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Determination of *p*-nitroaniline by the tartrate-acetone-Mn^{2+}-$KBrO_3$-H_2SO_4 double organic substrate oscillating system using non-equilibrium stationary state

Invited Paper

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Abstract: This paper described the determination of *p*-nitroaniline in a double organic substrate oscillating system of tartrate-acetone-Mn^{2+}-$KBrO_3$-H_2SO_4. Under the optimum conditions, temperature was chosen as a control parameter to design the bifurcation point and proposed a convenient method for determination of *p*-nitroaniline. Results showed that the system consisting of 3.5 mL 0.06 mol L^{-1} tartrate, 4.0 mL 0.7 mol L^{-1} H_2SO_4, 1.5 mL 1.5×10^{-4} mol L^{-1} $MnSO_4$, 4.0 mL 0.4 mol L^{-1} acetone and 7.0 mL 0.05 mol L^{-1} $KBrO_3$ was very sensitive to the surrounding at 33.5 °C. A good linear relationship between the potential difference and the negative logarithm concentration of *p*-nitroaniline was obtained to be in the range of 2.50×10^{-7}~3.75×10^{-5} mol L^{-1} with a lower detection limit of 2.50×10^{-8} mol L^{-1}.

Keywords: *Double organic substrate oscillating chemical system • Non-equilibrium stationary state • p-Nitroaniline • Determination*

1. Introduction

The application of oscillating chemical reaction to analytical chemistry has made a long progress during the last 20 years [1,2], in which the combination of the "continuously stirred tank reactor" (CSTR) [3] and the "analyte pulse perturbation technique" (APP) [4] was considered as a turning point. Most of organic compounds and some inorganic ions can be determined quantitatively in the range from 10^{-3} to 10^{-6} mol L^{-1} with a lower detection limit of 10^{-7} mol L^{-1}. To improve further the sensitivity of B-Z oscillating reaction, some of researchers pay more attention on the non-linearity or multi-stationary state. Examples are the use of the largest Lyapunov exponent [5] in the transient chaotic regime to create a new method for the determination of thallium and the use of a modified B-Z oscillating chemical system by sulfide [6] to detect the trace amount of some metal ions with very high sensitivity (detection limit ≤ 10^{-12} mol L^{-1}). Recently, Vukojević and Pejic *et al*. [7-9] studied the characteristics of a non-equilibrium stationary state close to the bifurcation point and proposed successfully a novel kinetic method for the determination of organic compounds and inorganic ions. In fact, the vicinity of a bifurcation point of non-equilibrium system gestates a fluctuation, which is very sensitive to the surrounding change. This behavior can be used in analytical determination.

The original Belousov-Zhabotinsky (B-Z) oscillating reaction was designed as a redox system consisting of malonic acid (reductant) and potassium bromate (oxidant) in a acidic solution (sulfuric acid). This reaction needs a catalyst (cerium ion Ce^{4+}) to speed up the rate of reaction. Here, malonic acid was considered as a single-substrate. The further investigations found that many organic compounds which have active methylene could also be considered as single-substrate

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to replace malonic acid in B-Z oscillating system such as lactic acid, tartaric acid, malic acid, tyrosine and so on. However, sometime the single-substrate could not offer a stable regular profile, even though the oscillating behavior occurs clearly. As a result, an attempt using two organic compounds (called the double organic substrate) to improve oscillator has emerged [2,10], for example, lactic acid-acetone, tartrate–acetone, and tyrosine-acetone. In the analytical determination, the application of double organic substrate can improve remarkably the sensitivity and selectivity.

p-Nitroaniline is an intermediate used in synthetic chemistry, which can pollute the environment during the applied process. For detecting contaminants, some detection techniques that have been used are spectrophotometry [11], capillary zone electrophoresis [12], voltammetry [13]. The experimental setups used in the above techniques are expensive, and their operations are time-consuming. In contrast to other instrumental techniques, the proposed method has many benefits, such as a simple set-up with ease of operation, less expensive, wide linear range and lower detection limit. In this paper, we propose a new method for the determination of *p*-nitroaniline in trace level.

