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Application of Oscillating Chemical Reaction to Analytical Chemistry: Recent Developments

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Abstract: This mini-review is limited in the real application of oscillating chemical reaction to analytical chemistry and it covers the research published from 1999 to 2004; a few of papers appeared in the early of 2005 were also included. The most used system was the Belousov-Zhabotinksy (B-Z) reaction. Some of methods were designed based on the Cu (II)-catalysed oscillating chemical reaction. The analytes include both organic and inorganic substances. Simple and convenient, rapidness and good reproducibility are the characteristics of the present technique. Largely linear range and lower detection limit are of benefit to the use in the really routine analysis.

Key words: Belosouv-Zhabotinsky reaction, oscillating chemical system, analytical method, review

INTRODUCTION

The first study dealing with the application of oscillating chemical reaction to analytical chemistry by Tikhonova *et al.*[1]. Then Jimenez-Prieto *et al.*[2] proposed an Analyte Pulse Perturbation Technique (APP) to promote the potentials in practical determination and they gave a critical review in 1998 in this field[3]. A recent review on the mechanism of oscillating chemical reaction was reported by Taylor[4], in which a detail analysis of the Belousov-Zhabotinksy (B-Z) reaction was made, meanwhile, the other reactions were also referenced. Therefore, this mini-review was just limited in really analytical application over a period from 1999 to 2004; a few of papers appeared in the early of 2005 were also included. That is to say, in the present paper we do not consider the history, the theory and the application of oscillating chemical reaction in other areas. Wherever, the oscillating phenomenon exists throughout nature such as heartbeat, breath, even the sleep cycle. A life process is a quite complex organism, concerning many subjects; one of them is chemical reaction. Using an oscillating chemical reaction in laboratory to understand the complex oscillating process in nature, at least, is an approach or idea. Perhaps, this is why this object is attracting many researchers.

Belousov-zhabotinsky oscillating chemical system: As an analytical tool, the most commonly used reaction is the Belousov-Zhabotinksy reaction. Up to now, it is one of the widely studied reaction systems. The original Belousov-Zhabotinsky 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. 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 instrument based on the change of potential or current against the reaction time. A potential-time curve as an example (Fig. 1).

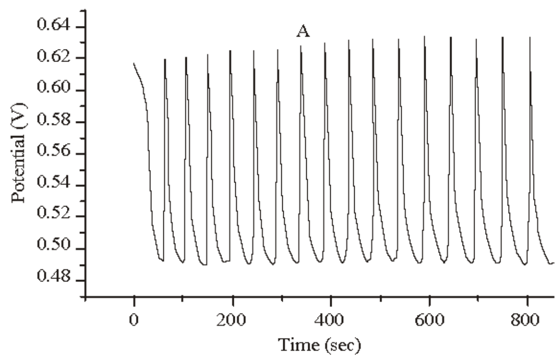

Fig. 1: The curve of potential against time
$[KBrO_3]$=0.2 M, $[CH_2(COOH)_2]$=0.5 M, $[Ce(SO_4)_2]$=0.04 M, $[H_2SO_4]$=0.8 M, T=303K

The general reaction is

$$2BrO_3^- + 3CH_2(COOH)_2 + 2H^+ = 2BrCH(COOH)_2 + 3CO_2\uparrow + 4H_2O$$

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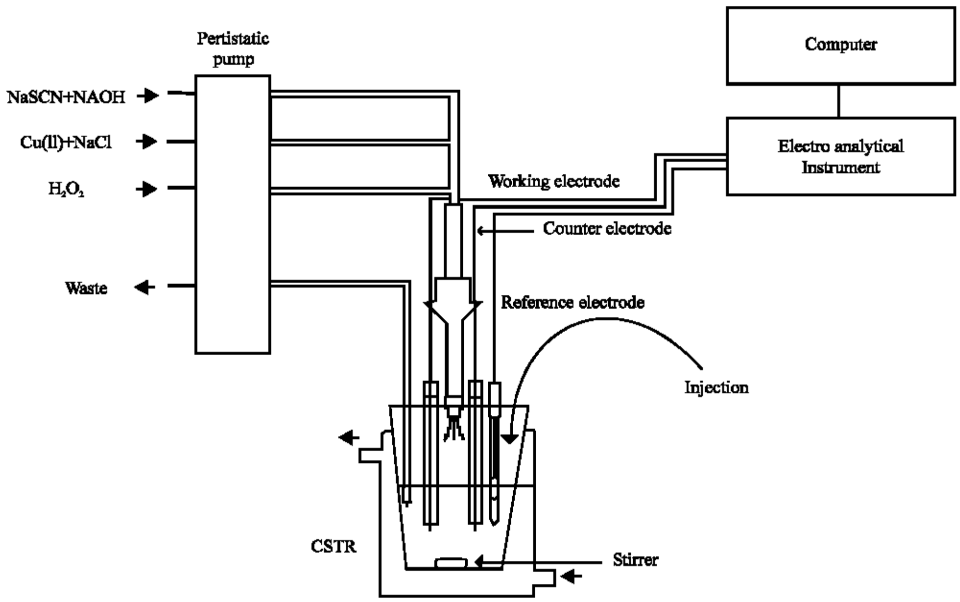

