

Determination of catechol based on an oscillating chemical reaction involving a macrocyclic complex as catalyst

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Abstract A novel methodological approach for the determination of catechol based on a Belousov-Zhabotinskii type oscillating system is presented. Such an oscillating reaction involves the oxidation of malic acid in an acidic bromate medium in the presence of a catalyst—macrocyclic complex $[\text{CuL}](\text{ClO}_4)_2$. The unsaturated ligand L in the complex $[\text{CuL}](\text{ClO}_4)_2$ is 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene. By perturbation of catechol on the oscillating chemical reaction, the increase in the oscillation amplitude is linearly proportional to the logarithm of the concentration of catechol in the range 2.1×10^{-6} – 2.1×10^{-4} M, with a correlation coefficient of 0.9976. The R.S.D obtained for 7.88×10^{-5} M catechol is 3.8% ($n = 5$). Cyclic voltammetry was applied to explore the mechanism of catechol perturbation on the oscillating chemical reaction.

Keywords Catechol · Belousov-Zhabotinskii reaction · Oscillating chemical system · Macrocyclic complex · Catalyst

1 Introduction

An oscillating chemical system is a mixture of several reactants that exhibits periodic changes in concentration of

some species (usually a reaction intermediate) [1]. Many oscillating chemical systems have been reported, among which the Belousov-Zhabotinskii (B-Z) system [2] is one of the most famous examples that exhibits most features of chemical oscillations [3, 4]. The driving force of this reaction is the oxidation of malonic acid by bromate ions in acid solution [5]. The oxidation is usually catalyzed by metal ions or complexes that can exist in two oxidation states ($\text{Ce}^{3+}/\text{Ce}^{4+}$, $\text{Mn}^{2+}/\text{Mn}^{3+}$, $\text{Fe}(\text{phen})_3^{2+}/\text{Fe}(\text{phen})_3^{3+}$) [6, 7].

Early researchers have so far been focused on physico-chemical terms with a view to elucidating the complicated mechanisms of these systems [8–10]. The famous FKN (Field–Körös–Noyes) mechanism [11] is one of the examples. Recently, some analysts have applied their discoveries on oscillation systems to analytical process. The pioneer work for kinetic determination based on the B-Z system was attributed to Tichonova et al. who first conducted their experiments in 1978 [12]. In addition, the emergence of the analyte pulse perturbation (APP) technique has opened a new outlook in analytical determinations [13]. However, the catalysts used in those B-Z systems are limited to the above mentioned metal ions. Recently, catalysts containing macrocyclic compounds, which include N_4 chelates as well as metal-chalcogenide, have aroused increasing attention. Oscillating reactions catalyzed by macrocyclic complex of Cu (II) or Ni (II) have been surveyed for their unique kinetic features [14]. An example of a macrocyclic complex-catalyzed oscillating reaction [15] is the system of NaBrO_3 – H_2SO_4 –Malic acid– $[\text{CuL}](\text{ClO}_4)_2$, where the ligand L in the complex $[\text{CuL}](\text{ClO}_4)_2$ is 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene. As the $[\text{CuL}](\text{ClO}_4)_2$ —catalyzed oscillating system has been used for kinetic determination of Ag^+ [16] and pyrogallol [17], we have surveyed the effect of catechol perturbation.

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Catechol, a biologically important phenol, exists naturally in many fruits and teas. It was widely used as an astringent, an antiseptic and a photographic developer. A number of conventional analytical methods [18–20], such as gas and liquid chromatography, have been reported for the determination of this compound. Although these methods are considered to be sensitive and practicable, high cost and complex procedures (time consuming) have limited their application.

As part of systematic studies of the analytical applications on oscillating chemical reactions, this paper aims to broaden the application of the novel oscillation system on analytical determination. Catechol, a strong reducing agent, is oxidized in the $[\text{CuL}]^{2+}$ catalyzed oscillation system, and in turn, elicits a quantitative response to the oscillating reaction. This kinetic method for determination of catechol provides a promising alternative to the classical methods due to its low cost of operation, relatively higher sensitivity and rapid detection procedures.

