

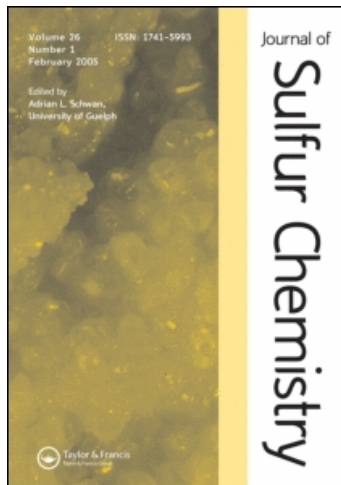
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RESEARCH ARTICLE

Determination of S^{2-} ion by using the B-Z oscillating chemical reaction

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A sensitive and convenient method is described for the determination of trace amounts of S^{2-} ion in aqueous solution based on the classical Belousov-Zhabotinskii (B-Z) oscillating reaction. The results showed that the change in the oscillating period was linearly proportional to the concentration of the S^{2-} ion with a wider range from 7.94×10^{-8} to 3.16×10^{-5} mol·L⁻¹. Various influencing factors are studied and a possible reaction mechanism is also discussed by means of the well-known FKN model. A comparison with the other methods used to determine the S^{2-} ion is given, too.

Keywords: B-Z oscillating reaction; Kinetic determination; Sulfur ion

1. Introduction

The application of Belousov-Zhabotinskii oscillating chemical reaction to analytical chemistry (or commonly called B-Z oscillating reaction) has been summarized [1, 2]. Thinking over its progress, two efforts must be reviewed: One is the early well-known FKN mechanism [3] and the recently theoretical analysis by Taylor [4]; the other is the combination of the “analyte pulse perturbation technique” (APP) and the “continuously stirred tank reactor” (CSTR) to make the use possible [5,6]. The classical B-Z reaction was designed as a redox system consisting of malonic acid (reductant) and potassium bromate (oxidant) in an acidic solution (sulfuric acid). This reaction needs a catalyst (cerium ion Ce^{4+}) to speed up the rate of reaction. During this process, an autocatalytic species $HBrO_2$ was formed to alter the intermediate reaction way. The oxidized cerium ion Ce^{4+} is pale yellow in color and the reduced state Ce^{3+} is clear. The oscillation for this reaction can be clearly observed owing to the change of cerium ion from yellow to clear and back to the yellow. This oscillation can be also recorded by a electrochemical instrumental based on the change of potential or current against the reaction time. The regular oscillating profile looks like the baseline in instrumental analysis. When an analyte was introduced into the oscillating system, the regular oscillating profile

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would be perturbed. And the change (e.g. amplitude, period, or induction time) is directly proportional to the amount of analyte added. With the aid of this relationship between the change of signal and the amount of added analyte, the B-Z oscillating reaction has been used for the determination of various samples.

Although the first paper reported dealing with analytical chemistry [7] was to determine the ruthenium ion, unfortunately, very few works were published on the inorganic ions [7–14] due to the poor sensitivity. Recently, there are two papers [8, 9] concerning the determination of inorganic ions with higher sensitivity, one is using the effect of Tl(I) ion on the transient chaotic regimes and the other is to modify the classical B-Z system with Na₂S solution. It is worth notice that the detection limits in both methods could be down to $1 \times 10^{-12} \text{ mol}\cdot\text{L}^{-1}$. These results imply that the B-Z reaction should be studied intensively as an analytical technique in future.

In the present paper, a convenient and sensitive method for determination of sulfide ion was reported based on the classical B-Z oscillating chemical reaction. The possible mechanism was also discussed.

2. Experimental

2.1 Apparatus

The experimental assembly consisted of an oscillation reactor (ca. 50 mL) and a potential measuring system. The reactor was coupled with a Model 501 thermostat and a Model ML-902 magnetic stirrer to keep the system at $308 \pm 0.1 \text{ K}$. A CHI-832 (CHI, USA) electrochemistry analyzer was connected to the reactor through two Pt electrodes (Rex. 213, China), in which one is as working electrode and the other as counter electrode, and a K₂SO₄ reference calomel electrode (Rex. 217, China) to record the potential changes. A Model 302 bromide selective electrode was used to measure the change of bromide ion concentration.