2. Experimental Procedures

2.1. Apparatus

The experimental set-up consists of a water-jacket glass reactor (*ca.* 50 mL) coupled with a Model 501 thermostat and a Model ML-902 magnetic stirrer to keep the temperature constant. A CHI-832 (CHI, USA) electrochemistry analyzer is directly connected to the reactor through two Pt-electrodes in which one is working electrode and the other is counter electrode and a K_2SO_4 reference electrode to record the potential changes. A micro-injector was used to inject sample solution.

2.2. Reagents

All chemicals used to establish the oscillating system were of analytical grade. Doubly distilled-deionized water was used throughout. Solutions of $KBrO_3$, tartrate, acetone and $MnSO_4$ were prepared in 0.7 mol L^{-1} sulfuric acid, respectively. Stock solutions of *p*-nitroaniline were prepared with acetone. Working solutions with lower concentrations were temporarily diluted just prior to use.

2.3. Procedure

The reaction was carried out in a glass vessel (*ca.* 50 mL) fitted with a Model 501 thermostat and a Model ML-902 magnetic stirrer. A mixture solution of 3.5 mL 0.06 mol L^{-1} tartrate, 4.0 mL 0.7 mol L^{-1} H_2SO_4, 1.5 mL 1.5×10^{-4} mol L^{-1} $MnSO_4$, 4.0 mL 0.4 mol L^{-1} acetone and 7.0 mL 0.05 mol L^{-1} $KBrO_3$ was added firstly into the reactor at 50.0 ℃ to make the total volume of 20.0 mL. Then, three electrodes were immersed into the reaction media under stirring and started to record the potential change of system. A regular steady oscillation profile was observed after some induction period. To find the bifurcation point of system, the temperature was reduced gradually during the experiment until the regular oscillation disappeared. The decrease in temperature causes the amplitude to decrease (as shown in Fig. 1). Recorded working temperature was 50.0 ℃, 47.5 ℃, 45.5 ℃, 42.2 ℃, 38.4 ℃, 35.2 ℃, 33.5 ℃, 30.6 ℃, 28.4 ℃ , respectively.

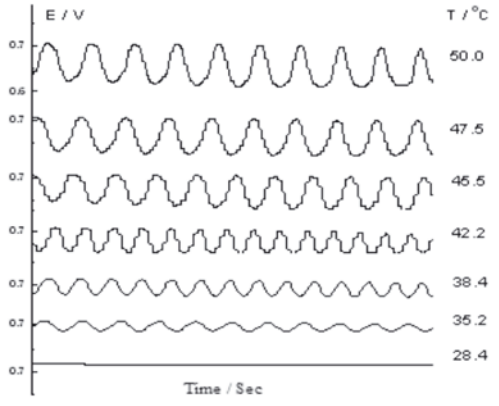


Figure 1. Time series profiles at different temperature. Common conditions: $[MnSO_4]=1.13\times10^{-5}$ mol L^{-1}, $[KBrO_3]=1.75\times10^{-2}$mol L^{-1},[Tartrate]$=1.05\times10^{-2}$ mol L^{-1}, $[H_2SO_4]=0.14$ mol L^{-1}, [Acetone]$=8.00\times10^{-2}$ mol L^{-1}.

3. Results and discussion

3.1. Finding bifurcation point

General speaking, temperature, the initial concentration of mixture and velocity can be chosen as control parameters to study non-equilibrium stationary state. In this paper, temperature was chosen as a preferred variable to design the bifurcation profile and concentrations of reactants were optimized at 50.0 ℃ . It was found that the appearance of a steady regular profile must be to meet the following conditions: $[MnSO_4]=1.13\times10^{-5}$ mol L^{-1}, $[KBrO_3]=1.75\times10^{-2}$ mol L^{-1}, [Tartrate]$=1.05\times10^{-2}$ mol L^{-1}, $[H_2SO_4]=0.14$ mol L^{-1}, [Acetone]$=8.00\times10^{-2}$ mol L^{-1}. With temperature decreasing gradually, the amplitude became smaller and smaller keeping other parameters

