

Determination of 1-naphthylamine by using oscillating chemical reaction

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Abstract

A simple and rapid analytical method for determining 1-naphthylamine was proposed by perturbation with different amounts of 1-naphthylamine on the classical Belousov–Zhabotinskii (B–Z) oscillating chemical system. The results show that the changes both in oscillating period and amplitude were linearly proportional to the logarithm of the concentration of 1-naphthylamine ($\log C$) very well ranging from 7.08×10^{-5} to $7.08 \times 10^{-6} \text{ mol L}^{-1}$ and 7.08×10^{-5} to $1.0 \times 10^{-6} \text{ mol L}^{-1}$, with the corresponding regression coefficient are 0.9957 and 0.9922, respectively. For the later, a lower detection limit of $5.64 \times 10^{-9} \text{ mol L}^{-1}$ was obtained. Influence of injection point, temperature and reactant variables on this oscillating system was also investigated in detailed. The results obtained were compared with other determination methods. A possible reaction mechanism was interpreted by using bromide ion selective electrode to inspect the concentration change of Br^- ion in the oscillating process.
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Keywords: Oscillating chemical reaction; Perturbation; Determination; Mechanism; 1-Naphthylamine

1. Introduction

1-Naphthylamine was widely used in organic chemical industry as an intermediate of dye and rubber antioxidant. With following the use, the pollution to environment was overspread into water source and soil, even clothes. Thereby, the simple and rapid analytical methods for determining 1-naphthylamine are required at first. Now, for the different purpose, various techniques have been chosen for the determination of 1-naphthylamine, e.g., gas chromatography/mass spectrometry/single ion monitor [1], spectrophotometry [2], and the other techniques for various purposes [3,4].

Generally speaking, the kinetic–catalytic reaction is one of the simple and rapid analytical techniques compared to other methods. In recent years, the B–Z oscillating chemical reaction as a new analytical technique has made a great progress, owing to the fact that the early FKN mechanism [5] and a recently theoretical analysis by Taylor [6] are easy able to understand those complex reactions. The combination of analyte pulse perturbation technique (APP) and continuous-flow stirred tank reactor (CSTR) established a milestone in the analytical application [7,8]. Compared to instrumental analysis, the oscillating

chemical reaction as an analytical tool has some advantages such as simple in set-up, easy for operation, largely linear range (*ca.* 10^{-7} to $10^{-3} \text{ mol L}^{-1}$) and lower detection limit (*ca.* 10^{-6} to $10^{-8} \text{ mol L}^{-1}$). Just due to having these characteristics, more and more analysts are moving their focus on this field. Many papers concerning the determination of organic and inorganic substances have been reviewed [9,10].

In the present paper, we reported the determination of 1-naphthylamine by using this technique and satisfactory results were obtained.

2. Experimental

2.1. Reagents

All chemicals used were of analytical-reagent grade without further purification and doubly distilled water was used to prepare the reagent solutions. $0.2 \text{ mol L}^{-1} \text{ KBrO}_3$, $0.5 \text{ mol L}^{-1} \text{ MA}$ and $0.04 \text{ mol L}^{-1} \text{ Ce(IV)}$ ion were prepared with $0.55 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$, respectively. All stock solutions were prepared separately in doubly distilled water. Solutions with lower concentration of 1-naphthylamine were prepared just prior to use.

2.2. Apparatus

The experimental assembly consisted of an oscillation reactor (*ca.* 50 mL) and a potential measuring system. The reactor

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was coupled with a Model 501 thermostat and a Model ML-902 magnetic stirrer to maintain the temperature of the reaction solution at 303 ± 0.1 K. A CHI-832 (CHI, USA) electrochemistry analyzer was directly connected to the reactor through two Pt electrodes in which one is as working electrode and the other as counter electrode, and a K_2SO_4 reference electrode to record the potential changes. A Type 302 bromide selective electrode was used to measure the change of bromide ion concentration. A micro-injector was used to inject sample solution. A Model 2550 UV Spectrophotometer was used to detect 1-naphthylamine in order to ensure the accuracy of the proposed method.