2.2 Reagents

All chemicals used to create the B-Z oscillating system such as KBrO₃, CH₂(COOH)₂, H₂SO₄, Ce(SO₄)₂·4H₂O, and Na₂S·9H₂O were of analytical-reagent grade and used as received. Solutions of KBrO₃, Ce(SO₄)₂ and CH₂(COOH)₂ were prepared in $0.7 \text{ mol}\cdot\text{L}^{-1}$ sulfuric acid. $0.01 \text{ mol}\cdot\text{L}^{-1} \text{ S}^{2-}$ ion was prepared by Na₂S·9H₂O and standardized by iodimetry and stored in the refrigerator. Working solution was diluted temporarily by the above solution prior to use. Meanwhile, a spectrophotometric method was used to check the concentration again. Doubly distilled water was used throughout in the study.

2.3 Procedure

A mixture solution containing 1.20 mL of $0.040 \text{ mol}\cdot\text{L}^{-1}$ Ce(IV), 6.30 mL of $0.50 \text{ mol}\cdot\text{L}^{-1}$ malonic acid, 6.20 mL of $0.80 \text{ mol}\cdot\text{L}^{-1}$ H₂SO₄ and 6.30 mL of $0.20 \text{ mol}\cdot\text{L}^{-1}$ KBrO₃ were loaded in a 50 mL water-jacket reactor and mixed well by stirring. Meanwhile, the indicator, counter and reference electrodes were immersed into the reaction solution and the data acquisition started. Once a regular oscillating profile was appeared, various amounts of S²⁻ ion were injected to perturb the profile. In order to get an accurate result, the position of adding analyte (or called injection point) should be carefully tested. In general, the position of adding analyte should be chosen at the maximum or minimum amplitude in the regular profile. Repeat adding

analyte at the same position to ensure the reproducibility is the key way for the determination precision. All of these data will be automatically recorded with computer.

3. Result and discussion

Figure 1 shows the potential-time profiles for the oscillating reaction system in the absence of S^{2-} ion perturbation. We found the period of the oscillating immediately increased a lot after some S^{2-} ion was injected into the reaction system. In order to balance perturbation-level on various concentration of S^{2-} ion, we defined a variational ratio of period (P_R) as following:

$$P_R = \frac{T}{T_0}$$

Where T and T_0 represent the periods of the oscillation with and without S^{2-} ion injection, respectively; and it was found that P_R changed linearly to the concentration of S^{2-} ion under certain operating conditions. So, the perturbation of period can be applied to the S^{2-} ion determination.

3.1 Optimization of experimental conditions

In order to evaluate the optimum conditions for determining the S^{2-} ion by B-Z oscillating system, we examined the following factors.

According to FKN model, the B-Z oscillating reaction was carried out in acidic medium and the concentration of H_2SO_4 could affect the shift of profile. Only when the concentration of H_2SO_4 was kept at a certain range, the regularly oscillating profile could be obtained. Too high or too low concentration of H_2SO_4 would make the oscillating profiles irregular. An acceptable range is ranging from 0.5–1.0 mol·L⁻¹ showed in figure 2a, and 0.8 mol·L⁻¹ of H_2SO_4 was chosen in this study.

The effect of $CH_2(COOH)_2$ concentration was studied and the result was exhibited in figure 2b over the range from 0.125–0.175 mol·L⁻¹. If the concentration was more than 0.18 mol·L⁻¹, with increasing the $CH_2(COOH)_2$ concentration, the amplitude increased while the period reduced. The optimum concentration of 0.158 mol·L⁻¹ was chosen.