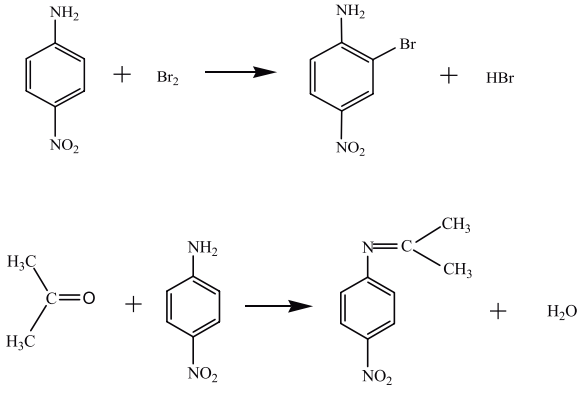
unchanged. When the temperature was equal to or less than 33.5℃, the regular oscillation disappeared, while the system was transformed from a non-equilibrium state to another one (as shown in Fig. 2).

The theoretical bifurcation point of system was just found by linear extrapolation method [7], *i.e.*, a plot of square of the amplitude in regular oscillations *vs.* corresponding temperatures with a linear intersecting abscissa. From Fig. 3 it can be seen that the critical value is 34.0℃.

If the temperature was chosen as a variable to design the bifurcation profile, the system would become very sensitive to the surrounding. Fig. 4 shows the sensitivities for determining the same amount of *p*-nitroaniline at the different temperatures. It is clear that the closer to the temperature of bifurcation point, the sensitivity is higher. That is to say, the temperature of injection sample must be as close as possible to the bifurcation point. In this work, 33.5℃ was chosen as the temperature for adding samples.

3.2. Determination of *p*-nitroaniline

The perturbation of *p*-nitroaniline on the B-Z oscillating system could be considered that there are two possible interactions between *p*-nitroaniline and/or Br_2 and acetone below:



As mentioned above, the addition of analyte would cause a change of potential of the system. Based on the potential change before (A) and after adding analyte (A_o), a quantitatively linear relationship between the concentration of *p*-nitroaniline and the potential difference (ΔA) was obtained, where, A_o and A referred to the potential of the system before and after adding the sample, respectively.

To ensure reproducibility, 0.1 mL of various concentrations of *p*-nitroaniline were repeatedly injected in the period of 1400 ~1600 seconds was carried out.

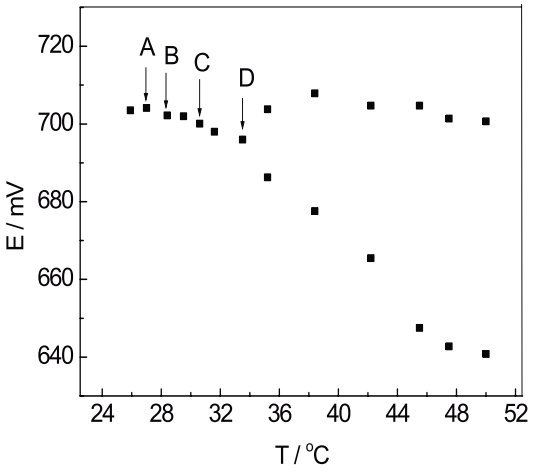


Figure 2. Bifurcation profiles using temperature as control parameter. Conditions: $[MnSO_4]=1.13\times10^{-5}$ mol L^{-1}, $[KBrO_3]=1.75\times10^{-2}$ mol L^{-1}, [Tartrate] $=1.05\times10^{-2}$ mol L^{-1}, $[H_2SO_4]=0.14$ mol L^{-1}, [Acetone] $=8.00\times10^{-2}$ mol L^{-1}. A=27.0℃; B=28.4℃; C=30.6℃; D=33.5℃.