2 Experimental

2.1 Reagents and apparatus

The catalyst $[\text{CuL}](\text{ClO}_4)_2$ was prepared according to a literature method [21] and was identified by IR spectra and elemental analysis. All chemicals used were of analytical reagent grade. Solutions of 0.5 M NaBrO_3 , 2 M malic acid, 0.0184 M $[\text{CuL}](\text{ClO}_4)_2$ were prepared in 1 M sulfuric acid. Solutions of 0.01 M catechol were made immediately before the experiment. Solutions with lower concentrations were prepared prior to use. Double distilled water was used in all cases.

Oscillating experiments were performed in a glass container with a Model 79-3 magnetic stirrer (Jiangsu, China) regulated by a thermostat at 20.0 ± 0.5 °C. Changes in potential were followed by a Type 213 platinum electrode (Shanghai, China), a Model 217 saturated calomel electrode (Shanghai, China) connected via a salt bridge containing 1 M Na_2SO_4 as reference electrode. Potentials of the electrode as a function of time were recorded with a PHS-25B digital voltmeter (Shanghai, China) connected with a Model XWTD-204 Y-t recorder (Shanghai, China) to record kinetic curves of the reaction. For the measurement of cyclic voltammetry: a Type 213 platinum electrode as the working electrode, a saturated calomel electrode (SCE) as reference, and a platinum wire as counter electrode were used.

2.2 Procedure

To a 50 mL glass thermostated at 20.0 ± 0.5 °C reactants were added in the following sequence: sodium bromate

solution, sulfuric acid solution, malic acid solution, and $[\text{CuL}](\text{ClO}_4)_2$ solution at intervals of 1 min. The volume of the reaction was 40 mL. The mixture was homogenized by continuous magnetic stirring. Then the platinum electrode and reference electrode were immersed in the reaction mixture and a Y-t recorder recorded the oscillating curve. When the oscillating system attaining steady state, 0.3 mL of sample containing variable amounts of catechol were injected to the reaction which cause the amplitude to increase sharply. Thus, changes of oscillating amplitude $\Delta A = A - A_0$ (A_0 and A are the oscillation amplitude before and after the injection, respectively) were used as parameter to determine catechol.

In order to obtain more information about the mechanism of the interaction of catechol on the macrocyclic complex of Cu (II)-catalyzed B-Z type oscillation, cyclic voltammetry was performed to monitor the species, which reacted with catechol.

3 Results and discussion

3.1 $[\text{CuL}](\text{ClO}_4)_2$ -catalyzed oscillating reaction

The NaBrO_3 - H_2SO_4 -Malic acid- $[\text{CuL}](\text{ClO}_4)_2$ system exhibits periodic changes of solution color (red–orange–red) during the oscillation [15]. The color changes are attributable to the concentration changes of the oxidized and reduced forms of $[\text{CuL}]^{3+}$ and $[\text{CuL}]^{2+}$, which demonstrate the color of orange and red, respectively.

Figure 1 shows typical oscillation profiles obtained in the presence of catechol perturbations under the selected experimental conditions. In order to ensure accurate and reproducible results, several injection points were tested, from the results of which we found that the analyte should be injected at the minimum of a cycle, for this is the optimal injecting point where the system will respond maximally to the perturbation. Perturbing the oscillating system by injecting 0.3 mL of sample containing a given amount of catechol caused a change in the oscillation amplitude and oscillation period. Because the changes of oscillation amplitude are proportional to the logarithm of catechol concentration and the system recovers from the perturbation quite rapidly, we are expecting to exploit this behavior of catechol perturbation.

