



The Potentiometric Effect of As(III) Ion on a Belousov–Zhabotinskii Oscillating Chemical Reaction. Application to the Determination of As(III)

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A novel analytical method that builds on specific features of non-linear chemical systems far from thermodynamic equilibrium is described. The used oscillating chemical system is the BZ (Belousov–Zhabotinskii) reaction in a non-equilibrium stationary state close to a bifurcation point. The method uses a Pt electrode for monitoring the potential response to a perturbation caused by As(III) ion. A linear response, in which the oscillating amplitude varies versus the logarithm of the As(III) concentration, was found in the range of 1.99×10^{-6} – 1.27×10^{-4} M. Under optimum conditions, a detection limit of 2×10^{-6} M for As(III) was obtained. The relative standard deviation (%RSD) for As(III) 1.59×10^{-5} M is 7.1 ($n = 6$).

Oscillating reactions are complex chemical systems that have aroused enormous interest since their discovery. Ever since Lotka developed what was probably the earliest chemical oscillator in 1920¹ a wide variety of oscillating reactions taking place in liquid and gas phases have been described, as have several mechanisms intended to account for the oscillating behaviour.²

These reactions involve a large number of chemical species, which can be categorized as reactants, products, and intermediates, that interact via unusual mechanisms.^{3,4} During an oscillating chemical reaction, the concentrations of reactants decrease and the concentrations of intermediates or catalyst species execute oscillation (sometimes over several orders of magnitude).⁴

The best known and most widely studied oscillating chemical systems is that based on the Belousov–Zhabotinskii (BZ) reaction,⁵ which was named after two Russian scientists who first studied the oscillatory chemical phenomenon. This reaction involves the oxidation of an organic species such as malonic acid by an acidified bromate solution in the presence of a metal ion catalyst. Among the catalysts, Ce(III)–Ce(IV) and $[\text{Fe}^{\text{II}}(\text{phen})]^{2+}$ – $[\text{Fe}^{\text{III}}(\text{phen})]^{3+}$ (ferroin–ferrin) couples are two of the most widely used catalysts. In a closed (batch) system, the B–Z system exhibits a short induction period, followed by an oscillatory phase. The colour of the solution alternates between yellow and colourless (for the Ce(III)–Ce(IV) couple) over a period of approximately 1 min. The oscillations may last over 2 h. Ultimately, with concentrations of the major reactants such as potassium bromate and malonic acid decreasing continuously during the reaction process, the system progresses in the direction of decreasing Gibbs free energy. As a consequence, the oscillations die out and the system then drifts slowly and monotonically towards its chemical equilibrium state.

Zhabotinskii obtained a linear correlation between the reactant concentration and the period of the BZ reaction and proposed the use of this phenomenon for chemical analysis. The first paper concerning the use of regular chemical oscillations

for the determination of trace amounts of ruthenium(III) ion was published in 1978.⁶ Since then, the advantages of the application of non-linear chemical systems under far from equilibrium conditions in quantitative analysis have been reported for numerous species including Cl^- ,⁷ Hg^{2+} and Ti^{3+} ,⁸ $\text{Fe}(\text{CN})_6^{3-}$,^{3,9} ascorbic acid,¹⁰ hydroquinone,¹¹ and a few others.

It is well known that arsenic compounds are highly toxic and strongly affect biochemical and physiological processes. In many initial substances, end products, and environmental material the concentration of arsenic is limited by national and international standards.¹² The toxicity and/or essentiality of this element depends not only on concentration, but also on the chemical forms (speciation).^{1,13} Many different sensitive and selective methods have been proposed for the determination of trace amounts of arsenic.¹⁴

In this paper, we have investigated the effect of arsenic(III) ion on the oscillating properties of the “ BrO_3^- –malonic acid– H_2SO_4 –Ce(IV)” (BZ) oscillatory system as a matrix for the determination of As(III) ion concentration. For this purpose, the influence of different variables on the As(III) perturbation were first optimized for the BZ oscillating system. Finally, a logarithmic calibration curve was obtained for As(III) ion.

