded. The  $t_{in}$  was found directly related on the concentrations of morin. As the concentration of morin increased the

 $t_{in}$  of the system increased. Thus, a linear curve was obtained in a concentration ranges  $2.44 \times 10^{-6}$  to  $1.30 \times 10^{-5}$  mol/L of morin vs.  $t_{in}$  with correlation coefficient of 0.98 as shown in the Figure 3(a). Following are the equation through which the calibration data was achieved.

 $t_{in} = -154.84 + 5.85E7*[Morin]; r = 0.98, n = 13$ 

The calculated RSD value is 2.56% which was achieved by the 5 measurement of  $1.30 \times 10^{-5}$  mol/L of morin and the LOD is  $1.20 \times 10^{-6}$  mol/L. Such precision is quite acceptable.

The same amount (35ul) of the same concentration  $(6.50 \times 10^{-6} \text{ mol/L})$  was used to perturb the active BR at a different cycle ranging from 2 to 10. The quite different variations in the t<sub>in</sub> were noticed which has the evidence that the t<sub>in</sub> is not only depended on the concentration of the reagents but also depended on the scheduled time commencing perturbation performance, counting from on setting of the oscillation (N: ordinal number of cycle for the oscillations). Thus, a linear curve between t<sub>in</sub> and N was obtained in N range from 2 to 10 with correlation coefficient of 0.99 as shown in the Figure 3(b).

The recovery experiments were performed in order to prove the accuracy of our proposed method. In the recovery experiments, the known amount of the morin were added into the standard solution and the same procedure was applied as shown in the Table 2. The percentage recovery obtained from our proposed method (lies in range between 91.00 to 96.10 %) is compared with the obtained percentage recovery of other reported instrumental techniques like voltammetry, HPLC, spectrofluorometric (as shown in Table 3) and assume that our proposed method is quite suitable and acceptable for practical analysis.

Techniques	Percentage recovery (%)	Relative	Standard	Deviation
		(RSD) %		
BR oscillator (this work)	91-96	2.56		
Sensitive Voltammetry [44]	97-100	3.9		
HPLC-DVD-UV [45]	98-100	3.16		
Spectrofluorometric [46]	97.4-100.5	1.4		

 Table 3. Comparison of morin determination by BR oscillator with some other instrumental techniques.

#### 3.5. Mechanism

In order to check the reactivity of morin with reagents, cyclic voltammetry (CV) experiments were carried out into the following solutions in the presence and absence of morin;

1).H<sub>2</sub>SO<sub>4</sub> + KIO<sub>3</sub>, 2) H<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>O<sub>2</sub>, 3) H<sub>2</sub>SO<sub>4</sub> + M.A, 4) H<sub>2</sub>SO<sub>4</sub> + [NiL](CLO<sub>4</sub>)<sub>2</sub>

From the results of cyclic voltammogram indicated that, only a redox reaction exist between morin and  $KIO_3$  as shown in the Figure 4 while the other reagents didn't shows reaction with morin. Here we didn't consider the direct reaction of  $KIO_3$  with morin because the morin were added in the lower amount compared with  $KIO_3$ . If we assume the direct reaction of morin with  $KIO_3$  there will be no  $t_{in}$  noticed. So it is our conclusion that morin reacted with intermediate species (HOO') that was produced during the oscillatory reaction. The involvement of the HOO' radical regarding  $t_{in}$  was noticed for the first time by Franz [47], who put the hydroperoxyl radical (HOO<sup>•</sup>) scavenger named superoxide dismutase pellet (SOD) into the BR system and he claimed that the HOO<sup>•</sup> was responsible for  $t_{in}$ . Later a lot of work were published by Cervellati et al [31,36,48] regarding the inhibitory effect caused by HOO<sup>•</sup>. Beside this, many authors (including our group) reported the similar evidence that the HOO<sup>•</sup> radical is responsible for  $t_{in}$  [30, 49-56]. In this paper we have the same claim that morin reacted with HOO<sup>•</sup> radical (as mention below in reaction (13) and (14)) and the system get inhibited ( $t_{in}$ ).