Fig. 2: A scheme of Continuously Stirred Tank Reactor (CSTR) for Cu (II)-catalysed oscillating reaction

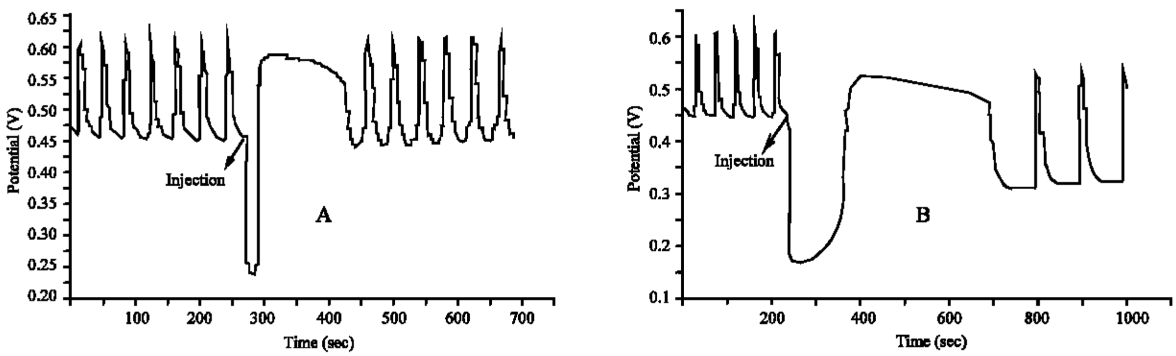

Fig. 3A and B: Addition of sodium diphenylamine sulfonate to perturb the B-Z oscillating system

A: [sodium diphenylamine sulfonate] = 1.96×10^{-3}M,

B: [sodium diphenylamine sulfonate]= 7.39×10^{-3}M, common conditions: 30±0.2 L, $[KBrO_3]$=0.02 M, $[CH_2(COOH)_2]$= 0.5 M, $[Ce(SO_4)_2]$= 0.04 M, $[H_2SO_4]$= 0.8 M

Due to the consuming of reactants with prolonging reaction, in a closed system the regular oscillation will be stopped. If the supplies of reactants were enough, a steadily regular profile would be unchanged. Generally, we call the former as a closed system, the latter as an open system. Of course, we prefer an open system to use for analytical purpose. Thereby, a Continuously Stirred Tank Reactor (CSTR) was designed (Fig. 2).

When an analyte was introduced into the above oscillating system, the regular oscillating profile 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, various analytical methods will be able to set up. The following example is for determining the sodium diphenylamine sulfonate (Fig. 3A and B). Li *et al.*[5] studied the sodium diphenylamine sulfonate to perturb the B-Z reaction in a closed system.

It was found that owing to a reaction between sodium diphenylamine sulfonate and Ce^{4+} ion existed, the adding of sodium diphenylamine sulfonate can caused the changes in both amplitude and period. Both changes are directly proportional to the added amount of analyte. In the range from 4.99×10^{-7} to 1.22×10^{-2} mol L^{-1}, using the change of amplitude can quantitatively determine the sodium diphenylamine sulfonate, with a correlation coefficient of 0.9948. If using the change of period in the range from 4.98×10^{-4} to 1.22×10^{-2} mol L^{-1} to determine the sodium diphenylamine sulfonate, the correlation coefficient is 0.9916. In a similar closed system, Fan *et al.*[6] using the change of amplitude and period to examine the vitamin B_1 in the range of 5.10×10^{-6} to 2.78×10^{-4} mol L^{-1}, the correlation coefficient are 0.995 and 0.993, respectively. As there is no ability to offer a continue injection of samples in closed system, many real samples were analyzed in open system with CSTR. Since many organic compounds are able to perturb the B-Z oscillating reaction, for this reason, there are a lot of papers concerning organic substances. Gao *et al.*[7] reported the determination of many organic substances and drugs using APP technique in the B-Z open system. For example, the adding of hydroquinone can perturb a regular B-Z oscillating system. The change of amplitude is linearly proportional to the logarithm of the concentration of hydroquinone in the range from 1.0×10^{-7} to 2.0×10^{-4} M (r=0.9965), whereas, when the concentration of hydroquinone over the range of 2.5×10^{-4} to 4.0×10^{-7} M, the curve fits a second-order polynomial equation very well (r=0.9983). The determination of traces of benzidine was made in the range from 3.5×10^{-9} to 1.0×10^{-4} M with a correlation coefficient of 0.9975[8]. In the range of 0.10 to 25 mg L^{-1}, the concentration of phenol was linear to the change of amplitude and period with a detection limit of 0.05 mg L^{-1} and a recovery of 97%[9]. For resorcinol[10], the linear range was from 6.5×10^{-7} to 1.0×10^{-5} M with a correlation coefficient of 0.9989. The determination of ninhydrin was given in the range of 6.9×10^{-7} to 4.2×10^{-2} M with a correlation coefficient of 0.9977[11]. Recently, Raoof *et al.*[12] investigated the effect of hydrazine on a B-Z oscillating chemical reaction, under the optimum conditions to determine traces of hydrazine. It was found that both the sensitivity and reproducibility are good. The above analyses have been used in wastewater samples and a satisfactory result was obtained. Based on the relationship between changes in the oscillation amplitude of the oscillating chemical system and the analyte concentration, Toledo *et al.*[13] have also made a systematic study on the polyphenol action and proposed a powerful analytical method. The dynamic range is 0.3 to 6.0 m mol L^{-1} with a RSD of 2%. The proposed method was used in the determination of hydroquinone, catechol, resorcinol, pyrogallol and gallic acid. A new trend in the analytical use is to determine the medicines in order that it may be able to serve in life science before long. Ren *et al.*[14] made a qualitative comparison of urine from patients on the B-Z oscillating reaction and an interesting idea was given. Gao *et al.*[15] proposed a method to examine the rifampicin in lotions. The linear range was 2.49×10^{-7} to 3.38×10^{-5} M with a correlation coefficient of 0.9987. Heroin, an excitant, has a strong perturbation to the B-Z oscillating reaction[16], both amplitude and period, it was examined sensitively in a large range of 1.8×10^{-8} to 2.1×10^{-3} M. The linear range for determining ascorbic acid was of 3.5×10^{-6} to 4.7×10^{-4} M with a correlation coefficient of 0.9975[17]. Dong *et al.*[18] described a method for determining nicotinamide adenine dinucleotide phosphate with a linear range of 1.0×10^{-8} to 1.0×10^{-6} M. Barbituric acid, as a starting material to synthesize tranquilizer, is important to the study of medicine mechanism, because it is a degradation product from tranquilizer in human body. It could also be examined by B-Z oscillating reaction[19] with a linear range of 6.4×10^{-7} to 3.1×10^{-3} M.