1. Experimental

1.1. Reagents. All reagents were analytical grade (Fluka) and used without further purification. All stock solutions of KBrO_3 , malonic acid, KBr , H_2SO_4 , and Ce(IV) salt were separately prepared in doubly distilled water. In any experiment, the reaction mixture was obtained by diluting stock solutions, properly. For analytical injection, we used an ion standard solution of As(III) (Fluka).

1.2. Apparatus. The experimental set-up used to implement the oscillating reaction consisted of a glass reaction vessel furnished with a thermostated jacket connected to a “polystat CCI” thermostat (Huber) and a magnetic stirrer (Jank & Kunkel). An “Ion-Analyzer 250” (corning) and a “E 586 labograph” x–y recorder (Metrohm) were used to record the potential changes. The elec-

trode system was a platinum electrode as an indicator and an Ag/AgCl electrode as a reference electrode, with a laboratory-constructed agar salt bridge containing 0.1 M KNO₃.

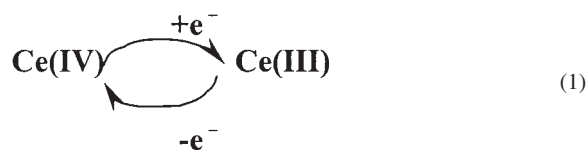
1.3. Procedure. The water-jacketed glass vessel was loaded with 2 mL of 0.35 M KBrO₃, 4 mL of 2 M malonic acid, 0.5 mL of 0.2 M potassium bromide, and 3 mL of 5 M H₂SO₄. After the solution had reached to thermal equilibrium (40 ± 0.1 °C), the electrodes were inserted into the solution with continuous and steady stirring. Then, the last species, that is 0.5 mL of 0.15 M Ce(IV), was added into the system. To prepare stock solution of Ce(IV), we dissolved 0.8223 g of (NH₄)₂Ce(NO₃)₆ in 10 mL of doubly distilled water. The total volume of reaction mixture always was 10 mL.

After adding the Ce(IV) solution, the oscillations were potentiometrically recorded. After the steady state had been reached, the system was perturbed by injecting a 0.5 mL sample of different concentrations of As(III) solution. Different stock solutions of As(III) were prepared from an arsenic(III) ion standard solution.

Changes in the oscillation amplitude, following perturbation, were used as an analytical signal that was investigated and used to construct the calibration plot.

Based on the FKN mechanism,¹⁵ two species were oscillating, Br⁻ and Ce(IV). Oscillations in Br⁻ concentration can be monitored using a Br⁻-ion selective electrode versus a reference electrode. Then, the oscillation is recorded.

One of cycles in this reaction is:



This causes variations in the medium potential. This variation in concentration and potential can be followed with a Pt electrode. On the other hand, we can measure potential due to redox couple of (Ce(IV)/Ce(III)) on the Pt electrode versus the reference electrode. We used the second method in this research.

The effect of different variables on the oscillating reaction was studied in order to establish the optimum working conditions for determination of interesting species. In order to ensure maximum sensitivity and precision of the determination, the influence of selected experimental variables in the presence and absence of analyte were investigated using different methods. For this purpose, we measured the difference in amplitude between the first oscillation after analyte injection (A) and the oscillation amplitude immediately before injection (A₀) and chose this difference as the analytical signal:

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

Figure 1 shows typical oscillation profiles obtained for the proposed oscillating chemical system in the absence and presence of an As(III) perturbation under the above described experimental conditions.

