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Article

Determination of *p*-Phenylenediamine by Perturbation of a Non-Equilibrium Stationary State in the B-Z Reaction

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Foi proposto um procedimento para a determinação de *para*-fenilenodiamina (PPD) em águas residuais, baseada na perturbação de uma reação oscilante em uma situação fora do equilíbrio, próximo a uma bifurcação pela reação Belousov-Zhabotinskii (B-Z), uma vez que este ponto encontra-se muito sensível à perturbação pela mudança de vizinhança. Os resultados indicam que a variação de potencial (ΔE) é linearmente proporcional ao antilogarítmo da concentração de PPD, (−logC), no intervalo de concentração correspondente a $4,68 \times 10^{-7}$ - $1,95 \times 10^{-5}$ mol L^{-1} (r = 0,9981) e com limite de determinação (LOD) de $9,50 \times 10^{-8}$ mol L^{-1}. Uma boa recuperação do analito foi obtida, em um intervalo de aproximadamente 95,1 a 102,3%.

A convenient method for determination of *p*-phenylenediamine (PPD) in wastewater has proposed, based on the perturbation of a non-equilibrium stationary state near a bifurcation for the Belousov-Zhabotinskii (B-Z) reaction, due to this point being very sensitive to the surrounding change. Results indicate that the change of the potential (ΔE) is linearly proportional to the negative logarithm concentration of PPD (−logC) in the range of 4.68×10^{-7} - 1.95×10^{-5} mol L^{-1} (r = 0.9981) with a limit of detection (LOD) of 9.50×10^{-8} mol L^{-1}. A good recovery was obtained at *ca.* 95.1 to 102.3%.

Keywords: non-equilibrium stationary state, Belousov-Zhabotinskii reaction, *p*-phenylenediamine determination

Introduction

Chemical reaction systems, which were far-from-equilibrium, could exhibit various dynamic regimes such as regular and irregular oscillations, chaos and so on.[1] Some of them have been widely used in analytical chemistry,[2,3] commonly based on the perturbation of a stationary oscillating system by analyte. The change of amplitude and/or period in regular oscillating system is proportional to the amounts of analyte added, in the range from 10^{-7} to 10^{-4} mol L^{-1} with a lower detection limit (*ca.* 10^{-6} - 10^{-8} mol L^{-1}). In general, it may satisfy the need of common determinations.

To improve the sensitivity of B-Z oscillating reaction, Perez-Bendito's group[4,5] and Strizhak's group[6,7] investigated theoretically the largest Lyapunov exponent in the transient chaotic regime with the B-Z oscillating system and developed a new analytical method with very high sensitivity (limit of detection, LOD ≤ 10^{-12} mol L^{-1}). Gao *et al.*[8] reported that a modified B-Z oscillating chemical system with sulfide is very sensitive to trace amounts of some metal ions. All of these facts demonstrated again that the oscillating chemical reaction as a novel analytical technique has been made a long progress, and applied successfully to the determination of trace amounts of organic and inorganic substances. Recently, Pejić *et al.*[9,10] 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. For this reason, it can be used in analytical chemistry. To assess the validity in the present paper we consider *p*-phenylenediamine (PPD) as analyte and compare with other analytical techniques such as capillary zone electrophoresis,[11] spectrophotometric,[12] and heat-gradient analytical technique.[13]

p-Phenylenediamine is one of main components in the oxidative-type hair dyes, which can react with hydrogen peroxide to turn hair to black. Now, it has been used widely in cosmetics except for application in synthetic

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chemistry. The sequel of large amounts of its use will be pollution of the surrounding such as water and soil. Thus, we proposed a more convenient and rapid method to determine *p*-phenylenediamine. Results showed that the proposed method could meet the need of many fields. Moreover, in contrast to other instrumental analysis, the proposed method has many benefits, such as simple set-up with ease of operation and low cost, broader linear range and lower limit of detection and so on.

Experimental

Reagents

All chemicals used were of analytical-reagent grade and doubly distilled water was used throughout. Stock solutions were prepared with doubly distilled water and standardized prior to use. Solutions with lower concentration of PPD were prepared and stored in the black polyethylene bottle.