2.3. Procedure

In the closed system, a 20 mL of mixed solution containing 1.8 mL 0.04 mol L^{-1} Ce(IV) salt, 6.7 mL 0.55 mol L^{-1} H_2SO_4 , 4.5 mL 0.2 mol L^{-1} KBrO_3 , 7.0 mL 0.5 mol L^{-1} malonic acid (MA) was added to the reactor thermostated at 308 ± 0.1 K, then the electrodes were immersed into the reaction mixture solution and the data acquired by computer were recorded. The system gave rise to a regular oscillating profile where the oscillation amplitude and period remained virtually constant. A few microliter of solution containing various amounts of 1-naphthylamine were injected at the moment as the platinum electrode potential dropped to the minimum. Because the lowest position of the regular oscillating profile was the optimal injection point, where the system will respond to the most changes both period and amplitude.

3. Results and discussion

Adding a trace amount of 1-naphthylamine could cause large changes both in the oscillation amplitude and period, the profiles were given as follows:

As shown in Fig. 1b, the perturbed profile would restore in a shorter time, this character offers the analytical application possible. The injection position was chosen generally at the top or the bottom of the profile in order to get the most responses. Before the determination, each injection point must be checked to ensure a good repeatability. The results were such that the changes of ΔT in period and ΔA in amplitude were exactly proportional to the concentration of analyte. That is,

$$\Delta T = T - T_0 \quad (1)$$

$$\Delta A = A - A_0 \quad (2)$$

where T_0 and T are the periods of oscillating profiles before and after injecting 1-naphthylamine, respectively. A_0 and A stand for the amplitudes of the oscillating profile before and after adding 1-naphthylamine, respectively.

3.1. Influence of experimental variables

To obtain the maximum responses of signals, in other words, ΔT and ΔA having the maximum values, the following parameters were examined.