2. Results and Discussion

2.1. Effect of Variables on the Oscillation Perturbation.

Point of Injection: In order to ensure accurate and highly sensitive results, where the injection was performed was a crucial variable. During a typical oscillation cycle (Fig. 1), the potential dropped to a minimum (zone A) and then increased gradu-

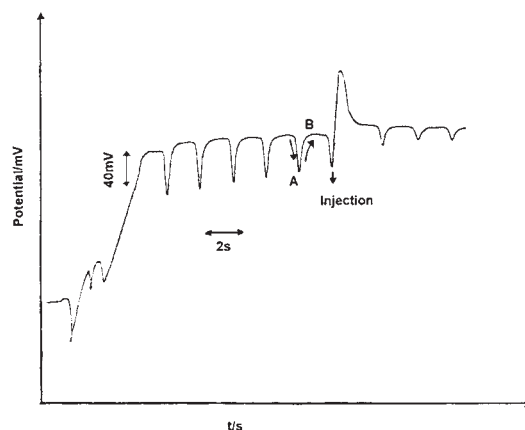


Fig. 1. A typical perturbation of As(III). 0.07 M KBrO₃, 1 M malonic acid, 10⁻⁴ M KBr, 0.75 M H₂SO₄ and 7.5 × 10⁻³ M Ce(IV) at 40 °C.

ally to the starting value (zone B), after which a new cycle began. For the effect of an As(III) perturbation to be large, we found the analyte should be injected at the potential minimum as the system began to return to the starting value.

KBrO₃: Increasing the KBrO₃ concentration from 0.02 to 0.25 M caused an increase in the amplitude and frequency of the the oscillations. Variation of the KBrO₃ concentration strongly affected the analyte perturbation also (Fig. 2a). In 0.07 M KBrO₃, the sensitivity to As(III) was maximum.

Malonic Acid: The effect of malonic acid was studied over the range from 0.4 to 1.2 M. The oscillation amplitude decreased, but the frequency increased with increasing malonic acid concentration. As can be seen from Fig. 2b, there is an optimum concentration (0.8 M) where the system responded to the analyte perturbation.

KBr: On the basis of the FKN mechanism,¹⁵ Br⁻ is an intermediate and plays an important role in the feedback mechanism and oscillation, and appears and disappears during the reaction. Br⁻ isn't required as a reactant to start the reaction, but decreases the induction period and the experiment time.¹⁶ As can be seen in Fig. 2c, the effect of Br⁻ on the analyte perturbation was studied over the range of 5 × 10⁻⁵ to 5 × 10⁻² M. As expected, Br⁻ didn't strongly affect the amplitude. However, 0.01 M Br⁻ concentration was chosen as the optimum.

H₂SO₄: Based on the BZ reaction and FKN mechanism, the reaction should take place in a strongly acidic medium.¹⁶ Therefore, the oscillating properties and sensitivity were investigated in the range of 0.5 to 2.5 M H₂SO₄ (Fig. 2d).

Ce(IV): The BZ reaction is catalyzed by a metal ion. In this work, Ce(IV) catalyzed the BZ reaction. For this purpose, the Ce(IV) concentration should be optimized. It was investigated in the range of 10⁻³ to 10⁻² M concentrations, with 7.5 × 10⁻³ M chosen as the optimum (Fig. 2e).

Effect of Temperature: Because of the kinetic mechanism, temperature strongly affects not only the original system but also the analyte perturbation signal. Therefore, we evaluated the effect of temperature on the BZ system and analyte signal. As can be seen in Fig. 3, at lower temperatures analyte injection caused an induction period that increased with decreasing temperature. At different temperatures, the analyte signal