With the increase of study on B-Z reaction, a well understanding has been obtained. General speaking, the organic substrate and/or catalyst in this system can be altered while the oscillating is still present. Some transition metal ions (whether free ion or complex ion) that possess two oxidation states differing in a single electron may be chosen as a catalyst. A lot of organic compounds can be as a reaction substrate. These oscillating reaction are roughly classified to be B-Z reaction, too. Recently, Berenstein *et al.*[20] observed an additive effect of methyl ketones in the B-Z reaction and pointed out that every ketone acts independently in a binary mixture of methyl ketones, but with an additive effect in the dynamics of the BZ reaction. Two groups form Wuhan University investigated the other B-Z reaction used Mn^{2+} as a catalyst and applied these systems to determine many samples. For example, Zhang *et al.*[21] described the perturbation of formaldehyde to the oscillating system of DL-Malic acid-BrO_3^--Mn^{2+}-H_2SO_4 . It was found that the presence of formaldehyde is able to perturb strongly both the induction time and the period of the oscillating system. A good linear relationship was obtained between the logarithms of formaldehyde concentration and the logarithms of derivative of the induction time, or of derivative of the period. The concentration of formaldehyde ranges from 5.0×10^{-5} to 1.0×10^{-2} M. They proposed a possible mechanism, that is, the presence of formaldehyde is able to consume rapidly BrO_3-and HOBr to form Br_2; Br_2 is a key in this system. Wang *et al.*[22] reported a method determination of uric acid in the system of lactic acid-acetone-BrO_3^--Mn^{2+}-H_2SO_4, based on the linear relationship between the oscillating period and the concentration of uric acid. The linear range was from 2.0×10^{-5} to 5.0×10^{-4} M. This oscillating system can also be used to determine the ascorbic acid in the range from 5.0×10^{-7} to 5.5×10^{-5} M with a RSD of 2.43%[23]. Recently, Dong *et al.*[24] reported a more sensitive method for determining the gibberellic acid, the linear range is from 1.0×10^{-8} to 1.0×10^{-6} M with a correlation coefficient of