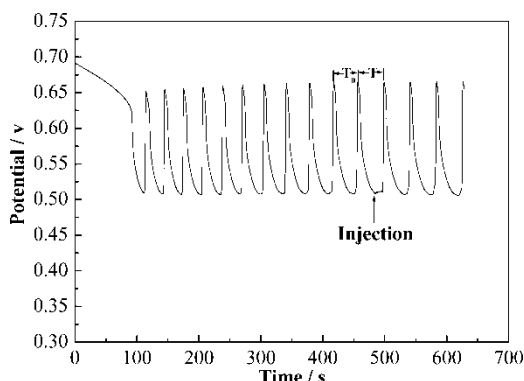


Figure 1. Potential-time profile of B-Z oscillating system after injected S^{2-} ion. Conditions: 0.0024 mol·L⁻¹ Ce^{4+} , 0.158 mol·L⁻¹ $CH_2(COOH)_2$, 0.063 mol·L⁻¹ $KBrO_3$, 0.8 mol·L⁻¹ H_2SO_4 [S^{2-}] = 10^{-7} mol·L⁻¹.

KBrO₃ was another important substrate and its change of concentration from 0.06 to 0.07 mol·L⁻¹ was examined (see figure 2c). It was found that if the concentration was more than 0.07 mol·L⁻¹, the amplitude become larger and the period shorter. Less than 0.06 mol·L⁻¹, the change both amplitude and period went to the other way round. Thereby, in this work a 0.063 mol·L⁻¹ of KBrO₃ was accepted.

The concentration of Ce⁴⁺, which was considered as a catalyst, was studied in the range of 0.0014–0.0030 mol·L⁻¹. Figure 2d showed the high sensitivity for determining S²⁻ ion was appeared at the Ce⁴⁺ concentration of 0.0024 mol·L⁻¹.

Besides the above variables, the temperature and the speed of stirring are also able to affect the oscillating profile. As showing in figure 2e, the temperature of 308 K and the stirring speed of 480 r/min would be the optimum choice for the determination of S²⁻ ion.

In sum, the following variables, *e.g.*, 0.0024 mol·L⁻¹ Ce⁴⁺, 0.158 mol·L⁻¹ malonic acid 0.8 mol·L⁻¹ H₂SO₄ 0.063 mol·L⁻¹ KBrO₃, 308 K and 480 r/min were considered as the optimum conditions for the determination of S²⁻ ion.

3.2 Determination of S²⁻ ion

Under the optimum conditions mentioned above, injecting different amounts of S²⁻ ion into the oscillating systems to perturb the regularly oscillating profile, a group data of P_R was obtained. A plot of P_R against -logC, (where C refers to the concentration of S²⁻ ion), exhibits a well linear relationship and it was obeyed the following equation (RSD < 5%) (figure 3):

$$P_R = 1.64 - 0.085 \times (-\log C); (N = 12, R = 0.9989)$$

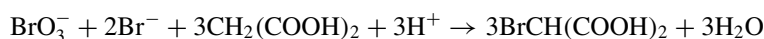
3.3 Interference study

In practice, the real water sample often contains a lot of other substances soluble. Thus, the common inorganic ions and a few of organic compounds with small molecular weight should be tested as foreign species listed in table 1. It was found that the concentration of 1000-fold of Zn²⁺, Mn²⁺, Ni²⁺, Fe²⁺, Fe³⁺ and 800-fold of MnO₄⁻, Cr₂O₇²⁻, NO₃⁻, HPO₄²⁻, CH₃COO⁻, as well as 200 fold NO₂⁻, F⁻ have no any interference the determination of S²⁻ ion. When the concentration of S²⁻ ion was more than 1.85 × 10⁻⁷ mol·L⁻¹, 80 fold of Cl⁻, I⁻ and 50 fold of methanol, ethanol, formic acid, formaldehyde are also tolerance.

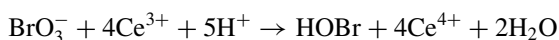
3.4 Possible mechanism

According to FKN model [3,4], a simplified interpretation could be proposed with the use of three processes as follows:

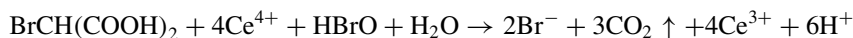
Process I:



Process II:



Process III:



