Kinetic determination of tannic acid using a Belousov-Zhabotinskii oscillating system catalyzed by a macrocyclic complex

Tingting Liu, Yangyang Chen, Gang Hu*, Xiaofeng Shen, Jimei Song, Lin Hu

Abstract: An analytical method for the determination of tannic acid is proposed by the sequential perturbation caused by different amounts of tannic acid on the Belousov-Zhabotinskii oscillating system. The oscillating system is catalyzed by tetraazamacrocyclic complex $[\text{CuL}](\text{ClO}_4)_2$, where L is 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene. The method relies on the linear relationship between the changes in the inhibition time and the logarithm of the concentration of tannic acid. The calibration curve obeys a linear equation very well when the concentration of tannic acid is over the range of $6.25 \times 10^{-7}$ to $1.56 \times 10^{-5}$ M ($n = 16$, $R = 0.9984$). This analytical method, equipped with a simple instrument, provides a new way to accurate determination of tannic acid.

Keywords: Belousov–Zhabotinskii oscillating system, tannic acid, determination

1 Introduction

Governed by complex nonlinear mechanism, a chemical oscillating reaction shows periodic changes in concentrations with some intermediates when system is far from equilibrium [1]. This type of system has attracted the attention of researchers [2-3] due to its potential applications in theoretical and practical chemistry since the first model for an oscillating chemical system was established [4]. Among all oscillating systems, both classical Belousov-Zhabotinskii (BZ) type of reaction [5-8] and Briggs-Rauscher (BR) type of reaction [9-10] have been extensively studied. BZ reaction, which involves the oxidation of an organic species in an acidic bromate solution, is usually catalyzed by a metal ion catalyst (Ce$^{3+}$, Mn$^{2+}$, for examples). BZ reaction involving macrocyclic complexes as catalysts was not reported until 1982 [11].

In recent years, great progress has been made by utilizing the oscillating chemical reaction as a new analytical method for determination of analytes. The first application of it was to determine trace amounts of ruthenium(III) which was the contribution from Tikhonova et al. [12]. Jimenez-Prieto proposed an Analyte Pulse Perturbation Technique (APP) that facilitates the use of oscillating reaction in determinations [13]. As an analytical tool, classical BZ reaction was designed to determine various analytes such as metal ions [14-15], organics [16], medicine [17-18], polyphenols [19], BZ oscillatory reaction catalyzed by macrocyclic copper complex (like tetraazamacrocyclic complex $[\text{CuL}](\text{ClO}_4)_2$) (Fig. 1) could be utilized in detection of some species and ions as well. As a catalyst, the tetraazamacrocyclic complex shows unusual features during its catalytic process compared with classical ones. Involving tetraazamacrocyclic complex as catalyst, such B-Z systems are more vulnerable to the external perturbations, and they oscillate in higher oscillating frequencies. We have used this $[\text{CuL}](\text{ClO}_4)_2$ catalyzed oscillating system for kinetic determination of Ag$^+$ [20], pyrogallol [21], calcium pantothenate [22], Alizarin red S [23], catechol [24], Paracetamol [25], Xylenol Orange [26] and vitamin B6 [27].

Tannic acid (Fig. 2) is a specific tannin obtained from Chinese gall. As a drug, tannic acid has antibacterial, anti-inflammatory effects and has resistance to a variety of pathogenic infection. It is directly applied in treating diaper rash and prickly heat. It is also used in cosmetics and pharmaceuticals for skin conditioning purposes. Tannic acid is a typical acyl-glucose compound, and its
phenolic hydroxyl structure gives it a unique chemical property and physiological activity.

At present, the analytical method for determination of tannic acid includes high-performance liquid chromatography [28], flow-injection chemiluminescence [29] and reversed-phase liquid chromatographic methods [30]. Although the results of these methods are accurate, it needs the support of more expensive testing instruments. Our analytical method equipped with a simple instrument provides an accurate determination of analyte. In this article, we proposed a kinetic approach for determination of tannic acid by using its perturbation effects, seeking to broaden the application of the above-mentioned oscillation system on analytical field. Such a B-Z system being used is catalyzed by a macrocyclic complex [CuL](ClO$_4$)$_2$, where the ligand L is 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene.