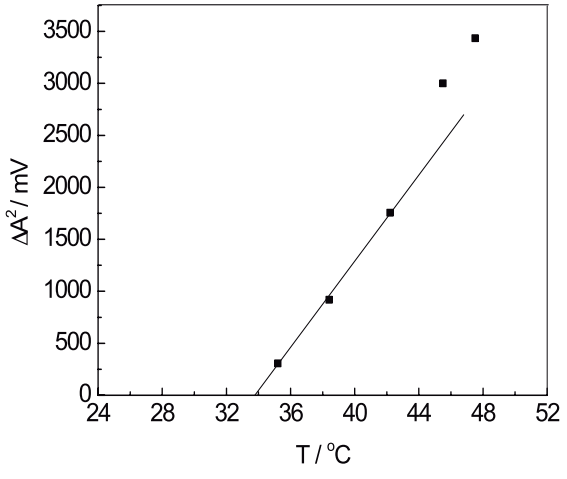


Figure 3. The plot of square of the amplitude *vs.* temperature.

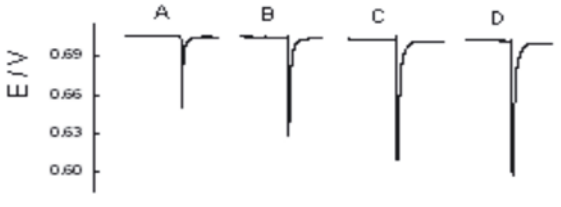


Figure 4. The profiles of adding samples close to the point of bifurcation.
Conditions: A=27.0℃; B=28.4℃; C=30.6℃; D=33.5℃.
Common Conditions: $[MnSO_4]=1.13\times10^{-5}$ mol L^{-1}, $[KBrO_3]=1.75\times10^{-2}$ mol L^{-1}, [Tartrate] $=1.05\times10^{-2}$ mol L^{-1}, $[H_2SO_4]=0.14$ mol L^{-1}, [Acetone] $=8.00\times10^{-2}$ mol L^{-1}, [*p*-nitroaniline] $=4.50\times10^{-4}$ mol L^{-1}

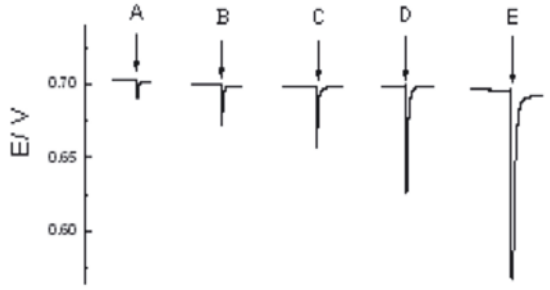


Figure 5. The perturbation of *p*-nitroaniline on the non-equilibrium stationary state in B-Z oscillating system. Conditions: [*p*-nitroaniline]: (A)=3.75×10^{-7} mol L^{-1}; (B)=3.75×10^{-6} mol L^{-1}; (C)=3.75×10^{-5} mol L^{-1}; (D)=1.00×10^{-4} mol L^{-1}; (E)=5.00×10^{-3} mol L^{-1}. Common conditions: [$MnSO_4$]=1.13×10^{-5} mol L^{-1}, [$KBrO_3$]=1.75×10^{-2} mol L^{-1}, [Tartrate]=1.05×10^{-2} mol L^{-1}, [H_2SO_4]=0.14 mol L^{-1}, [Acetone]=8.00×10^{-2} mol L^{-1}, T= 33.5°C.

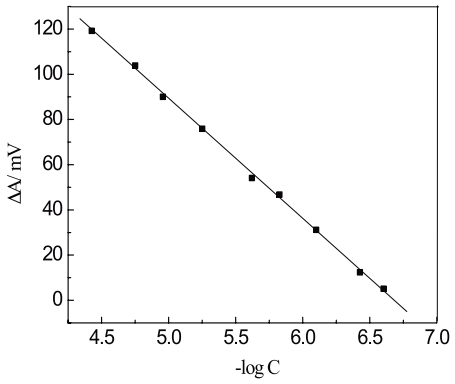


Figure 6. Calibration curve for determination of *p*-nitroaniline. Conditions: [$MnSO_4$]=1.13×10^{-5} mol L^{-1}, [$KBrO_3$]=1.75×10^{-2} mol L^{-1}, [Tartrate]=1.05×10^{-2} mol L^{-1}, [H_2SO_4]=0.14 mol L^{-1}, [Acetone]=8.00×10^{-2} mol L^{-1}, T= 33.5°C.