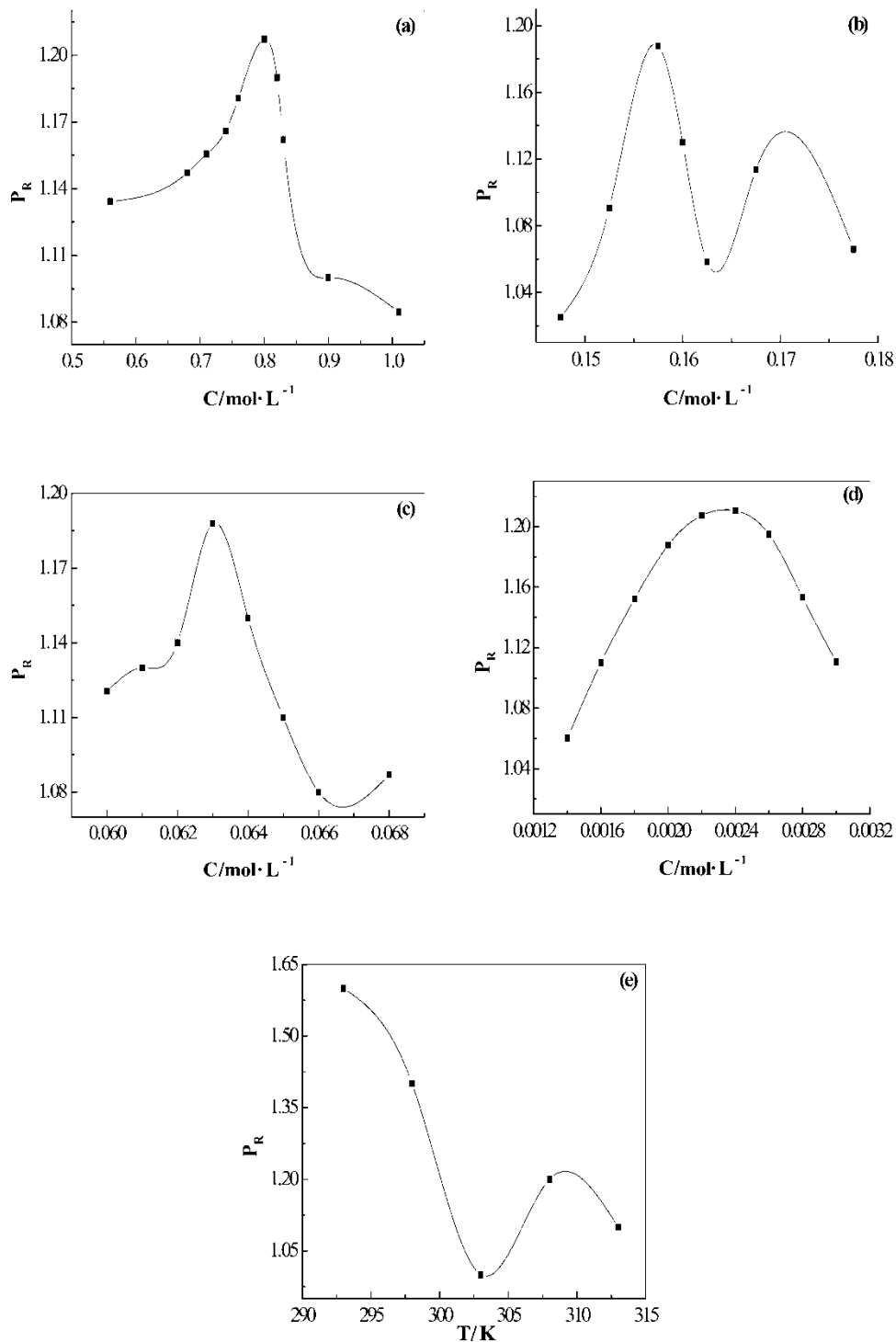


Figure 2. Influence of concentration of (a) H_2SO_4 ; (b) $\text{CH}_2(\text{COOH})_2$; (c) KBrO_3 ; (d) Ce(IV) ; (e) and the temperature on the oscillating profiles. Common condition: $[\text{S}^{2-}] = 10^{-5} \text{ mol}\cdot\text{L}^{-1}$; a) $0.002 \text{ mol}\cdot\text{L}^{-1} \text{ Ce}^{4+}$, $0.168 \text{ mol}\cdot\text{L}^{-1} \text{ CH}_2(\text{COOH})_2$, $0.062 \text{ mol}\cdot\text{L}^{-1} \text{ KBrO}_3$ $T = 308 \text{ K}$; b) $0.002 \text{ mol}\cdot\text{L}^{-1} \text{ Ce}^{4+}$, $0.062 \text{ mol}\cdot\text{L}^{-1} \text{ KBrO}_3$, $0.8 \text{ mol}\cdot\text{L}^{-1} \text{ H}_2\text{SO}_4$ $T = 308 \text{ K}$; c) $0.002 \text{ mol}\cdot\text{L}^{-1} \text{ Ce}^{4+}$, $0.158 \text{ mol}\cdot\text{L}^{-1} \text{ CH}_2(\text{COOH})_2$, $0.8 \text{ mol}\cdot\text{L}^{-1} \text{ H}_2\text{SO}_4$ $T = 308 \text{ K}$; d) $0.158 \text{ mol}\cdot\text{L}^{-1} \text{ CH}_2(\text{COOH})_2$, $0.063 \text{ mol}\cdot\text{L}^{-1} \text{ KBrO}_3$, $0.8 \text{ mol}\cdot\text{L}^{-1} \text{ H}_2\text{SO}_4$ $T = 308 \text{ K}$; e) $0.0024 \text{ mol}\cdot\text{L}^{-1} \text{ Ce}^{4+}$, $0.158 \text{ mol}\cdot\text{L}^{-1} \text{ CH}_2(\text{COOH})_2$, $0.063 \text{ mol}\cdot\text{L}^{-1} \text{ KBrO}_3$, $0.8 \text{ mol}\cdot\text{L}^{-1} \text{ H}_2\text{SO}_4$.

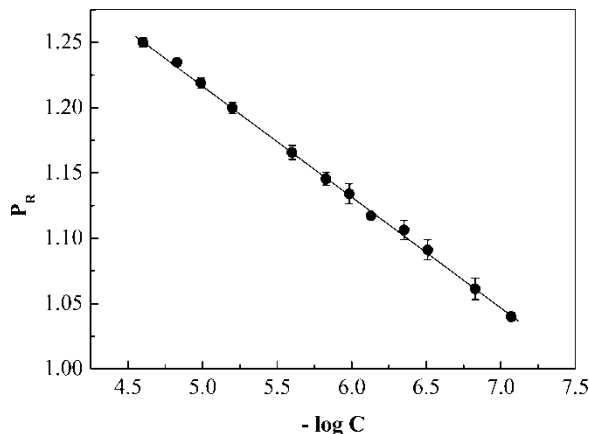


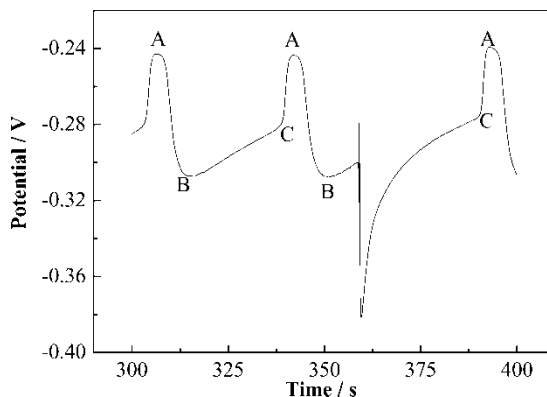
Figure 3. Calibration curve of P_R versus $-\log C$ (C means concentration of S^{2-} ion in oscillating system) ranging from 7.94×10^{-8} to 3.16×10^{-5} mol·L $^{-1}$.

Table 1. Effect of foreign species on the determination of 5×10^{-7} mol·L $^{-1}$ S^{2-} ion.

Foreign species	Tolerated ratio (foreign/ S^{2-})
Zn $^{2+}$, Mn $^{2+}$, Ni $^{2+}$, Fe $^{2+}$, Fe $^{3+}$	1000
MnO $_4^-$, Cr $_2$ O $_7^{2-}$, NO $_3^-$, HPO $_4^{2-}$, CH $_3$ COO $^-$	800
NO $_2^-$, F $^-$	200
Cl $^-$, I $^-$	80
Methanol, Ethanol, Formic acid, Formaldehyde	50