Table 1: The B-Z oscillating chemical system

Analyte	Oscillating chemical system	Comments	Ref.
Sodium diphenylamine sulfonate	Malonic acid-BrO_3^--Ce(IV)-H_2SO_4; Closed system	Range: 4.99×10^{-7} to 1.22×10^{-2} M; correlation coefficient : 0.9948	[5]
Vitamin B_1	Malonic acid-BrO_3^--Ce(IV)-H_2SO_4; Closed system	Range: 5.10×10^{-6} to 2.78×10^{-4} M; 0.995 (amplitude); 0.993(period)	[6]
Hydroquinone	Malonic acid-BrO_3^--Ce(IV)-H_2SO_4; Open system	Range: 1.0×10^{-7} to 2.0×10^{-4} M; correlation coefficient: 0.9965	[7]
Benzidine	Malonic acid-BrO_3^--Ce(IV)-H_2SO_4; Open system	Range: 3.5×10^{-9} to 1.0×10^{-4} M; correlation coefficient: 0.9975	[8]
Phenol	Malonic acid-BrO_3^--Ce(IV)-H_2SO_4; Open system	Range: 0.10 to 25 mg L^{-1}; Detection Limit: 0.05 mg L^{-1}	[9]
Resorcinol	Malonic acid-BrO_3^--Ce(IV)-H_2SO_4; Open system	6.5×10^{-7} to 1.0×10^{-5} M; Correlation coefficient: 0.9989	[10]
Polyphenol	Malonic acid-BrO_3^--Ce(IV)-H_2SO_4; Open system	Range: 0.3 to 6.0 m mol L^{-1}; RSD: 2%	[13]
Ninhydrin	Malonic acid-BrO_3^--Ce(IV)-H_2SO_4; Open system	Range: 6.9×10^{-7} to 4.2×10^{-2} M; Correlation coefficient: 0.9977	[11]
Rifampicin	Malonic acid-BrO_3^--Ce(IV)-H_2SO_4; Open system	Range: 2.49×10^{-7} to 3.38×10^{-5} M; Correlation coefficient: 0.9987	[15]
Heroin	Malonic acid-BrO_3^--Ce(IV)-H_2SO_4; Open system	Range: 1.8×10^{-8} to 2.1×10^{-3} M; Correlation coefficient: 0.9931	[16]
Ascorbic acid	Malonic acid-BrO_3^--Ce(IV)-H_2SO_4; Open system	Range: 3.5×10^{-6} to 4.7×10^{-4} M; Correlation coefficient: 0.9975	[17]
Nicotinamide adenine dinucleotide phosphate	Malonic acid-BrO_3^--Ce(IV)-H_2SO_4; Open system	Range: 1.0×10^{-8} to 1.0×10^{-6} M; Correlation coefficient: 0.9999	[18]
barbituric acid	Malonic acid-BrO_3^--Ce(IV)-H_2SO_4; Open system	Range: 6.4×10^{-7} to 3.1×10^{-3} M; Correlation coefficient: 0.9954	[19]
Formaldehyde	DL-Malic acid-BrO_3^--Mn^{2+}-H_2SO_4; Open system	Range: 5.0×10^{-5} to 1.0×10^{-2} M; Correlation coefficient: 0.9970	[21]
Uric acid	Lactic acid-acetone-BrO_3^--Mn^{2+}-H_2SO_4; Open system	Range: 2.0×10^{-5} to 5.0×10^{-4} M; Detection limit: 3.28×10^{-6} M	[22]
Ascorbic acid	Lactic acid-acetone-BrO_3^--Mn^{2+}-H_2SO_4; Open system	Range: 5.0×10^{-7} to 5.5×10^{-5} M; Correlation coefficient: 0.9990	[23]
Gibberellic acid	L-alamine-malonic acid-BrO_3^--Mn^{2+}-H_2SO_4;	Range:1.0×10^{-8}to1.0×10^{-6}M; Correlation coefficient: 0.9998	[24]
Caffeine	Tyrosine-acetone-BrO_3^--Mn^{2+}-H_2SO_4; Open system	Range: 4.0×10^{-6} to 1.2×10^{-4} M; correlation coefficient: 0.9968	[27]
NO_2^- ion	Lactic acid-acetone-BrO_3^--Mn^{2+}-H_2SO_4; Open system	Range: $7.66\times10^{-5}$to 2.99×10^{-3} M; Correlation coefficient: 0.9980	[30]
As (III)	Malonic acid-BrO_3^--Ce(IV)-H_2SO_4; Open system	Range: 1.99×10^{-6} to 1.27×10^{-4} M; Detection limit: 2×10^{-6} M	[31]
Halogen ion	Malonic acid-BrO_3^--Ce(IV)-H_2SO_4; Open system	The perturbation mechanismare not the same	[32,33]
Ag^+ ion	Malonic acid-BrO_3^--Ce(IV)-H_2SO_4; Open system	Range: 9.42×10^{-6} to 2.54×10^{-4} M; Detection limit: 8.9×10^{-6} M	[34]
Tl (I) ion	Chaotic regime (in B-Z system)	Observed range:1.0×10^{-4} to 1.0×10^{-12} M; Detection limit: 1.0×10^{-12} M	[35]
Gas: NO, CO, Cl_2	A mixed-mode BZ oscillating profile	Different effects	[36]
H_2O_2	Diacetone-BrO_3^--Mn^{2+}-H_2SO_4	Possible mechanism	[37]

0.9998. And the detection limit is down to 5.0×10^{-9} M. Yang *et al.*[25] and Cai *et al.*[26] took this kind of oscillating chemical system as a probe to study the anti-oxygenation in biological system and proposed some analytical methods. This is maybe a good idea using oscillating chemical reaction to approach the life science, because the chemical system is simpler than biological system. The examination of drug is beneficial to the understanding of pathogeny. Gao *et al.*[27] described a method for the determination of caffeine by the Mn (II)-catalysed reaction with a linear range from 4.0×10^{-6} to 1.2×10^{-4} M. Yu and Jwo[28] developed a systematic study, examining the effect of Ce (III), Mn (II), or ferroin on the B-Z oscillating reaction with allyl malonic acid. It was found that under the different conditions the catalysed activity is not the same. The mechanism of the above mentioned could be explained by the FKN model in 1972[29].