2 Experimental

2.1 Reagents

All chemicals used were of analytical-reagent grade. They were used without further purification and doubly distilled water was used to prepare the reagent solutions. The catalyst [CuL](ClO$_4$)$_2$ was prepared according to a published procedure [31] and was identified by its IR spectra and elemental analysis. Solutions of 0.5 M NaBrO$_3$, 2.0 M malic acid and 0.0184 M [CuL](ClO$_4$)$_2$ were prepared with 1.0 M sulfuric acid. Aqueous solution of 0.0025 M tannic acid was freshly prepared before the experiment. Solutions with lower concentration of tannic acid were prepared just prior to use.

2.2 Apparatus

The experimental assembly consisted of a glass beaker (ca. 50 mL) and a potential measuring system. The beaker was coupled with a model DZCS-IIIC thermostat to maintain the temperature of the reaction solution at 298 ± 0.5 K. The oscillation was monitored by means of Pt electrode (Rex, 213, China) and a saturated calomel electrode (Rex, 217, China), which were connected to a computer equipped with a software (Vernier, Logger Lite). An amplifier (Vernier software, USA) and Go!Link sensor interface (Vernier software, USA) were introduced between electrodes and the computer. Signals were recorded as a function of time with a time interval of 0.5 s.

Solutions of sulfuric acid (29.5 mL), malic acid (4.0 mL), NaBrO$_3$ (1.5 mL) and [CuL](ClO$_4$)$_2$ (5.0 mL) were added to a 50 mL glass beaker, which was thermostated at 298 ± 0.5 K. The platinum electrode and reference electrode were placed into the beaker. Then, the mixture was continuously stirred at a rate of 500 rpm and the potential as a function of time was recorded by a computer equipped with software (Vernier, Logger Lite). Aqueous solution samples containing variable amounts of tannic acid were injected into the reaction system at the bottom of the potentiometric cycle. After addition of tannic acid, there were an immediate quenching and successive regeneration of the oscillations after the inhibition time ($t_{in}$). The inhibition time (the length of time in seconds before oscillations restart (Fig. 3b) was selected as analytical data to construct the calibration plot.
3 Results and discussion

Adding a trace amount of tannic acid could cause temporary inhibition of the oscillation, and the profiles were given as Fig. 3, which shows typical oscillation profiles for the [CuL](ClO$_4$)$_2$-catalyzed oscillating system in the presence and absence of variable amounts of tannic acid under the above experimental conditions.

It was found that $t_{in}$ is linearly proportional to the logarithm of tannic acid concentration over the range of $6.25 \times 10^{-7}$ ~ $1.56 \times 10^{-5}$ M (Fig. 4). The linear regression equation can be expressed as $t_{in} = 424.8 + 60.0 \times \log_{10} \text{[tannic acid]}$ ($n = 16$, $R = 0.9984$). The relative standard deviation (RSD) of $t_{in}$ in five replicate determinations for $1.5 \times 10^{-4}$ M tannic acid was 4.50%.

In order to ensure the maximum possible sensitivity and precision in the determination, the influences of the experimental variables on the proposed oscillating reaction were studied (Fig. 5).

Acidity not only affects the perturbation effects of tannic acid, but the oscillation behavior of the system as well. The effect of H$_2$SO$_4$ concentration was studied in the range of 0.8~1.25 M. When the concentration exceeds this range, it can cause unstable oscillation behavior. Though $t_{in}$ shows a decreasing tendency with increasing concentration of sulfuric acid, a concentration of 1.0 M was chosen as optimal.

The effect of NaBrO$_3$ concentration was studied over the range from $1.1125 \times 10^{-2}$ to $1.875 \times 10^{-2}$ M. As the concentration was increased, $t_{in}$ decreased. However, when the concentration of NaBrO$_3$ is too high or too low, it leads to a marked drift of oscillation. In order to obtain optimal $t_{in}$, $1.875 \times 10^{-2}$ M concentration of NaBrO$_3$ was selected.