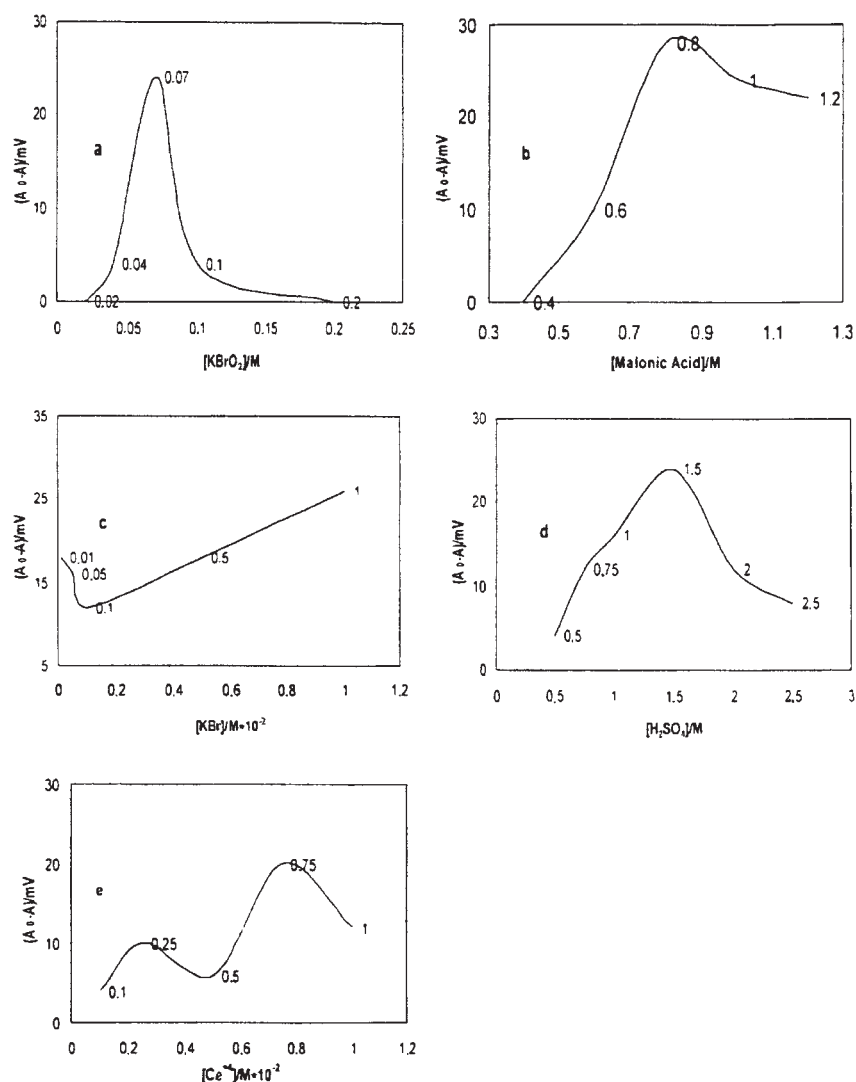


Fig. 2. Influence of (a) KBrO_3 , (b) malonic acid, (c) KBr , (d) H_2SO_4 , (e) Ce(IV) on the As(III) perturbation. Condition: (a) 1 M malonic acid, 0.01 M KBr , 0.75 M H_2SO_4 and 7.5×10^{-3} Ce(IV) ; (b) 0.07 M KBrO_3 and the others such as (a); (c) 0.07 M KBrO_3 , 1 M malonic acid and the others such as (a); (d) 0.07 M KBrO_3 , 1 M malonic acid, 10^{-4} M KBr , 7.5×10^{-3} Ce(IV) ; (e) 1.5 M H_2SO_4 and the others such as (d); all at 40°C .

$(A_0 - A)$ was different also. Therefore, a constant temperature was necessary for obtaining a stable background for optimum sensitivity. We kept the temperature constant at 40°C , the temperature with a maximum signal.

2.2. Determination of Arsenic. The oscillating system was perturbed with various concentrations of As(III) under the above described optimum conditions. When As(III) is added to the system, the oscillation period increased slightly, but the amplitude of oscillation almost decreased (Fig. 1). Several repeated experiments indicated that there is a good linear relationship between the changes in the oscillation amplitude (ΔA) and the logarithm of As(III) concentration in the range of 1.99×10^{-6} to 1.27×10^{-4} M (Fig. 4). If the As(III) concentration is below 1.99×10^{-6} M, the effect can hardly be measured, and if the concentration of As(III) exceeds 1.27×10^{-4} M the decrease in oscillation amplitude doesn't hold a linear relationship with logarithmic concentration.