The determination of inorganic ion and compound, as well as gas, by B-Z oscillating reaction has been reported, too. Yang *et al.*[30] studied the effect of NO_2^- ion on the system of lactic acid-acetone-BrO_3^--Mn^{2+}-H_2SO_4. It was found that in the presence of NO_2^- ion, both period and induced time were changed strongly. In the range of 7.66×10^{-5} to 2.99×10^{-3} M, NO_2^- ion can be determined. Ojani *et al.*[31] reported the determination of As (III) using B-Z reaction. The change of amplitude was directly proportional to the logarithm of the As (III) concentration. The linear range was from 1.99×10^{-6} to 1.27×10^{-4} M. Liu *et al.*[32] and Yang *et al.*[33] examined the effect of

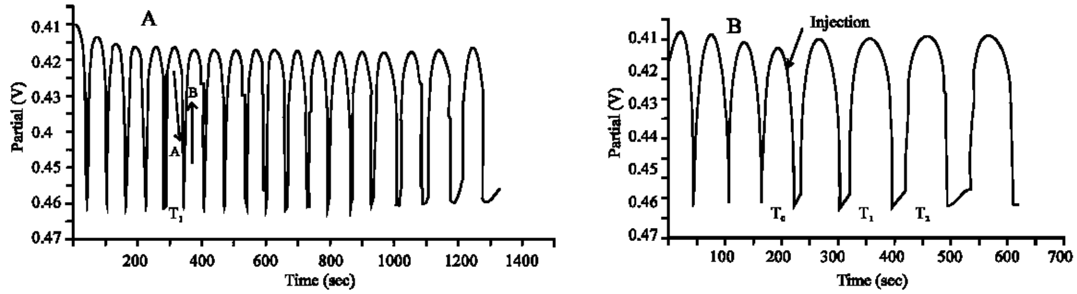

Fig. 4A and B: Typical Cu (II) catalyze oscillation profiles
A: in the absence of L-value
B: in the presence of 8.26×10^{-5} M of L-value

halogen ion on the B-Z system and analyzed their reaction mechanism. Since F^- ion reacts with Ce^{3+} ion to form an insoluble compound of CeF_3 to decrease the concentration of cerium ion, the oscillating profile could be inhibited. However, Cl^- and I^- ions can also react with the intermediate HBrO or $HBrO_2$ to perturb the oscillating profile. Base on these reactions a simply determined method for three ions were proposed. The determination of metal ion exhibits more sensitivity. Raoof *et al.*[34] reported that in the B-Z oscillating system using a platinum wire as an indictor electrode, the Ag^+ ion could perturb the amplitude. In the range from 9.42×10^{-6} to 2.54×10^{-4} M the change of amplitude is linear to the Ag^+ ion concentration and the detection limit is 8.85×10^{-6} M with a good correlation coefficient of 0.999. Except Hg^{2+}, most of inorganic ions have no interferences in the determination. A more sensitive method used to determine Tl (I) ion was developed by Strizhak *et al.*[35]. The method is based on the effect of Tl (I) ion on the transient chaotic regimes in B-Z reaction. The detection limit is down to 10^{-12} M in aqueous solution. No doubt, there are a few of interferences.

Strizhak and Khavrus[36] has extended the application of B-Z reaction to the determination of gases, for example, some of gas such as NO, CO, or Cl_2 can affect a mixed-mode profile, which was a largely single amplitude followed by a few of small amplitude. A new set-up for gas determination and a possible mechanism were given in this paper. Gan *et al.*[37] studied the effect of peroxide hydrogen on the oscillating system of diacetone-BrO_3^--Mn^{2+}-H_2SO_4 and a possible mechanism was given.

Now, the application of B-Z system to analytical chemistry was summarized in Table 1.

Cu (II)-catalysed oscillating chemical reaction: The other oscillating system used for analytical chemistry is the Cu (II)-catalysed oscillating reaction. That is, taking Cu (II) as a catalyst to catalyze a redox reaction in a strongly basic medium, e.g., H_2O_2-$CuSO_4$-KSCN, H_2O_2-$CuSO_4$-KSCN-Luminol, H_2O_2-$Na_2S_2O_3$-$CuSO_4$-KSCN and so forth. The oscillating profile is similar to those of the BZ system. Gao *et al.*[38] gave a few of reports on the Cu (II)-catalysed oscillating reaction. For example, L-valine was determined in a closed system involving H_2O_2-$CuSO_4$-NaSCN; the perturbation was directly proportional to the change of the oscillating period (both first and secondary oscillating period). The range is from 2.77×10^{-5} to 5.52×10^{-4} M with a relative standard deviation of 0.83%. Owing to the regularly steady pattern showing in Fig. 4A and B, the precision of method is very good.