3.2 Influence of experimental variables

The behavior of an oscillating chemical reaction is easily influenced by the variables of reactants in the system [22]. To obtain a steady oscillating profile and a maximum change in amplitude in the determination of catechol, the effect of the concentrations of sulfuric acid, $[\text{CuL}](\text{ClO}_4)_2$,

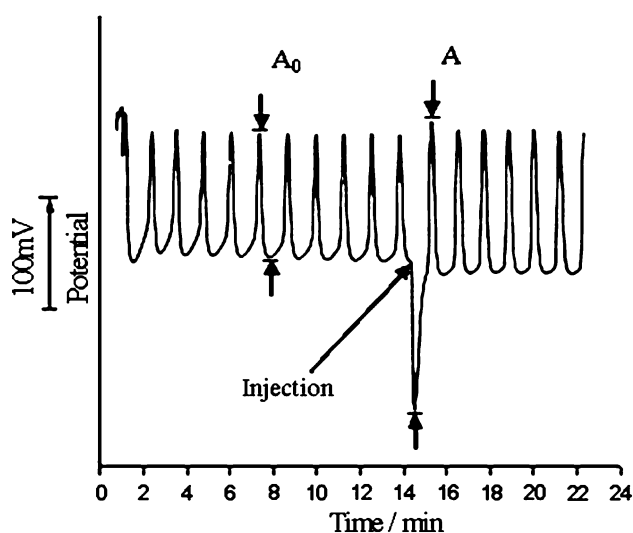


Fig. 1 Typical oscillation profiles for the proposed oscillation system in the presence of variable amounts of catechol perturbation using platinum electrode: $[\text{NaBrO}_3] = 1.25 \times 10^{-2} \text{ M}$; $[\text{malic acid}] = 0.2 \text{ M}$; $[\text{H}_2\text{SO}_4] = 1 \text{ M}$; $[[\text{CuL}](\text{ClO}_4)_2] = 3.68 \times 10^{-3} \text{ M}$; $[\text{catechol}] = 1.05 \times 10^{-5} \text{ M}$

sodium bromate and malic acid were examined. The optimum working conditions were established with three criteria in mind: (a) the oscillating system should oscillate

steadily; (b) oscillation amplitude (A) due to catechol perturbation should be accurately determined and (c) a maximum change of oscillation amplitude (ΔA) for a higher sensitivity of catechol determination should be obtained. The three aspects should be compromised when possible. An aqueous solution of catechol ($1.05 \times 10^{-5} \text{ M}$) was used for perturbation in all cases when surveying the effects of reactants.

The effect of H_2SO_4 concentration was studied over the range 0.78–1.22 M. From the experimental results, oscillation amplitude (A) increased dramatically as H_2SO_4 concentration increased. However, when the H_2SO_4 concentration fell below 0.93 M and above 1 M, ΔA decreased sharply (Fig. 2a), and the oscillation curves did not oscillate steadily. A 1 M sulfuric acid concentration was selected as optimal since it caused the system to oscillate highly uniformly prior to the perturbation and responded quite sharply in the presence of catechol. Similar results were obtained when surveying the effect of NaBrO_3 concentration (Fig. 2b).

The influence of malic acid concentration was investigated over the range 0.15–0.25 M. When the concentration of malic acid was 0.2 M (Fig. 2c), it resulted in a maximum response (ΔA) of catechol perturbation with a steady oscillation curve. High concentration of malic acid caused