The calibration data obeys the following logarithmic regres-

sion equation:

$$\Delta A = 2.8603 \log[\text{As}] \times 10^4 + 17.89. \quad (3)$$

The detection limit was found to be 2×10^{-6} M (according to the IUPAC method).¹⁷ Table 1 shows our work versus other As(III) determinations.

2.3. Interferences. We investigated the effect of more than 15 foreign ions that may exist with As(III) in real samples for their possible influence on the determination of As(III) ion concentration in the above described optimum conditions. According to Table 2, large amounts of some cations and anions such as alkali and alkaline earth ions, La^{3+} , Pb^{2+} , Cu^{2+} , and NO_3^- , H_2PO_4^- , HPO_4^{2-} have no effect on the determination, but ions such as I^- , Cl^- and Hg^{2+} have a large effect on the determination.

2.4. Proposed Mechanism for Arsenic(III) Ion Perturbation. According to the famous FKN mechanism proposed by Field et al.,¹⁵ there are two major processes (process A

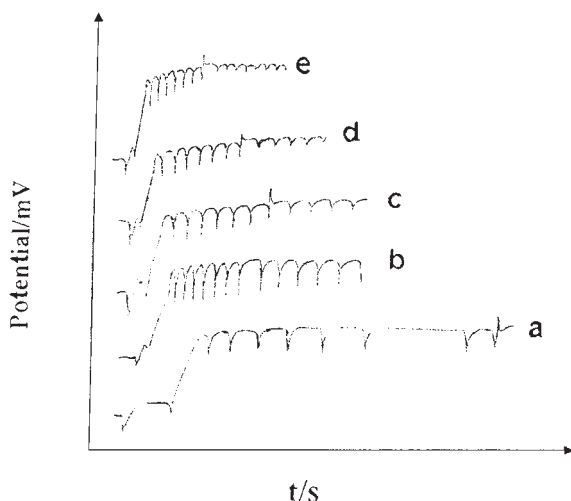


Fig. 3. Influence of temperature on BZ reaction and As(III) perturbation. (a) 32 °C, (b) 35 °C, (c) 37.5 °C, (d) 40 °C, (e) 45 °C. 0.04 M KBrO₃, 1 M malonic acid, 10⁻⁴ M KBr, 1.5 M H₂SO₄ and 0.1 M Ce(IV).

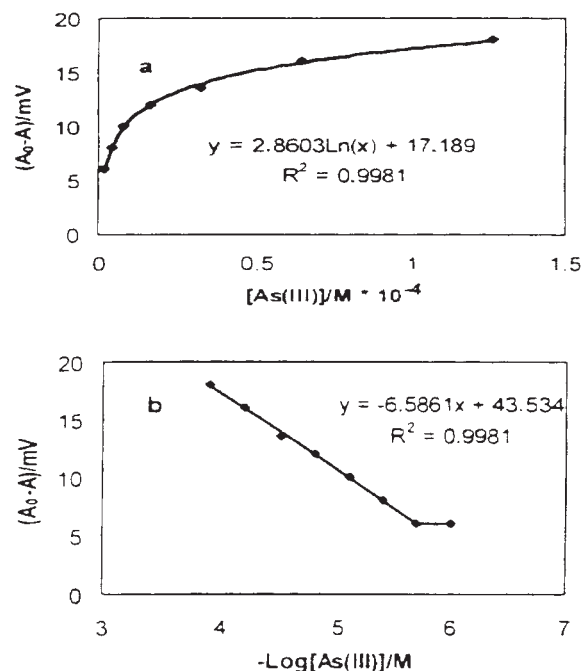


Fig. 4. Calibration curve for determination of As(III). (a) Signal versus concentration of As(III) and (b) signal versus negative of logarithmic concentration of As(III).