The determination of glutamic acid[39] was carried out in the open system of H_2O_2-$CuSO_4$-NaSCN, using the linear relationship between the change of amplitude and the concentration of analyte. The linear range was from 2.5×10^{-6} to 3.2×10^{-4} M and the correlation coefficient was 0.9987. The common inorganic ions and some organic compounds such as aspargine, lysine and glycine have not interfered the determination. Ren *et al.*[40] developed that the trace amount of heroin can perturb the oscillating period and amplitude in the above system and the change of period was very clear. Based on this perturbation, a rapid, simple method for the determination of heroin was proposed. Over the range from 2.0×10^{-6} to 1.2×10^{-5} M, a linear relationship between the change of period and the concentration of heroin was existed. The detection limit was 4.0×10^{-7} M. with the aid of the change of the first oscillating period, Xiang *et al.*[41] reported an analytical determination of vitamin K_3. A largely linear range of 5.3×10^{-7} to 2.2×10^{-4} M was obtained (Table 2).

Over the past five years, there is no paper concerning the application of peroxidase-oxidase oscillating system in analytical chemistry. Surveying the new oscillating chemical system is still an object followed with interest by analysts. Some new oscillating reactions have been reported[42-46], by mean of the modified substrate and catalyst, the mixtures of substrate and so on. The introduction of new oscillating system may be extending the field of analytical use.

In summary, the oscillating chemical reaction is a fascinating and important area, which is triggering many subjects, such as mathematics, physics, life science, chemistry and so forth. Intense studies in all directions

Table 2: The Cu (II)-catalysed oscillating chemical reaction

Analyte	Oscillating chemical system	Comments	Ref.
L-valine	H_2O_2-$CuSO_4$-NaSCN; Closed system	Range: 2.77×10^{-5} to 5.52×10^{-4} M; Relative standard deviation: 0.83%	[38]
Glutamic acid	H_2O_2-$CuSO_4$-NaSCN; Open system	Range: 2.5×10^{-6} to 3.2×10^{-4} M; Correlation coefficient: 0.9987 Relative standard deviation: 0.68%	[39]
Heroin	H_2O_2-$CuSO_4$-NaSCN; Open system	Range: 2.0×10^{-6} to 1.2×10^{-5} M; Correlation coefficient: 0.9971 Relative standard deviation: 0.98%	[40]
Vitamin K3	H_2O_2-$CuSO_4$-NaSCN; Open system	Range: 5.3×10^{-7} to 2.2×10^{-4} M; Correlation coefficient: 0.9981	[41]

indicate that how to understand and how to use those oscillating reactions continue to be an important object, attracting many researchers to explore. One of them is the application in analytical chemistry. The analyte pulse perturbation technique combined with a continuously stirred tank reactor has strongly improved the really applied valuation. Generally, the equipment used is cheap in price than other analytical instruments; largely linear range (ca. 10^{-7} to 10^{-4} M) and lower detection limit (ca. 10^{-6} to 10^{-8} M; rarely down to 10^{-12} M) could satisfy the need of common determination. As an analytical method, oscillating chemical reaction would be investigated extremely in future.

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REFERENCES

1. Tikhonova, L.P., L.N. Zakrevskaya and K.B. Yasimirskii, 1978. Catalytic determination of ruthenium based on an oscillating chemical reaction. J. Anal. Chem., 33: 1991-1998.
2. Jimenez-Prieto, R., M. Silva and D. Perez-Bendito, 1995. Analyte pulse perturbation technique: A tool for analytical determination in far-from-equilibrium dynamic systems. Anal. Chem., 67: 729-734.
3. Jimenez-Prieto, R., M. Silva and D. Perez-Bendito, 1998. Approaching the use of oscillating reactions for analytical monitoring. Analyst, 123: 1R-8R.
4. Taylor, A.F., 2002. Mechanism and phenomenology of an oscillating chemical reaction. Progress in Reaction Kinetics and Mechanism, 27: 247-325.
5. Li, Q.Z., X.H. Liu, J. Ren, H. Yang, W. Yang and J.Z. Gao, 2002. Effects of sodium diphenylamine sulfonate on the B-Z oscillating reaction. J. Northwest Normal Uni. (Natural Science) (Ch.), 38: 51-54.
6. Fan, S.H., C.J. An, L. Zhuang, N.Q. Gan and Z.X. Lin, 1999. The effect of concentration of vitamin B1 on the B-Z oscillating chemical reaction and the kinetics. Acta Physico-Chimica Sinica (Ch.), 15: 178-181.
7. Gao, J.Z., J. Ren, W. Yang, X.H. Liu, H. Yang, Q.Z. Li and H.L. Deng, 2002. Kinetic determination of hydroquinone by Belousov-Zhabotinsky oscillating chemical reaction. J. Electroanalytical Chem., 520: 157-161.
8. Gao, J.Z., K.J. Sun, W. Yang, F.W. Yang and G.H. Zhao, 2004. Determination of benzidine using the analyte pulse perturbation technique in BZ oscillating chemical system. Pak. J. Biol. Sci., 7: 1721-1726.
9. Liu, X.H., J. Ren, H. Yang and J.Z. Gao, 2001. Kinetic determination of phenol by oscillating chemical reaction in open system. J. Instru. Analysis (Ch.), 20: 9-11.
10. Lv, D.Y., J.Z. Gao, W. Yang and J. Ren, 2003. Kinetic determination of trace amount of resorcinol by B-Z oscillating chemical reaction. J. Northwest Normal Uni. (Ch.), 39: 48-50.
11. Gao, J.Z., Sounan, W. Yang, L. Wang, G.H. Zhao and K.J. Sun, 2004. Effect of ninhydrin on the B-Z oscillating chemical reaction Chinese J. Analysis Laboratory (Ch.), 23: 5-7.
12. Raoof, J.B., R. Ojani, A. Kiani, M. Khosravi and A. Adnani, 2005. The potentiometric effect of hydrazine on a B-Z oscillating chemical reaction: Application to the determination of hydrazine. Bull. Chemical Soc. Japan, 78: 258-261.
13. Toledo, R., M. Silva, V.O. Khavrus and P.E. Strizhak, 2000. Potential of the analyte pulse perturbation technique for the determination of polyphenols based on the Belousov-Zhabotinskii reaction. Analyst, 125: 2118-2124.
14. Ren, J., W. Yang, X.H. Liu, H. Yang, Q.Z. Li and J.Z. Gao, 2002. Perturbation of urine on the oscillating chemical system. J. Northwest Normal Uni. (Natural Science) (Ch.), 38: 55-57.