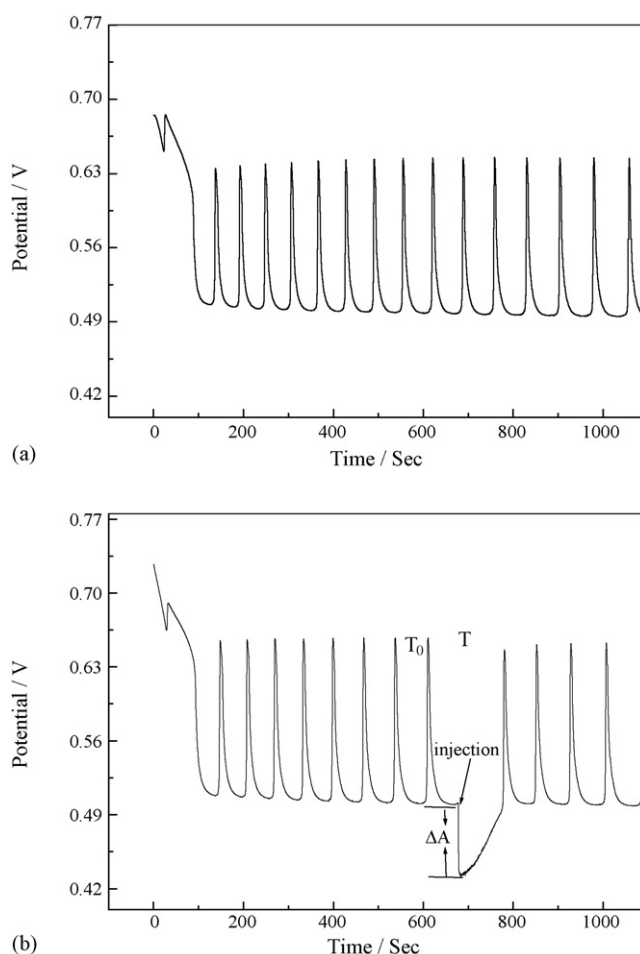


Fig. 1. Typical oscillating profiles before and after perturbation. Common conditions: $[\text{H}_2\text{SO}_4] = 0.56 \text{ mol L}^{-1}$; $[\text{KBrO}_3] = 0.045 \text{ mol L}^{-1}$; $[\text{MA}] = 0.175 \text{ mol L}^{-1}$; $[\text{Ce(IV)}] = 0.0036 \text{ mol L}^{-1}$; $T = 308 \pm 0.1$ K; (a) $[\text{1-naphthylamine}] = 0$; (b) $[\text{1-naphthylamine}] = 1.52 \times 10^{-5} \text{ mol L}^{-1}$.

The effect of the sulfuric acid concentration was studied over the range from 0.5 to 0.8 mol L^{-1} ; as shown in Fig. 2a, the 0.56 mol L^{-1} of sulfuric acid was the optimal choice. Less or more than this value the changes of period and amplitude were decreased significantly.

The concentration of potassium bromate used in the oscillating system was tested from 0.035 to 0.06 mol L^{-1} , showing in Fig. 2b. It was found that the effect of potassium bromate on the change of period difference (ΔT) is more than on the change of amplitude difference (ΔA). If the amounts of potassium bromate used were not enough, the profile would be drifted remarkably, even out of use for determination. An acceptable amount was compromised at 0.045 mol L^{-1} .

Malonic acid is one of the essential substrates in B–Z oscillating system. The effect of amount of malonic acid used, in the presence of 1-naphthylamine with $6.93 \times 10^{-6} \text{ mol L}^{-1}$, on the oscillating profile was examined over the range from 0.150 to 0.200 mol L^{-1} (see Fig. 2c). At the concentration of 0.175 mol L^{-1} , the better responses were obtained both from period and amplitude.

Ce(IV) ion, which was considered as a catalyst, the concentration change was examined over the range from