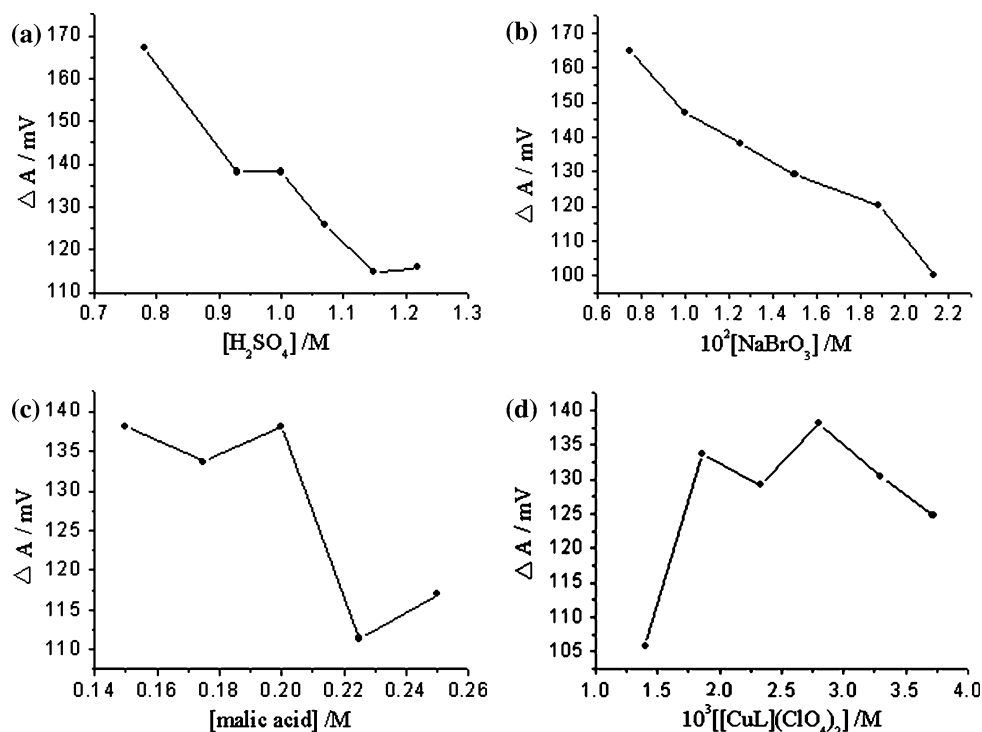


Fig. 2 Influence of the concentration (a) Sulfuric acid, (b) Sodium bromate, (c) Malic acid and (d) $[\text{CuL}](\text{ClO}_4)_2$, on the oscillation system in the presence of $1.05 \times 10^{-5} \text{ M}$ catechol (● refers to ΔA) (a) $[\text{malic acid}] = 0.2 \text{ M}$, $[[\text{CuL}](\text{ClO}_4)_2] = 3.68 \times 10^{-3} \text{ M}$, $[\text{Sodium bromate}] = 1.25 \times 10^{-2} \text{ M}$. (b) $[\text{malic acid}] = 0.2 \text{ M}$,

$[[\text{CuL}](\text{ClO}_4)_2] = 3.68 \times 10^{-3} \text{ M}$, $[\text{Sulfuric acid}] = 1 \text{ M}$. (c) $[[\text{CuL}](\text{ClO}_4)_2] = 3.68 \times 10^{-3} \text{ M}$, $[\text{Sodium bromate}] = 1.25 \times 10^{-2} \text{ M}$, $[\text{Sulfuric acid}] = 1 \text{ M}$. (d) $[\text{malic acid}] = 0.2 \text{ M}$, $[\text{Sodium bromate}] = 1.25 \times 10^{-2} \text{ M}$, $[\text{Sulfuric acid}] = 1 \text{ M}$

oscillation curves to drift, which seriously affected the determination of catechol. As a result, 0.2 M malic acid concentration was chosen. The effect of [CuL] (ClO_4)₂ concentration to catechol perturbation was similar to that of malic acid (Fig. 2d). In conclusion, 3.68×10^{-3} M [CuL] (ClO_4)₂, 1 M sulfuric acid, 0.2 M malic acid, and 1.25×10^{-2} M sodium bromate were chosen as optimal.

The effect of temperature on oscillation systems in some autocatalytic procedures has been reported by Körös et al. [23]. Thus, this system was investigated over a temperature range of 15.0–25.0 °C. The oscillation period decreased gradually as temperature increased, whereas oscillation amplitude (A) and change of oscillation amplitude (ΔA) were almost unchanged. A temperature of 20.0 °C was chosen as optimal as it ensured good, reproducible oscillations.