When the concentration of Br $^-$ ion was enough high, the whole oscillating reactions were dominated by the Process I, showing in position A of the cyclic curve (see point A in figure 4). With the reactions prolonging, the concentration of Br $^-$ ion was gradually decreased by the following reactions: Br $^-$ + BrO $_3^-$ + 2H $^+$ \rightarrow HBrO $_2$ + HOBr, which is a rate-controlling step in Process I, and 5Br $^-$ + BrO $_3^-$ + 6H $^+$ \rightarrow 3Br $_2$ + 3H $_2$ 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 low, that is, reached a critical value (see point B in figure 4), BrO $_3^-$ ion will react with Ce $^{3+}$ ion to start the Process II, in which two intermediate reactions, BrO $_3^-$ + HBrO $_2$ + H $^+$ \rightarrow 2BrO $_2$ + H $_2$ O and BrO $_2$ + Ce $^{3+}$ + H $^+$ \rightarrow HBrO $_2$ + 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, another reaction between Ce $^{4+}$ ion and BrCH(COOH) $_2$ would be occurred to regenerate the Br $^-$ ion. That is, Process II was switched automatically to Process III (see point C in figure 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 illustrating in the left part of figure 4.

The reduction ability of S $^{2-}$ ion is stronger than Ce $^{3+}$ ion. Adding S $^{2-}$ ion to the above oscillating system, Process II would be perturbed remarkably to cause S $^{2-}$ reacting with BrO $_3^-$. The result was that the regeneration of Br $^-$ ion would be ceased until the S $^{2-}$ ion is used up, and then, the regular cycle started (see the right part in figure 4). The perturbed profile is easy to be restored so that a regularly oscillating profile can be used many times for determination.

Figure 4. Single oscillating cycle of $[Br^-]$.Table 2. Determination of S^{2-} ion in artificial water sample.

Sample No:	Concentration (mol·L ⁻¹)	Added (mol·L ⁻¹)	Spectrometry (mol·L ⁻¹)	Present method (mol·L ⁻¹)	Recovery (%)
1	1.85×10^{-7}	0	1.80×10^{-7}	1.81×10^{-7}	98.09
2	1.85×10^{-7}	1.85×10^{-6}	2.03×10^{-6}	2.00×10^{-6}	98.46
3	1.85×10^{-7}	9.25×10^{-6}	9.44×10^{-6}	9.46×10^{-6}	100.26
4	1.85×10^{-7}	1.23×10^{-5}	1.25×10^{-5}	1.27×10^{-5}	103.24

Table 3. Methods of determination of sulfide.

Method	Linear dynamic range(mol·L ⁻¹)	Reference
Extraction Catalytic Kinetic Spectrophotometric method	1.56×10^{-8} – 2.80×10^{-7}	15
Reverse flow-injection chemiluminescence method	2.50×10^{-8} – 1.56×10^{-4}	16
Catalytic photometric determination method	3.12×10^{-8} – 3.75×10^{-7}	17
Methylene blue spectrophotometric method	6.25×10^{-7} – 1.25×10^{-6}	18
Mercuric nitrate-dithione spectrophotometric method	1.56×10^{-7} – 2.19×10^{-5}	18
Present method	7.94×10^{-8} – 3.16×10^{-5}	

3.5 Sample analysis

An artificial sample containing the following inorganic ions such as 1.85×10^{-7} mol·L⁻¹ of S^{2-} , 1×10^{-6} mol·L⁻¹ of Cl^- , 1×10^{-6} mol·L⁻¹ of I^- , 1×10^{-6} mol·L⁻¹ of Na^+ and 1×10^{-6} mol·L⁻¹ of K^+ , was determined by spectrophotometric method [18]. At the same time, it was also examined by means of the proposed method. The results were listed in table 2. Table 3 gave the linear ranges for determination of S^{2-} ion by the aid of various methods. It is obvious that the proposed method was able to meet the need of commonly routine analysis.

4. Conclusion

Sulfide was existed widely in water sources. The determination of S^{2-} ion has been recognized as a routine analysis in many fields. Compared with the other techniques, the proposed method has some of advantages such as simple set-up and convenient operation, good reproducibility,

as well as largely linear range and lower detection limit. All the characters are able to match the needs in routine analysis.

Acknowledgement

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