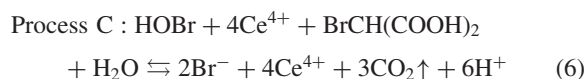
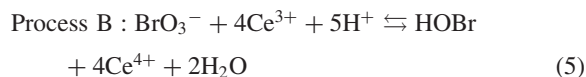
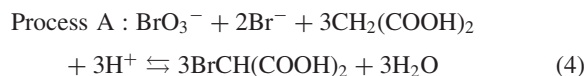
Table 1. Comparing This Work Results with Some Other Researches

Method	Detection Limit	Dynamic Range	%RSD	Reference
Spectrophotometry	0.003 mg L ⁻¹	0.008–0.12 mg L ⁻¹	2–8%	17
Stripping voltammetry	6.3 × 10 ⁻⁷ M	10 ⁻⁷ –10 ⁻⁶ M	—	18
Hidride generation-glow discharge	0.2 mg L ⁻¹	up to 250 mg L ⁻¹	2.1%	19
-optical emission				
Coulometric stripping	—	0.01–2 mg L ⁻¹	—	20
potentiometry				
Liquid chromatography	0.07 mg L ⁻¹	—	—	21
Anodic stripping-voltammetry	0.19 ppb	—	2%	22
Titration of As(III) with electrogenerated iodine	7 × 10 ⁻⁶ M	—	—	23
BZ oscillating reaction	2 × 10 ⁻⁶ M	1.99 × 10 ⁻⁶ –1.27 × 10 ⁻⁴ M	7.1%	This work

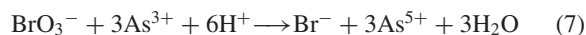
Table 2. Effect of 18 Foreign Ions on the Determination of 2 × 10⁻⁵ M As(III)

Foreign ion	Maximum of tolerated molar ratio
La ³⁺ , Fe ²⁺ , Pb ²⁺ , Cu ²⁺ , NO ₃ ⁻ , H ₂ PO ₄ ⁻	2500
Ca ²⁺ , K ⁺ , Na ⁺ , Mg ²⁺ , HPO ₄ ²⁻	2000
Zn ²⁺ , Mn ²⁺ , Cd ²⁺ , Ag ⁺	4500
Cl ⁻ , I ⁻	15
Hg ²⁺	2

and process B) which alternately control the B–Z reaction and result in oscillations in the concentration of the intermediate species (Ce(IV) and Br⁻). In addition, a third process (process C) links processes A and B as following:



As is well known, As(III) ion is oxidized in strongly acidic medium, which suggests that BrO₃⁻ oxidizes As(III) to As(V) in concentrated sulfuric acid according to the reaction:



Thus, the perturbation effect of As(III) includes decreasing the bromate ion concentration. As mentioned above (process

B), decreasing the bromate ion concentration leads to a decrease in the Ce(IV) concentration as a product of this process. Thus, the concentration of Ce(IV) in the system decreases, and that of Ce(III) increases, so the value of $\ln([Ce(IV)]/[Ce(III)])$ as a potentiometric signal sharply decreases and the potential oscillations are seen to decrease.

3. Conclusion

As described above, kinetic methods of analysis, especially chemical reactions, are currently regarded as highly effective tools in analytical chemistry. Thus, we attempted to determine As(III) ion using its perturbation effect on the classic BZ reaction, because of its possible effect on BrO_3^- ion concentration in the oscillating reaction.

As expected, injection of As(III) solution changed the oscillating amplitude. This change had a logarithmic relationship with As(III) concentration. Comparing the results with other methods (Table 1) shows that, although this method doesn't have the most ideal analytical attributes (e.g., detection limit, %RSD, ...), the results are acceptable and comparable with other results. This aside, the largest advantage of this technique is its simplicity and instrumental set-up.

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