3.3 Determination of catechol

We performed perturbation experiments under the optimal experimental conditions described above. The response to the catechol perturbation was tested by employing changes in oscillation amplitude (ΔA) for the cycle following the sample injection as the measured parameter. The change in oscillation amplitude (ΔA) obtained is linearly proportional to the logarithm of the catechol concentration over the range 2.1×10^{-6} to 2.1×10^{-4} M (Fig. 3). The calibration data obtained obey the following linear regression equation:

$$\Delta A = (873.91 \pm 17.20) + (148.54 \pm 3.64) \log [\text{catechol}/\text{M}]$$

$$(r = 0.9976, n = 10)$$

The precision (R.S.D), calculated from five perturbations of 7.88×10^{-5} M catechol, was 3.8%. The detection

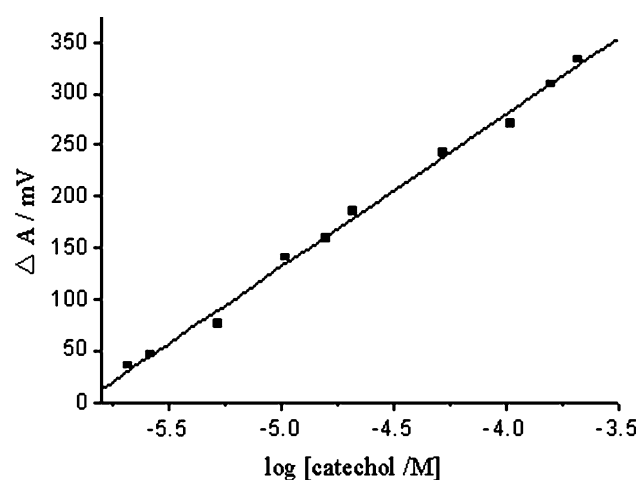


Fig. 3 Calibration curve of the increase in amplitude versus the logarithm of [catechol/M] in the range 2.1×10^{-6} – 2.1×10^{-4} M. Conditions: $[\text{NaBrO}_3] = 1.25 \times 10^{-2}$ M; [malic acid] = 0.2 M; $[\text{H}_2\text{SO}_4] = 1$ M; $[\text{CuL} (\text{ClO}_4)_2] = 3.68 \times 10^{-3}$ M

Table 1 Influence of foreign ions and species on the determination of 1×10^{-5} M catechol

Foreign ions and species	Tolerated ratio
Mg^{2+} , Al^{3+} , Cu^{2+} , Zn^{2+} , Co^{2+} , AcO^-	1,000
Ni^{2+}	500
Glucose	25
Fe^{2+} , Fe^{3+}	10
F^- , Cl^-	2
Vc, I^-	0.2
Resorcinol, pyrogallol	0.02

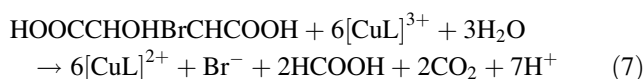
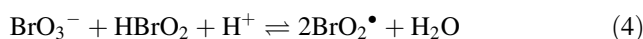
limit obtained is 1.37×10^{-6} M. Such a precision is quite acceptable.

3.4 Effects of some foreign species

The behavior of the oscillating systems is very easily altered in the presence of foreign species in the reaction medium. The effects of some common ions and strong reductive species, such as resorcinol and pyrogallol, on catechol determination were studied. The amount of interference causing an error of less than 5% in the determination of 1×10^{-5} M catechol was taken as the tolerance limit. The results obtained are shown in Table 1. It can be concluded that the reducing character of some species has a strong effect on the determination of analyte, the more reductive, the more interfering.

3.5 Mechanism of action of catechol on the oscillating system

Based on the well known FKN mechanism, the $[\text{CuL}]^{2+}$ -catalyzed oscillating system was proposed in reactions (1)–(7) [15, 17]:



Reactions (1)–(7) are explained in our previous papers [15, 17]. To clarify the perturbation effect of catechol on the oscillating system, cyclic voltammetry was applied in the absence and presence of catechol to the acidic solutions of