Apparatus

The set-up used to implement the determination of PPD consisted of a glass vessel with 50 mL capacity wrapped in a water recirculation jacket. A Model 501 thermostat (Shanghai Experimental Instrumental Factory, China) with an accuracy ± 0.1°C and a Model ML-902 magnetic stirrer (Shanghai Pujiang Analytical Instrumental Factory, China) were used to maintain the temperature of the reaction solution. Reactants were added to the CSTR and products were lead away from it by using a Model DDB-600 six-channel peristaltic pump (Zhejiang Xiaoshang Haitian Instrumental Factory, China). A CHI-832 electrochemical analytical instrument (Shanghai Chenhua Instrument Company, China) was used to record the changes in potential, which were monitored by using two Pt-electrodes (Rex, 213, China) as the working electrode and auxiliary electrode separately, and an Ag/AgCl/KCl electrode (Rex, 217, China) as the reference electrode. A microinjector was used for introducing sample solution.

Procedure

The experiments were performed in a 50 mL CSTR thermostatted at 303 ± 0.1 K. The reactants were supplied to the reactor by using the following concentrations: $[KBrO_3]_o = 0.14$ mol L^{-1}, $[MA]_o = 0.30$ mol L^{-1}, $[H_2SO_4]_o = 0.20$ mol L^{-1}, $[Fe(phen)_3]_o^{2+} = 1.25$ mmol L^{-1}, keeping the total volume of 25.20 mL. Then the electrodes were immersed in the solution and the mixture was homogenized by continuous magnetic stirring with a rate of 800 rpm, and the time-potential curve was recorded immediately. Perturbations were performed by adding a volume of 0.2 mL of the sample solution with a microinjector.

Results and Discussion

Procedure of finding the bifurcation

Theoretically, changing any dynamic parameters, such as temperature, specific flow rate (j_o), the concentration of reactants, could make the oscillating profile both in amplitude and period from oscillatory to non-oscillatory phase. In this paper, we considered the specific flow rate as a control parameter to find the bifurcation in the range of 0.0125 - 0.0450 min^{-1}. The specific flow rate j_o is a parameter in the CSTR being equal to the overall volume flow rate divided by the volume of the reaction mixture with a unit of (time)$^{-1}$. By introducing this parameter, the flow rates of all species can be described as first order reactions.[14] By decreasing the value of j_o, the amplitude of system decreased gradually and eventually disappeared at $j_o = 0.0275$ min^{-1} (see Figure 1A). In other words, the system approaches to a critical value of a dynamic regime and over this point a bifurcation phenomenon would be observed. Based on the data shown in Figure 1A, a plot of potentials (both maximum and minimum) *versus* the j_o was made as shown in Figure 2B. It is easy to understand that for a regular oscillating profile there are two potential points (*i.e.*, the highest and the lowest values); for a non-oscillating straight-line only one point can be acquired, meaning that the bifurcation point should be limited the range from 0.0125 to 0.0450 min^{-1}. In fact, a theoretical bifurcation point ($j_o = 0.0268$ min^{-1}) was obtained only by linear extrapolation rather than experimental observation ($j_o = 0.0275$ min^{-1}). Figure 1C shows an example, *i.e.*, how to find the value of $j_o = 0.0268$ min^{-1} by linear extrapolation. That is, a plot of the square of amplitude of the limit cycle oscillations *versus* j_o. This is why the bifurcation point must be determined experimentally several times (see the arrows in Figure 1B).

Determination of PPD

As the matrix reaction system was suitable for the quantitative determination of PPD, the B-Z oscillatory system catalyzed by $[Fe(phen)_3]^{2+}$ was chosen. That is, in the vicinity of bifurcation point, the matrix system is extremely sensitive to the surrounding. Even very small changes in reaction system caused by the addition