15. Gao, J.Z., Q.Z. Li, W. Yang, X.H. Liu, J. Ren and H. Yang, 2004. Determination of rifampicin based on the BZ oscillating chemical reaction by the analyte pulse perturbation technique. Current Topics in Electrochem., 10: 203-209.
16. Gao, J.Z., Sounan, W. Yang, L. Wang, G.H. Zhao and K.J. Sun, 2004. Effect of heroin on the B-Z oscillating chemical reaction and its analytical application. Chinese J. Analytical Chem. (Ch.), 32: 611-614.
17. Gao, J.Z., H. Yang, X.H. Liu, J. Ren, X.Q. Lu, J.G. Gou and J.W. Kang, 2001. Kinetic determination of ascorbic acid by the BZ oscillating chemical system. Talanta, 55: 99-107.
18. Dong, Y.J., K. Gai and X.X. Gong, 2004. Determination of nicotinamide adenine dinucleotide phosphate by B-Z oscillating chemical system. Chinese J. Analytical Chem. (Ch.), 32: 923-926.
19. Gao, J.Z., Sounan, L. Wang and W. Yang, 2004. Effect of barbituric acid on the B-Z oscillating chemical reaction and its analytical application. J. Northwest Normal Uni. (Natural Science) (Ch.), 39: 62-65.
20. Berenstein, I. and D. Barragan, 2004. Additive effects of methyl ketones in the Belousov-Zhabotinsky reactions. J. Brazilian Chem. Soc., 15: 844-848.
21. Zhang, Z.Q., C.J. An, Z.Z. Zhang, Y.Z. Zheng, D. Zheng and Z.Y. Wu, 2004. Kinetic study of chemical oscillatory reaction in the system of $HCHO_2$-(malic acid)-BrO_3^--Mn^{2+}-H_2SO_4. J. Wuhan Uni. (Ch.), 50: 177-181.
22. Wang, J., S.T. Yang, R.X. Cai, Z.X. Lin and Z.H. Liu, 2005. A new method for determination of uric acid by the lactic acid-acetone-BrO_3^--Mn^{2+}-H_2SO_4 oscillating reaction. Talanta, 65: 799-805.
23. Yang, S.T., X.Z. Lin, R.X. Cai and N.Q. Gan, 2002. Determination of ascorbic acid using a new oscillating chemical system of latic acid-acetone-BrO_3^--Mn^{2+}-H_2SO_4. Chinese J. Chem., 20: 1019-1024.
24. Dong, Y.J., K. Gai and X.X. Gong, 2004. Kinetic determination of gibberellic acid by the BZ oscillating chemical system. J. Chinese Chem. Soc., 51: 7-11.
25. Yang, S.T., N.Q. Gan, X.Z. Lin and R.X. Cai, 2002. Determination of activity of anti-oxygenation of glutathione by the probe of the latic acid-acetone-BrO_3^--Mn^{2+}-H_2SO_4 oscillating system. Chemical J. Chinese Uni. (Ch.), 23: 1026-1029.
26. Cai, R.X., K. Zhang, W.H. Ma, N.Q. Gan and Z.X. Lin, 1999. Non-linear chemical reaction charactistics of diacetone-malic acid-BrO_3^--Mn^{2+}-H_2SO_4 and the application in biological anti-oxidation. J. Fuzhou Univ. (Ch.), 27: 49-50.
27. Gao, J.Z., J. Ren, W. Yang, X.H. Liu and H. Yang, 2003. Determination of caffeine using oscillation chemical reaction in a CSTR. J. Pharmaceutical and Biomedical Analysis, 32:393-400.
28. Yu, Y.O. and J.J. Jwo, 2000. Kinetic study of the Ce(III)-, Mn(II)-, or ferroin-catalysed Belousov-Zhabotinsky reaction with allylmalonic acid. J. Chinese Chem. Soc., 47: 433-439.
29. Field, R.J., E. Koros and R.M. Noyes, 1972. Oscillations in chemical systems. II. Through analysis of temporal oscillation in the bromate-cerium-malonic acid system. J. Am. Chem. Soc., 94: 8649-8664.
30. Yang, B., C.J. An, D. Zheng and Z.Z. Ding, 2002. Influence of NO_2^- on lactic acid-acetone-BrO_3^--Mn^{2+}-H_2SO_4 chemical oscillation reaction. Chinese J. Inorganic Chem. (Ch.), 18: 874-878.
31. Ojani, R., J. Raoof and F. Mahdavi, 2003. The potentiometric effect of As(III) ion on a Belousov-Zhabotinsky oscillating chemical reaction. Bull. Chemical Soc. Japan, 76: 2117-2121.
32. Liu, X.H., H. Yang, J.Z. Gao, Y.J. Ma and X.Q. Lu, 2001. Effect of fluoride on the B-Z oscillating reaction. Chinese J. Analytical Chem. (Ch.), 29: 1318-1321.
33. Yang, H., J.Z. Gao, W. Yang, X.H. Liu and G.H. Zhao, 2003. The effect of halogen on the B-Z oscillating chemical system. J. Northwest Normal Uni. (Natural Science) (Ch.), 39: 45-48.
34. Raoof, J., R. Ojani and K. Kiani, 2004. Kinetic determination of silver ion by its perturbation on Belousov-Zhabotinsky oscillating chemical reaction using potentiometric method. Analytical Sci., 20: 883-886.
35. Strizhak, P.E., O.Z. Didenko and T.S. Ivashchenko, 2001. Determination of traces of thallium using the transient chaotic regime in the Belousov-Zhabotinskii oscillating chemical reaction. Analytica Chimica Acta, 428: 15-21.
36. Strizhak, P.E. and V.O. Khavrus, 2000. Determination of gases (NO, CO, Cl_2) using mixed-mode regimes in the Belousov-Zhabotinskii oscillating chemical reaction. Talanta, 51: 935-947.
37. Gan, N.Q., R.X. Cai and Z.X. Lin, 2000. The effect of peroxide hydrogen on a chemical oscillating reaction. Analytical Sci., 16: 1327-1330.
38. Gao, J.Z., Q.Z. Li, W. Yang, X.H. Liu, J. Ren, H. Yang and H.L. Deng, 2002. Determination of L-valine based on an oscillating chemical reaction. Electroanalysis, 14: 1191-1196.