Fig. 5 showed the perturbation of different amount of *p*-nitroaniline on the system at the same temperature. A good linear range from 2.50×10^{-7} to 3.75×10^{-5} mol L^{-1} was obtained with a lower detection limit of 2.50×10^{-8} mol L^{-1} (see Fig. 6). The linear relationship can be expressed by the following regression equation:

$$\Delta A\ (mV) = 353.585 - 52.918\ (-\log C) \quad (r=0.9995, n=9)$$

3.3. Interferences

It is well known that the oscillating chemical reaction is highly vulnerable to foreign species in general. For this reason, the interferences of some possible inorganic ions and organic compounds with small molecular weight on detection of *p*-nitroaniline were tested. The results were shown in Table 1. It can be seen that common inorganic ions have no effect on the determination of *p*-nitroaniline. Methanol, ethanol, ether, and acetic acid can affect slightly the determination. The tolerable ratio for *m*-nitroaniline, having a similar structure to *p*-nitroaniline, was limited to be less than 10-fold.

3.4. Compared with other methods

Linear range and detection limit are two figures of merit for assessing the instrumental analysis methods. Table 2 gives the comparison results in the determination of *p*-nitroaniline with different techniques. It can be seen

Table 1. The influence of foreign species on the determination of *p*-nitroaniline ([*p*-nitroaniline]=1.0×10^{-5} mol L^{-1}).

Foreign species	Tolerable ratio (foreign / *p*-nitroaniline)
Zn^{2+}, Ni^{2+}, Mg^{2+}, Fe^{2+}, Fe^{3+}	2000
Cl^-, I^-, Br^-	500
Methanol, ethanol, ether, acetic acid	20
m-Nitroaniline	10

Table 2. Compared the proposed method with others used for determining *p*-nitroaniline.

Method	Linear range (mg L^{-1})	Detection limit (mg L^{-1})	References
Spectrophotometry	0.1~17.0	6.00×10^{-2}	[11]
Capillary zone electrophoresis	0.017~331.49	3.31×10^{-3}	[12]
Voltammetry	0.0014~0.97	1.10×10^{-3}	[13]
The present paper	0.0345~5.18	3.45×10^{-3}	-

Table 3. The determination results and recovery analysis of *p*-nitroaniline sample.

Sample no.	Original (mol L^{-1})	Added (mol L^{-1})	Found (mol L^{-1})	Recovery
1	2.50×10^{-6}	1.30×10^{-5}	1.53×10^{-5}	98.7%
2	2.50×10^{-6}	1.85×10^{-5}	2.08×10^{-5}	99.0%
3	2.50×10^{-6}	2.10×10^{-5}	2.36×10^{-5}	100.4%
4	2.50×10^{-6}	2.90×10^{-5}	3.07×10^{-5}	97.5%
5	2.50×10^{-6}	3.45×10^{-5}	3.80×10^{-5}	102.7%
6	2.50×10^{-6}	3.90×10^{-5}	4.12 ×10^{-5}	99.3%

that the proposed method has a large linear range with low detection limit.

3.5. Sample analysis

The following artificial wastewater samples were analyzed, and the recoveries of samples were determined. Results in Table 3 indicate that this method could be used in the routine wastewater analysis of *p*-nitroaniline with a recovery of 97.5% - 102.7%.

4. Conclusion

A rapid and simple method for the determination of *p*-nitroaniline has been developed in the present paper. The method developed in this work has advantages such as large linear range, low detection limit, convenient operation and lower cost. In addition the proposed technique could be adopted more easily in the routine analysis as compared to existing techniques.

Acknowledgements

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