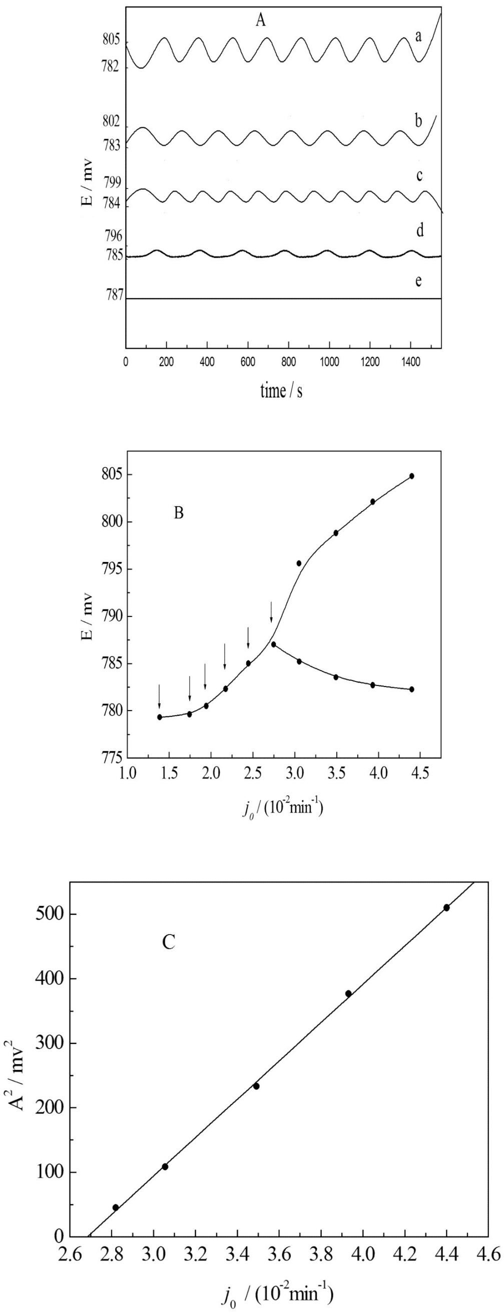

Figure 1. A: Time series showing stable dynamic structures observed in the B-Z reaction at different j_o, a: 0.0440 min^{-1}, b: 0.0393 min^{-1}, c: 0.0349 min^{-1}, d: 0.0306 min^{-1}, e: 0.0275 min^{-1}. Common condition: $[KBrO_3]_o$ = 0.14 mol L^{-1}, $[MA]_o$ = 0.30 mol L^{-1}, $[H_2SO_4]_o$ = 0.20 mol L^{-1}, $[Fe(phen)_3]_o^{2+}$ = 1.25 mmol L^{-1}, T = 303 ± 0.1 K; B: Bifurcation diagram for j_o as control parameter. The points, j_o = 0.0139, 0.0175, 0.0194, 0.0217, 0.0245 and 0.0275 min^{-1}are indicated by arrows; C: Plot of the square of oscillation amplitudes as a function of j_o. The bifurcation point was determined from the intercept on the abscissa.

of analytes may perturb extremely fragile balance and induce detectable changes in the dynamic pattern. When the PPD was injected into the system, the potential of system was impacted (see Figure 2). The change in the potential difference (ΔE) was linearly proportional to the negative logarithm concentration of PPD (–logC) over the range 4.68 ×10^{-7}- 1.95 × 10^{-5} mol L^{-1}, with a LOD 9.50 × 10^{-8} mol L^{-1}, as shown in Figure 3. The linear relationship can be expressed by the following regression equation 1:

$$\Delta E_m(\text{mV}) = 311.85 - 47.92\,(-\log C)$$
$$(\,r = 0.9981,\ RSD = \pm\,2.35\%) \qquad (1)$$

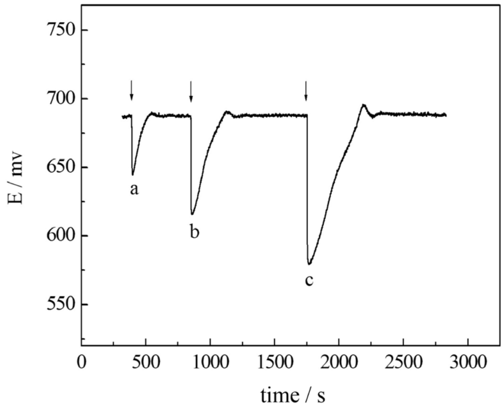

Figure 2. Typical potentiometric responses of the B-Z matrix, obtained after perturbing by PPD. a: [PPD] = 2.57 ×10^{-6} mol L^{-1}; b: [PPD] = 9.77 × 10^{-6} mol L^{-1}; c: [PPD] = 4.79 × 10^{-5} mol L^{-1}. Arrows indicate the moments at which stationary states were perturbed.