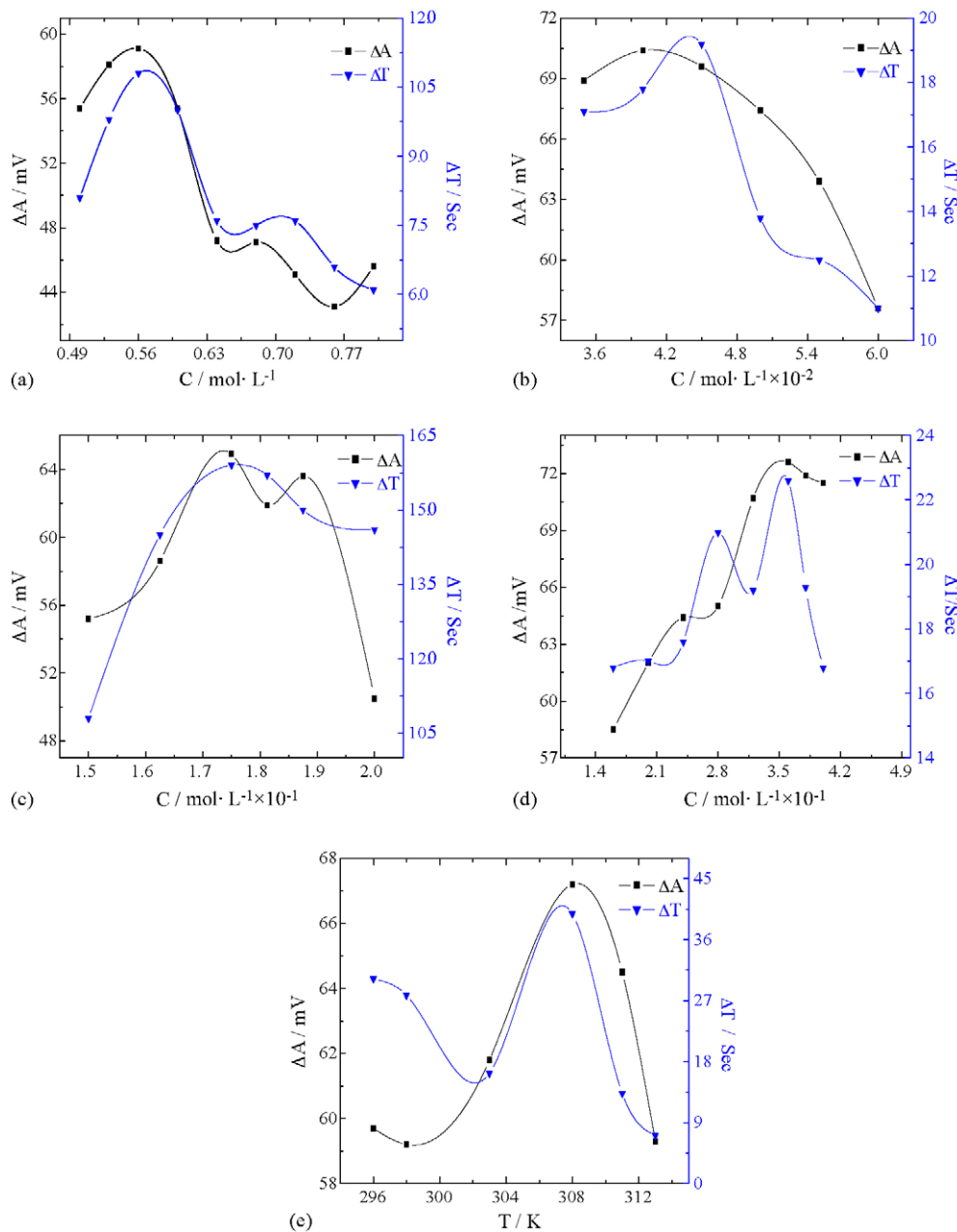


Fig. 2. Influence of: (a) $[\text{H}_2\text{SO}_4]$, (b) $[\text{KBrO}_3]$, (c) $[\text{MA}]$, (d) $[\text{Ce(IV)}]$ and (e) temperature on the oscillating reaction. Common condition: $[\text{1-naphthylamine}] = 6.93 \times 10^{-6} \text{ mol L}^{-1}$. (a) $[\text{KBrO}_3] = 0.055 \text{ mol L}^{-1}$; $[\text{MA}] = 0.188 \text{ mol L}^{-1}$; $[\text{Ce(IV)}] = 0.025 \text{ mol L}^{-1}$; $T = 303 \text{ K}$. (b) $[\text{H}_2\text{SO}_4] = 0.56 \text{ mol L}^{-1}$; $[\text{MA}] = 0.188$; $[\text{Ce(IV)}] = 0.025 \text{ mol L}^{-1}$; $T = 303 \text{ K}$. (c) $[\text{H}_2\text{SO}_4] = 0.56 \text{ mol L}^{-1}$; $[\text{KBrO}_3] = 0.045 \text{ mol L}^{-1}$; $[\text{Ce(IV)}] = 0.025 \text{ mol L}^{-1}$; $T = 303 \text{ K}$. (d) $[\text{H}_2\text{SO}_4] = 0.56 \text{ mol L}^{-1}$; $[\text{KBrO}_3] = 0.045 \text{ mol L}^{-1}$; $[\text{MA}] = 0.175 \text{ mol L}^{-1}$; $T = 303 \text{ K}$. (e) $[\text{H}_2\text{SO}_4] = 0.56 \text{ mol L}^{-1}$; $[\text{KBrO}_3] = 0.045 \text{ mol L}^{-1}$; $[\text{MA}] = 0.175 \text{ mol L}^{-1}$; $[\text{Ce(IV)}] = 0.045 \text{ mol L}^{-1}$.

0.0016 to 0.0040 mol L⁻¹. Fig. 2d showed that the value of 0.0036 mol L⁻¹ was the optimum concentration for determining 1-naphthylamine.