39. Gao, J.Z., H. Yang, X.H. Liu, J. Ren, Q.Z. Li and J.W. Kang, 2002. Determination of glutamic acid by an oscillating chemical reaction using the analyte pulse perturbation technique. Talanta, 57: 105-114.
40. Ren, J., J.Z. Gao, Sounan, G.H. Zhao, W. Yang, D.Y. Lv, K.J. Sun and C.Y. Li, 2004. Determination of heroin based on analyte pulse perturbation to an oscillating chemical reaction. Chem. Res. Chinese Uni., 20: 534-538.
41. Xiang, X.M., D.Y. Lv, J. Ren and J.Z. Gao, 2004. The effect of vitamin K3 on Cu(II)-H_2O_2-NaSCN oscillating chemical reaction. J. Northwest Normal Univ. (Natural Science) (Ch.), 40: 53-56.
42. Gao, J.Z., L. Wang, W. Yang and F.W. Yang, 2005. Electrical potential oscillation in an anionic surfactant system with barbitone in octanol as an oil phase. J. Iranian Chemical Soc., 2: 71-77.
43. Gao, J.Z., K.J. Sun and W. Yang, 2003. Nonlinear behavior and domain feature at oil/water interface. Chinese Chemical Lett., 14: 1062-1065.
44. Yang, W., J. Ren, J.Z. Gao, H. Yang, D.Y. Lv and X.H. Liu, 2003. A novel chemical oscillator with tyrosine as the substrate. Chinese Chemical Lett., 14: 1281-1284.
45. Shen, S.G., C.Q. Ynag, H.W. Sun, J.H. Shan and Y. Liu, 2003. The kinetic study of the chemical oscillating system of 1,3-propanediol/acetone as the organic substrate. Turkish J. Chem., 27: 243-250.
46. Strizhak, P.E., A.B. Basylchuk, I. Demjanchyk, F. Fecher, F.W. Schneider and A.F. Munster, 2000. Oxidation of ascorbic acid by air oxygen catalysed by copper (II) ions in batch and continuous flow stirred tank reactors: Bistability, oscillations and stochastic resonance. Physical Chem. Chemical Physics, 2: 4721-4727.