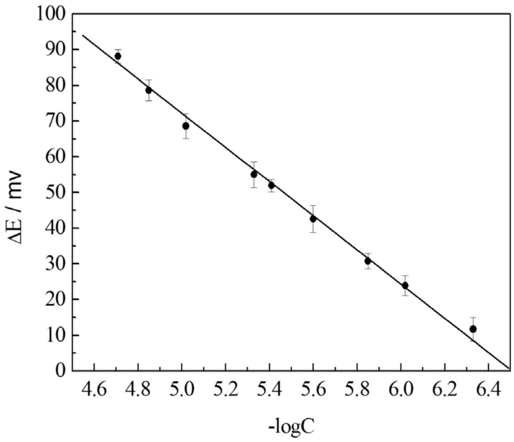

Figure 3. Calibration curve for the ΔE *vs.* the negative logarithm concentration of PPD (–logC) over the range of 4.68 × 10^{-7} - 1.95 × 10^{-5} mol L^{-1} (r = 0.9981).

Interferences

As we know that the non-equilibrium stationary state is highly vulnerable to the foreign species. For determining PPD, some of common inorganic ions and organic compounds were investigated. The tolerance level was defined as the maximum amount of foreign species causing an error, being limited less than ±5%

(RSD) for determining the PPD of 2.90×10^{-5} mol L^{-1}, as listed in Table 1.

Generally, commonly inorganic ions and organic compounds with small molecular weight have little influence on the determination. Tolerated ratio (foreign/PPD) for anilin (its structure similar to PPD), as well as phenol and formaldehyde were found to be less than 10.

Comparison with other methods

In order to ensure the sensitivity response of the proposed method, PPD determination was compared with other techniques and results were listed in Table 2.

Table 1. Effect of foreign species on the determination of [PPD] = 2.90×10^{-5} mol L^{-1}

Foreign species	Tolerated ratio (foreign/PPD)
K^+, Na^+, Ca^{2+}, Mg^{2+}, Ba^{2+}, Al^{3+}, Cl^-	1000
CO_3^{2-}, SO_4^{2-}, NO_3^-, PO_4^{3-}	500
Co^{2+}, Ni^{2+}, methanol, toluene	100
Pb^{2+}, Cd^{2+}	20
Anilin, phenol, formaldehyde	10

Table 2. Compared the proposed method with others used for determining PPD

Method	Linear range (mol L^{-1})	Ref.
Capillary zone electrophoresis coupled with amperometric detection	2.00×10^{-4} - 2.00×10^{-6}	11
Spectrophotometric	1.38×10^{-5} - 9.25×10^{-4}	12
Heat-gradient analytical technique	3.70×10^{-6} - 5.36×10^{-5}	13
Present work	4.68×10^{-7} - 1.95×10^{-5}	

Table 3. Results and recovery for determining PPD in water samples, (n = 6)

Sample No.	Original (mg L^{-1})	Added (mg L^{-1})	Found (mg L^{-1})	Recovery (%)
1	0.566	0.500	1.09	102.3
2	0.562	0.500	1.01	95.1
3	0.557	0.500	1.05	99.3
4	1.035	1.00	2.04	100.2
5	1.029	1.00	2.02	99.6
6	1.026	1.00	2.06	101.7

Sample analysis

Six artificial wastewater samples containing PPD were determined for testing the proposed method, and satisfactory results were obtained (Table 3).

Conclusion

Although some methods for determining PPD have been used widely, the proposed technique has its advantages, such a broader linear range and lower LOD, convenient operation and low cost set-up. Relative to other instrumental analysis, the proposed technique could be adopted easily in the routine analysis.

Acknowledgements

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