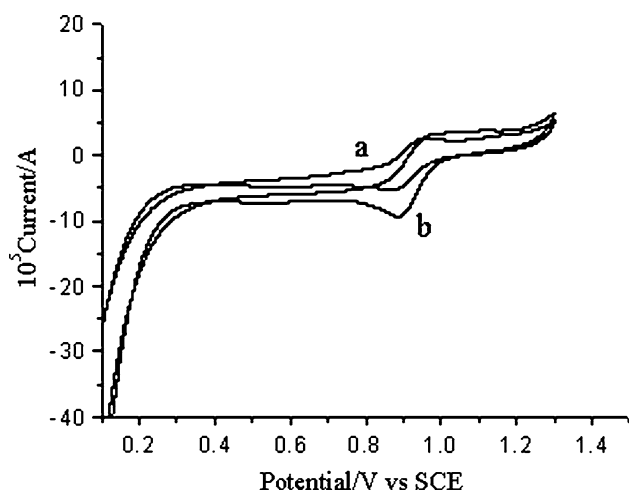


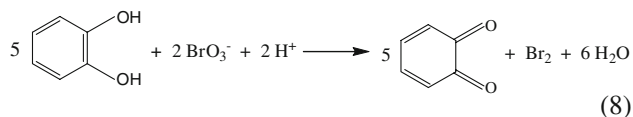
Fig. 4 Cyclic voltammograms of the reactions between catechol and BrO_3^- obtained in the absence and in the presence of catechol: (a) [catechol] = 0; (b) [catechol] = 4×10^{-5} M; Common conditions: [Sodium bromate] = 1.25×10^{-2} M, [Sulfuric acid] = 1 M. Scan rate = 100 mV/s

NaBrO_3 , $[\text{CuL}]^{2+}$ and malic acid, respectively. From the cyclic voltammetry it may be concluded that only BrO_3^- can react with catechol.

Cyclic voltammetric curves a and b in Fig. 4 show the cyclic voltammograms of the acidic NaBrO_3 solution in the absence of catechol and in the presence of 4×10^{-5} M catechol, respectively. The reduction current of acidic NaBrO_3 solution in 0.9 V increases after catechol is introduced. Since catechol is a strong anti-oxidant, such an increase in the reduction current is due to the reduction of BrO_3^- by catechol.

We may understand the reduction product of BrO_3^- in view of the standard redox potentials of $\text{BrO}_3^-/\text{Br}_2$ (1.51 V), $\text{BrO}_3^-/\text{HOBr}$ (1.49 V) and $\text{BrO}_3^-/\text{Br}^-$ (1.44 V), respectively [11]. As the potential of $\text{BrO}_3^-/\text{Br}_2$ (1.51 V) is the highest among the above three potentials, we draw the conclusion that Br_2 is the reduction product of BrO_3^- .

Catechol possesses an aromatic ring bearing two hydroxyl substitutes and it can be easily oxidized to quinone. The process of catechol oxidation by BrO_3^- can be expressed as follows:



BrO_3^- , which is the reactant of reactions (1) and (4), is consumed in this reaction, so reactions (1) to (4) are inhibited to some extent. The decrease in free radical (BrO_2^\bullet) concentration in reaction (4) causes the $[\text{CuL}]^{3+}$ concentration to decrease (BrO_2^\bullet is responsible for the generation of $[\text{CuL}]^{3+}$ in reaction (6)). Therefore the value

of $\ln [\text{CuL}]^{3+}/[\text{CuL}]^{2+}$ decreases suddenly, the result of which is reflected in the decrease in the potentiometric oscillation curves (Fig. 1).

Reactions (1)–(4) are reversible. The accumulation of Br_2 in reaction (8) causes reaction (3) to occur in the reverse direction causing the generation of HOBr and Br^- . Then reaction (2) takes place in the negative direction giving an increase in HBrO_2 concentration. When the HBrO_2 concentration reaches a sufficient amount, reaction (1) occurs in the reverse direction producing BrO_3^- . Reaction (4) occurs in succession as the concentration of BrO_3^- and HBrO_2 increase. As it turns out, reactions (1)–(4) proceed according to the original rate. Then, the accumulation of Br_2 and BrO_2^\bullet induce reactions (5)–(7) to take place at their original rates. Therefore, the system adopts its initial oscillating state.

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