On the basis of FCA mechanism [31,57], the perturbation effect caused by morin on Nicatalyzed BR is suitable to explain. Furrow et al, put forward the FCA mechanism from the union combination of two quantitative NF [58] and DE [59] Models. Based on the NF [58] and the FCA model [31, 57], we put a tentative mechanism which consists of below 12 oscillatory reactions;

$HOI + I^- + H^+ \leftrightarrow I_2 + H_2O$	(1)
$\mathrm{HIO}_2 + \mathrm{I}^- + \mathrm{H}^+ \! \rightarrow \! 2\mathrm{HOI}$	(2)
$IO_3^- + I^- + 2H^+ \leftrightarrow HIO_2 + HOI$	(3)
$2\text{HIO}_2 \rightarrow \text{IO}_3^- + \text{HOI} + \text{H}^+$	(4)
$IO_3^- + HIO_2 + H^+ \leftrightarrow 2IO_2^{\bullet} + H_2O$	(5)
$2\text{HOO}^{\bullet} \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	(6)
$HOI + H_2O_2 \rightarrow I^- + O_2 + H^+ + H_2O$	(7)
$IO_2^{\bullet} + [NiL]^{2+} + H^+ \leftrightarrow [NiL]^{3+} + HIO_2$	(8)
$\mathrm{H_2O_2} + \mathrm{[NiL]}^{3+} \rightarrow \mathrm{[NiL]}^{2+} + \mathrm{HOO}^{\bullet} + \mathrm{H}^+$	(9)
$\mathrm{HOO}^{\bullet} + \mathrm{IO_3}^{-} + \mathrm{H}^+ \longrightarrow \mathrm{O_2} + \mathrm{H_2O} + \mathrm{IO_2} \bullet$	(10)
$MA \leftrightarrow MA(enol)$	(11)
$I_2 + MA(enol) \rightarrow MAI(IMAI) + I^- + H^+$	(12)

In Reaction (13) morin reacted with HOO' radical forming their respective radicals and in reaction (14) the self-reaction of morin radicals forms products. Reaction (13) and (14) should be included to FCA mechanism [60].



The perturbation of morin (reaction 13) disturbed mostly the reaction (10), because in both reactions (10) and (13), HOO<sup>•</sup> radical was consumed.



Figure 4. Cyclic Voltammogram of the reaction between morin and iodate at different concentrations of morin,  $[KIO_3] = 2.275 \times 10^{-2} \text{ M}$ , Common condition;  $[H_2SO_4] = 2.50 \times 10^{-2} \text{ M}$ . Scan rate = 100 mV / s.

Since the inhibitory effect was noticed, we consider that reaction (13) become dominated in consumption of HOO' and thus caused the deficiency of  $IO_2^{-1}$  radicals via reaction (10). The lower amount of  $IO_2^{-1}$  led to disturbed the oxidation of  $[NiL]^{2+}$  into  $[NiL]^{3+}$  in reaction (8) result in low production of  $[NiL]^{3+}$ . The reduced amount of  $[NiL]^{3+}$  has greatly affect the reduction of  $[NiL]^{3+}$  into  $[NiL]^{2+}$  via reaction (9). Thus, the oscillation was temporary stopped until the concentration of morin was consumed via reaction (13), than reactions (8), (9), and (10) become predominate again and oscillation regain.

## **4. CONCLUSION**

The assessable method for the determination of morin was proven for the first time by using Ni-complex catalyzed BR oscillator. The addition of morin cause the inhibitory effect on the Ni-complex catalyzed system and such  $t_{in}$  was directly proportional to the concentration of morin. Concentration ranging from  $2.44 \times 10^{-6}$  to  $1.30 \times 10^{-5}$  mol L<sup>-1</sup> of morin has been tested over BR system and the different data in the  $t_{in}$  were obtained through which a linear regression curve was achieved with correlation coefficient of 0.98. Redox reaction between morin and potassium iodate was confirmed through CV experiments, but the explanation that morin reacts with intermediate species (HOO') sounds reasonable. On the basis of FCA mechanism, the perturbation effect caused by morin was deliberated.