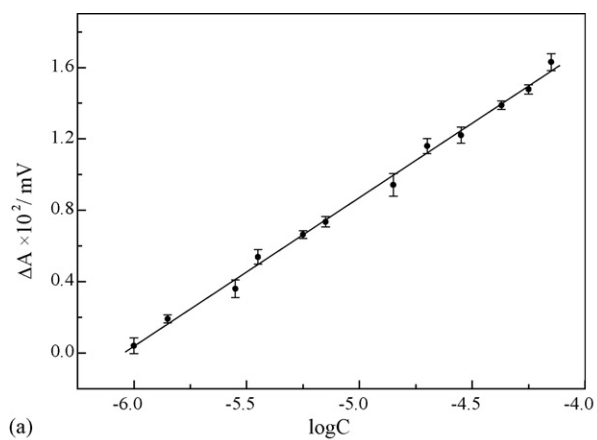
As shown in Fig. 2e, the temperature also played an important role in the oscillation system. From 296 to 308 K, the changes both the ΔT and ΔA were decreased at first and then increased till 308 K. It means that at the temperature of 308 K, the maximum responses to the 1-naphthylamine could be obtained.

Finally, the influence of stirring speed was also considered. With increasing the stirring speed the period would be shortened

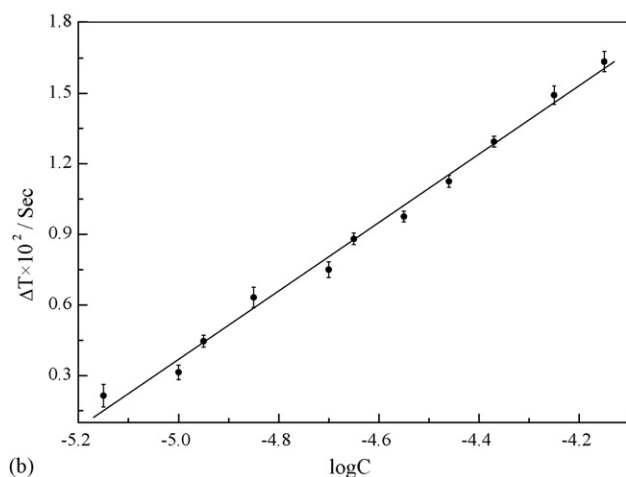
while the amplitude remains constant. In this study, the stirring speed of 300 rpm was adopted.

3.2. Calibration curve

By adding a trace amount of 1-naphthylamine to perturb the oscillating system, changes in the oscillation period and amplitude are quantitatively related to the concentration. Under the optimal conditions mentioned above, the responses to the perturbation can be calculated by using the oscillation period and amplitude; where C is the concentration of 1-naphthylamine.



(a)



(b)

Fig. 3. Calibration curve of ΔA (or ΔT) vs. $\log C$. Common conditions: $[\text{H}_2\text{SO}_4] = 0.56 \text{ mol L}^{-1}$; $[\text{KBrO}_3] = 0.045 \text{ mol L}^{-1}$; $[\text{MA}] = 0.175 \text{ mol L}^{-1}$; $[\text{Ce(IV)}] = 0.045 \text{ mol L}^{-1}$; $T = 308.5 \text{ K}$. (a) $[\text{1-Naphthylamine}] = 1.00 \times 10^{-6}$ to $7.08 \times 10^{-5} \text{ mol L}^{-1}$. (b) $[\text{1-Naphthylamine}] = 7.08 \times 10^{-6}$ to $7.08 \times 10^{-5} \text{ mol L}^{-1}$.