Changes in malic acid concentration were over the range of 0.125~0.375 M. The result showed that, with increasing concentration, $t_{in}$ decreased to its minimum at 0.3 M malic acid and then increased. In lower concentration, the system needs longer time of induction process. A concentration of 0.2 M was finally adopted as optimal.

The effect of the catalyst [CuL](ClO$_4$)$_2$ concentration also was investigated. The concentration of the catalyst is the key to maintain a stable oscillation. The result
showed that the inhibition time changes irregularly with increasing $\text{[CuL(CIO}_4\text{)]}_2^-$ concentration. A very high level of catalyst could give rise to a marked drift of oscillation. The value of $2.75 \times 10^{-3}$ M was chosen for the optimum concentration.

The recovery experiments were employed to ensure the accuracy of the proposed method. Different concentrations of standard tannic acid were added into analyte (tannic acid solution) with different concentrations and the same procedure was applied. The recovery experiments indicate that the accuracy of the proposed method is very good (Table 1). From above experimental results, we observe that this method is suitable for sample analysis.

The macrocyclic Cu(II) complex-catalyzed oscillating system is vulnerable to foreign species in the reaction medium. The oscillating system was perturbed with a sample, which contained tannic acid and variable amounts of interference. The amount of interference causing an error of less than 5% in the determination of $1.5 \times 10^{-4}$ M tannic acid was taken as the tolerance limit.

The results obtained were shown in Table 2. As it is shown, it can be concluded that some species (such as I -, Ag+, Fe2+) have strong effects on the determination of analyte, but Na+, Cu2+ and some other common ions have no effects on the determination.

4 Mechanism of Action of Tannic acid on the Oscillation System

The mechanisms of oscillation reaction are rather complex. Elucidating the nature of the interaction of tannic acid with the oscillating system was not an easy task. Often, oscillation systems consist of many kinetic steps involving several independent variables [32]. According to the well-known FKN mechanism [33], the $\text{[CuL]}^{2+}$ – catalyzed oscillating system can be described by the following seven-step reactions. The rate constants are listed in Table 3:

![Figure 5: Influence of the concentration of (a) sulfuric acid; (b) sodium bromate; (c) malic acid; (d) $\text{[CuL(CIO}_4\text{)]}_2^-$ on the oscillation system in the presence of $6.25 \times 10^{-7}$ M tannic acid. (a)$[\text{[CuL(CIO}_4\text{)]}_2^-]=2.75 \times 10^{-3}$ M; $[\text{NaBrO}_3]=1.875 \times 10^{-2}$ M; [malic acid] = 0.20 M; (b) $[\text{H}_2\text{SO}_4]=1.0$ M; $[\text{[CuL(CIO}_4\text{)]}_2^-]=2.75 \times 10^{-3}$ M; [malic acid] = 0.20 M; (c) $[\text{H}_2\text{SO}_4]=1.0$ M; $[\text{[CuL(CIO}_4\text{)]}_2^-]=2.75 \times 10^{-3}$ M; [NaBrO3] = 1.875 $\times 10^{-2}$ M; (d) $[\text{H}_2\text{SO}_4]=1.0$ M; [NaBrO3] = 1.875 $\times 10^{-2}$ M; [malic acid] = 0.20 M.](image-url)
We explore tannic acid perturbation mechanism in an attempt to identify which species react with tannic acid by using cyclic voltammetry.

Fig. 6 shows the cyclic voltammograms of NaBrO₃ solution in the absence of tannic acid and in the presence of 2.50 × 10⁻⁶ M tannic acid. It was observed that, when the 2.50 × 10⁻⁶ M tannic acid was added into the NaBrO₃ solution, there was a decrease both in the reduction and in oxidation current. In addition, such a decrease in current suggests that redox reaction between NaBrO₃ and tannic acid could occur.