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## References

- 1. T. M. Hermans, P.S. Stewart, and B.A. Grzybowski, J. Phys. Chem. Lett., 6 (2015) 760-766.
- 2. E. N. Harvay, A History of Luminescence from the Earliest Times until 1900 (Am. Philos. Soc. Philadelphia, 1957).
- 3. R. J. Field, and F. W. Schneider, J. Chem. Educ., 66 (1989) 195-204.
- 4. A. T. Fechner, and Schweigg Jahrbuch d. Chemie und Physik, Halle H, 53 (1828) 61-76.
- 5. D. Alba, S. Di Lorenzo, and C. Lucarini, J. Appl. Electrochem., 28 (1998) 711-716.
- 6. F. Crisan, and E. Sallo, J. Serb. Chem. Soc., 73 (2008) 221-226.
- 7. S. Lin, J. Keizer, P. A. Rock, and H. Stenschke, Natl. Acad. Sci., 71 (1974) 4477-4481.
- 8. W. C. Bray, and H. A. Liebhafsky, J. Am. Chem. Soc., 53 (1931) 38-44.
- 9. W. C. Bray, J. Am. Chem. Soc., 43 (1921) 1262-1267.
- 10. A. M. Zhabotinsky, and A. B. Rovinsky, J. stat. Phys., 48 (1987) 959-975.
- 11. S. Scott, New Sci., 1693 (1989) 53-59.
- 12. I. Lamprecht, and B. Schaarschmidt, Thermochim. Acta, 112 (1987) 95-100.
- 13. W. Uddin, G. Hu, X. Sun, H. Chang, Y. Wang, and L. Hu, Arabian Journal of Chemistry, (2017), doi: 10.1016/j.arabjc.2017.09.010.
- 14. T. S. Briggs, and W. C. Rauscher, J. Chem. Educ., 50 (1973) 496-496.
- 15. K. R. Kim, D. J. Lee, and K. J. Shin, J. Chem. Phys., 117 (2002) 2710-2717.
- 16. Z. Noszticzius, and J. Bodiss, J. Am. Soc., 101 (1979) 3177-3182.
- 17. M. C. Guedes, and R. B. Faria, J. Phys. Chem., 102 (1998) 1973-1975.
- 18. K. Kurin, Csorgei, A. M. Zhabotinsky, M. Orban, and I. R. Epstein, *J. Phys, Chem.*, 100 (1996) 5393-5397.
- 19. R. J. Field, E. Koros, and R. M. Noyes, J. Am. Chem. Soc., 94 (1972) 8649-8653.
- K. B. Yatsimirskii, L. P. Tikhonova, and L. N. Zakrevskaya, React. Kinet. Catal. Lett., 21 (1982) 381-386.
- 21. L. Hu, G. Hu, and H. H. Xu, J. Anal. Chem., 61 (2006) 1021-1025.
- 22. G. Hu, P. Chen, W. Wang, L. Hu. J. Song, and L. Qiu, *Electrochim. Acta*, 52 (2007) 7996-8002.
- 23. G. Hu, Z. D. Zhang, L. Hu, and J. M Song, Transition Met. Chem., 30 (2005) 856-860.
- 24. G. Hu, and L. Hu, React. Kinet. Catal. Lette., 88 (2006) 349-355.
- 25. G. Hu, and Z. Zhang, Chem. Lett., 35 (2006) 1154-1155.
- 26. P. Chen, G. Hu, W. Wang, J. Song, L. Qiu, H. Wang, L. Chen, J. Zhang, and L. Hu, *J. Appl. Electrochem.*, 38 (2008) 1779–1783.
- 27. L. Chen, G. Hu, J. Zhang, and L. Hu, Medeleev Commun., 19 (2009) 224-226.
- 28. G. Hu, L. Chen, J. Zhang, P. Chen, W. Wang, J. Song, L. Qiu, L. Song, and L. Hu, *Cent. Eur. J. Chem.*, 7 (2009) 291–297.
- 29. G. Hu, Q. Zheng, Y. Hu, X. Shen, and J. Song., Electrochimica. Acta, 136 (2014) 33-40.
- 30. R. Cervellati, K. Honer, S. D. Furrow, and F. Mazzanti, Helv. Chim. Acta, 85 (2000) 2523-2537.
- 31. R. Cervellati, N. Crespi-Perellino, and S. D. Furrow, Helv. Chim. Acta, 83 (2000) 3179-3190.
- 32. S. D. Furrow, K. Honer, and R. F. Cerellati, Helv. Chim. Acta, 87 (2004) 735-739.
- 33. J. G. Kljusuric, S. Djakovic, I. Kruhak, K. K. Ganic, D. Komes, and Z. Kurtanjek, *Acta Aliment. Hung* 34 (2005) 483-490.
- 34. N. F. Curtis, J. Chem. Soc. Dalton Trans., 13 (1972) 1357-1361.
- 35. N. F. Curtis, and R. W. Hay, Chem. Commun. London, 0 (1966) 524-525.