It was found that the relationship between the concentration of 1-naphthylamine and the changes in the amplitude and period followed a simple equation in the ranging from 1.0×10^{-6} to $7.08 \times 10^{-5} \text{ mol L}^{-1}$ (see Fig. 3a); meanwhile, a plot of ΔT against $\log C$ over the range of 7.08×10^{-6} to $7.08 \times 10^{-5} \text{ mol L}^{-1}$ provided the following linear regression equation (see Fig. 3b).

$$\Delta T \text{ (s)} = 763.67 + 145.35 \log C \quad (R = 0.9922, N = 11)$$

$$\Delta A \text{ (mV)} = 504.02 + 83.39 \log C \quad (R = 0.9955, N = 12)$$

3.3. A possible mechanism for 1-naphthylamine perturbations on BZ oscillating system

According to FKN model [5], a simplified interpretation could be proposed with the use of three processes as follows:

- Process I:

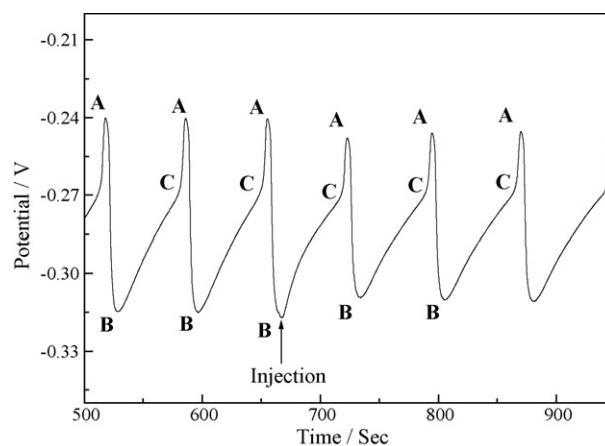
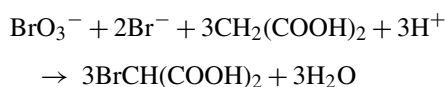
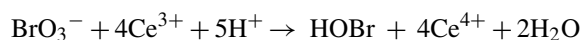
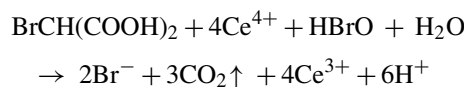


Fig. 4. The oscillation profile recorded by bromide selective electrode.

- Process II:



- Process III:



When the concentration of Br^- ion was high enough, the whole oscillating reactions were dominated by the Process I, showing in position A of the cyclic curve (see point A in Fig. 4). With the reactions prolonging, the concentration of Br^- ion was gradually decreased by the following reactions: $\text{Br}^- + \text{BrO}_3^- + 2\text{H}^+ \rightarrow \text{HBrO}_2 + \text{HOBr}$, which is a rate-controlling step in Process I, and $5\text{Br}^- + \text{BrO}_3^- + 6\text{H}^+ \rightarrow 3\text{Br}_2 + 3\text{H}_2\text{O}$. Furthermore, the bromination reaction of malonic acid with Br_2 was occurred to consume Br^- ion. When the concentration of Br^- ion was reduced enough small, that is, reached a critical value (see point B in Fig. 4), BrO_3^- ion will react with Ce^{3+} ion to start the Process II, in which two intermediate reactions, $\text{BrO}_3^- + \text{HBrO}_2 + \text{H}^+ \rightarrow 2\text{BrO}_2 + \text{H}_2\text{O}$ and $\text{BrO}_2 + \text{Ce}^{3+} + \text{H}^+ \rightarrow \text{HBrO}_2 + \text{Ce}^{4+}$, help the transform from Ce^{3+} to Ce^{4+} ion. Obviously, HBrO_2 is an important intermediate and affects the Process II. Owing to the large accumulation of Ce^{4+} ion, the another reaction between Ce^{4+} ion and $\text{BrCH}(\text{COOH})_2$ would be occurred to regenerate the Br^- ion. That is, Process II was switched automatically to Process III (see point

Table 1

Effect of foreign species on the determination of $8.0 \times 10^{-6} \text{ mol L}^{-1}$ 1-naphthylamine

Foreign species	Tolerated ratio (foreign/1-naphthylamine)
Zn^{2+} , Ni^{2+} , Fe^{2+} and Fe^{3+}	1000
NO_3^- , HPO_4^{2-} and CH_3COO^-	500
Cl^- , I^- ,	100
Methanol, ethanol, formic acid and formaldehyde	50
Sulfanilamide salicylic	20