However, an assumption of occurrence of reaction between NaBrO₃ and tannic acid seems has difficulty in explaining the resumption of oscillations. Nor it can explain the existence of inhibition time. Because the concentration of NaBrO₃ is larger, and the concentration of tannic acid added was relatively lower in the system, tannic acid would be consumed rapidly. There would be no inhibition time that could be observed. Then intermediate species (BrO₂⁻ radicals) should be taken into account. Tannic acid reacts with BrO₂⁻ radicals to form tannic acid radicals, which react with each other to form the final products – quinones. Reference [37] confirmed that polyphenols could be oxidized into quinones, so tannic acid could be oxidized into quinone. As tannic

Table 1: Determination results and recovery for tannic acid sample.

| Experiment | Determined concentration/10⁻⁶ mol L⁻¹ | Added concentration/10⁻⁶ mol L⁻¹ | Found concentration/10⁻⁶ mol L⁻¹ | Recovery (%) |
|------------|--------------------------------------|----------------------------------|----------------------------------|--------------|
| 1          | 0.437                                | 0.500                            | 1.024                            | 91.504       |
| 2          | 0.750                                | 0.500                            | 1.324                            | 94.411       |
| 3          | 1.375                                | 0.500                            | 1.676                            | 111.873      |
| 4          | 1.188                                | 1.000                            | 2.014                            | 108.639      |
| 5          | 1.500                                | 1.000                            | 2.554                            | 97.885       |
| 6          | 2.125                                | 1.000                            | 3.142                            | 99.458       |
| 7          | 1.750                                | 2.000                            | 3.607                            | 103.964      |
| 8          | 2.375                                | 2.000                            | 4.353                            | 100.505      |
| 9          | 3.000                                | 2.000                            | 5.067                            | 98.677       |
| 10         | 3.625                                | 2.000                            | 5.653                            | 99.504       |

Table 2: The effect of foreign ions on oscillation.

| Foreign ions and species | Tolerated ratio* |
|--------------------------|------------------|
| Na⁺, Cu²⁺, Zn²⁺         | 2000             |
| Mg²⁺, Ca²⁺              | 200              |
| F⁻, Cl⁻                 | 5                |
| Br⁻                     | 1                |
| I⁻, Ag⁺, Fe⁺           | 0.2              |

* Tolerated ratio is the ratio between the concentration of foreign ions (or species) and concentration of tannic acid (1.5 × 10⁻⁴ M), on the condition that interference of foreign ions (or species) causes an error of less than 5% in the determination.

Table 3: The rate constant.

| Reaction | Rate constant | Ref. |
|----------|---------------|------|
| (1)      |                | [34] |
| BrO₃⁻ + HBrO₂⁻ + H⁺ ⇌ 2BrO• + H₂O |            |
| (2)      |                | [35] |
| HBrO₂⁻ + Br⁻ + H⁺ ⇌ 2HBrO⁻ |            |
| (3)      |                | [35] |
| BrO⁻ + H₂O ⇌ BrO⁻ + H₂O |            |

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The occurrence of reaction of tannic acid and BrO₂− leads to the decrease in BrO₂− radicals. As BrO₂− radicals decrease, there will not be sufficient BrO₂− radicals to oxidize [CuL]²⁺ into [CuL]³⁺. Oscillations between [CuL]²⁺ and [CuL]³⁺ were terminated. Therefore, oscillation temporarily ceases. That is why the inhibition time was observed. The relationship between the off-time of the oscillation and the logarithm of the tannic acid concentration makes very likely that the consumption of the tannic acid takes place in a first-order reaction, and once the tannic acid concentration decreases below a certain level, the oscillation can restart.

5 Conclusion

Kinetic determination of tannic acid by a [CuL](ClO₄)²⁻ catalyzed oscillating system is reported. The change in inhibition time is linearly proportional to the logarithm of tannic acid concentration over the range from 6.25 × 10⁻⁷ ~ 1.56 × 10⁻⁵ M. Compared with other analytical techniques, the set-up used in the proposed method is rather cheap in price. This analytical method equipped with a simple instrument provides a new tool for accurate determination of analytes.

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