- 36. R. Cervellati, and S. D. Furrow, Russ. J. Chem. A, 87 (2013) 2121-2126.
- 37. G. Hu, L. Zhu, M. M. Guo, and H. Liu, Asian Journal of Chemistry, 22 (2010) 6393-6396.
- 38. S. D. Furrow, R. Cervellati, and E. Greco, Z. Naturforsh, B, 67 (2012) 89-97.
- 39. J. Gao, Y. Lin, J. Ren, X. Zhang, M. Li, and W. Wang, J. Serb. Chem. Soc., 77 (2012) 95-104.
- 40. M. Milos, and D. Makota, Food Chemistry, 113 (2012) 296-299.
- 41. W. Uddin, G. Hu, L. Hu, X. Shen, Z. Fang, Y. Zhang, and J. Song, *Int. J. Electrochem. Sci.*, 12 (2017) 178-191.
- 42. W. Uddin, G. Hu, L. Hu, Y. Hu, Z. Fang, S. Ullah, X. Sun, X. Shen, and J. Song, *Int. J. Electrochem. Sci.*, 12 (2017) 4193-4203.
- 43. W. Uddin, G. Hu, L. Hu, Y. Hu, Z. Fang, R. Ullah, X. Sun, Y. Zhang, and J. Song, *Journal of Electroanalytical Chemistry*, 803 (2017) 135-140.
- 44. P. Xiao, Q. Zhou, F. Xiao, F. Zhao, and B. Zeng, Int. J. Electrochem. Sci., 1 (2006) 228-237.
- 45. A. Zhang, L. Wan, C. Wu, Y. Fang, G. Han, H. Li, Z. Zhang, and H. Wang, *Molecules*, 18 (2013) 14241-14257.
- 46. L. Pavan, D. Dikanovic, P. Durdevic, M. J. Stankov, D. Malesev, and A. Ciric, *Acta Chim, Slov.*, 56 (2009) 967- 972.
- 47. D. A. Franz, J. Chem. Educ., 68 (1991) 57-57.
- 48. R. Cervellati, K. Honer, S. D. Furrow, C. Neddens, and S. Costa, *Helv. Chim. Acta*, 84 (2001) 3533–3547.
- 49. R. Cervellati, E. Greco, and S. D. Furrow, J. Phys. Chem. A, 114 (2010) 12888-12892.
- 50. E. Szabo, and P. Sevcik, J. Phys. Chem. A, 113 (2009) 3127-3132.
- 51. R. Cervellati, C. Renzulli, M. C. Guerra, and E. Speroni, *J. Agric. Food Chem.*, 50 (2002) 7504-7509.
- 52. T. Cecchi, P. Passamonti, and P. Cecchi, Food Anal. Methods, 3 (2010) 1-6.
- 53. N. Muntean, G. Szabo, M. Wittmann, T. Lawson, J. Fulop, Z. Noszticzius, and L. Onel, J. Phys. Chem. A, 113 (2009) 9102–9108.
- 54. T. Lawson, J. Fulop, M. Wittmann, Z. Noszticzius, N. Muntean, and G. Szabo, *J. Phys. Chem. A*, 113 (2009) 14095–14098.
- 55. M. Li, G. Hu, and Y. Chen, Food Chemistry, 197 (2016) 987–991.
- 56. J. Hu, G. Hu, J. Song, Z. Fang, X. Shen, and L. Hu, J. Chin. Chem. Soc., 63 (2016) 572-579.
- 57. R. Cervellati, K. Höner, S. D. Furrow, F. Mazzanti, and S. Costa, *Helv. Chim. Acta*, 87 (2004) 133-155.
- 58. R. M. Noyes, and S. D. Furrow, J. Am. Chem. Soc., 104 (1982) 45-48.
- 59. P. D. Kepper, and I. R. Epstein, J. Am. Chem. Soc., 104 (1982) 49-53.
- 60. S. Fujisawa, T. Atsumi, Y. Kadoma, and H. Sakagami, Toxicology, 177 (2002) 39-54.

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