Table 2
Compared the proposed method with others used for determining 1-naphthylamine

Method	Linear dynamic range (mg L ⁻¹)	Detection limit (mg L ⁻¹)	References
Gas chromatography/mass spectrometry/single ion monitor	0.5–100	0.005	[1]
Spectrophotometry	1.0–20.0	1	[2]
Photometric	0.0014–0.20	–	[4]
Catalytic photometry	0.050–0.5	1.0 × 10 ⁻⁵	[11]
The present work	0.15–1.01	8.07 × 10 ⁻⁴	

C in Fig. 4). When the concentration of Br⁻ ion was reached up to point A, the next new cycle will begin. These are the most simplified interpretation on the oscillating curve by the use a bromide selective electrode to monitor the change of Br⁻ ion concentration in whole oscillating processes, illustrating in the left part of Fig. 4.

The perturbation of 1-naphthylamine on the oscillating profile are very complex, because there are, at least, three reactions between sample and substrates could perhaps occur, such as, in the presence of H₂SO₄, the 1-naphthylamine was easily oxidized to transform 1,4-naphthaquinone, which could react with Br₂ to decrease the concentration of Br⁻ ion and react with Ce³⁺ ion to coordinate to form a complex ion. All of those reactions can change the original boundary conditions to perturb the regularly oscillating profile.

3.4. Interferences

As we know that the oscillating chemical reaction is highly vulnerable to the external species. For the determination of 1-naphthylamine, 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% (R.S.D.) in the determination of 8.0 × 10⁻⁶ mol L⁻¹ 1-naphthylamine, listing in Table 1.

Generally, the inorganic ions and organic compounds with small molecular weight such as methanol, ethanol, formic acid, and formaldehyde have little influence on the determination.

3.5. Comparison with other methods

In order to ensure the sensitivity responsible of the proposed method, 1-naphthylamine was determined by using other techniques, which were listed in Table 2.

3.6. Sample analysis

Six samples were prepared artificially to illustrate the reliability of detecting 1-naphthylamine in this approach, listed in Table 3.

Three given water samples containing 1-naphthylamine of 1.57 × 10⁻⁵, 6.80 × 10⁻⁵, and 5.58 × 10⁻⁶ mol L⁻¹ were detected, respectively. The results by using spectrophotometry and the proposed method are listed in Table 4.

From Tables 3 and 4, it can be seen that the proposed method has higher sensitivity and good reproducibility.

Table 3
Determination results and recovery of 1-naphthylamine in water sample

Sample no. (n=6)	Determine result (mg L ⁻¹)	Added (mg L ⁻¹)	Found (mg L ⁻¹)	Recovery (%)
1	0.329	0.500	0.841	102.4
2	0.361	0.500	0.837	95.2
3	0.235	0.700	0.958	103.3
4	0.218	0.700	0.913	99.3
5	0.112	0.900	1.026	102.0
6	0.107	0.900	1.036	103.2

Table 4
Determination of 1-naphthylamine by using different analyzing methods

Method	Samples (mol L ⁻¹)		
	1.57 × 10 ⁻⁵	6.80 × 10 ⁻⁵	5.58 × 10 ⁻⁶
Spectrophotometry	1.59 × 10 ⁻⁵	6.85 × 10 ⁻⁵	5.62 × 10 ⁻⁶
Present method	1.52 × 10 ⁻⁵	6.93 × 10 ⁻⁵	5.49 × 10 ⁻⁶

4. Conclusion

Compared with other analytical instruments, the set-up used in the proposed method is rather cheap in price. However, the sensitivity and reproducibility are very well. Simple set-up, convenient operation would be easy received by routine analysis. Largely linear range and lower detection limit are able to meet the needs in water sources for determining 1-naphthylamine. Of course, as an analytical method, oscillating chemical reaction would be investigated extremely in future.

Acknowledgements

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