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The application of oscillating chemical reactions to analytical determinations

Review Article

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Abstract: Oscillating chemical reactions, which are far from equilibrium, are extremely sensitive to certain species and may provide new analytical methods using the regular oscillations as well as the non-equilibrium stationary state after system bifurcation. This review of their application to analytical chemistry from 2005 to 2012 includes other appropriate references. Both organic and inorganic analytes are included.

Keywords: *Oscillating chemical reactions • Applications • Analytical determination*

1. Introduction

Oscillations of chemical origin have been present as long as life itself. Every living system contains scores, perhaps hundreds of chemical oscillators [1]. The phenomenon of chemical oscillation - the periodic or nearly periodic temporal variation of concentrations in a reacting system - provided the initial impetus for the development of nonlinear chemical dynamics. It has been the most thoroughly studied phenomenon in this rich field. Epstein and Pojman summarized some of the early theoretical and experimental work that led to the ideas of Prigogine on non-equilibrium thermodynamics and to the experimental and theoretical work of Belousov, Zhabotinsky, Field, Körös and Noyes in 1998 [1]. Later the features, occurrence and spatiotemporal patterns of oscillating reactions were reviewed by Ferino and Rombi [2]. The mechanism of an oscillating chemical reaction was reviewed by Taylor in 2002 [3].

Tikhonova *et al.* first proposed using an oscillating chemical reaction for trace ruthenium determination in 1978 [4]. Then the analyte pulse perturbation (APP) technique in a continuous flow stirred tank reactor (CSTR) [5] proposed by Jimenez-Prieto *et al.* promoted wider application. They gave a critical review in 1998 [6]. Later, Vukojevic′ *et al.* [7,8] proposed a new analytical approach by changing the control parameters of an oscillating system to bifurcate from regular oscillation to a non-equilibrium stationary state, then performing the determination in the stationary state. This improved sensitivity. Gao reviewed real applications to analytical chemistry published from 1999 to 2004 [9]; detailed analyses of the Belousov-Zhabotinsky (B-Z) and Cu(II)-catalyzed reaction applications were cited. This review focuses primarily on analytical applications reported from 2005 to 2012.

2. Regular oscillations in analytical determinations

Studies of oscillating chemical reactions have concentrated on the physical chemistry, elucidating the intricate nonlinear behaviors observed. However, many recent analytical applications have been reported, focused on the B-Z and Cu(II)-catalyzed oscillating reactions. Quantitative determinations have been based on analyte-caused changes in the characteristic

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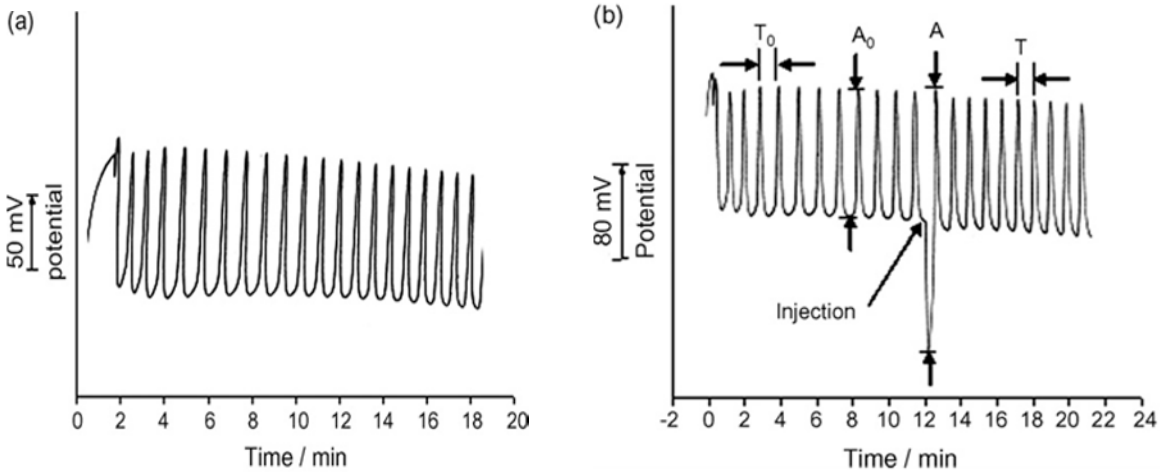

Figure 1. Typical oscillation profiles in the absence and presence of pyrogallol using a platinum electrode: (a) [pyrogallol] = 0.000 M, (b) [pyrogallol] = 7.5×10^{-6} M. Common conditions: [$NaBrO_3$] = 0.0175 M; [malic acid] = 0.2 M; [H_2SO_4]=1 M; [CuL](ClO_4)$_2$ = 2.76×10^{-3} M. (Adapted from [10]).

parameters of the regular oscillations, such as induction time, period, or amplitude. The analytes include organic species, some medicines and inorganic species.

2.1. Use of regular oscillations in organic determinations

Reactions which are far from equilibrium can display oscillations in intermediate concentrations through positive and negative feedback in the mechanism. Thus, any species which can react with the reactants or intermediate can in principle be determined by this method. The effects have been ascribed to two factors: (1) coordination between the analyte and a catalyst; and (2) redox reaction between the analyte and the system oxidant. Most determinations are of organic compounds.

Hu *et al.* [10] noted that due to its three active hydroxyls pyrogallol could be easily oxidized to the corresponding quinone by acidic $NaBrO_3$. Pyrogallol addition to the B-Z reaction catalyzed by the macrocyclic complex [CuL](ClO_4)$_2$ caused changes in the potentiometric oscillation amplitude linearly proportional to log[pyrogallol] from 1.5×10^{-6} to 1×10^{-4} M (Fig. 1), with a correlation coefficient of 0.9959. The relative standard deviation (RSD) with eight samples was 1.6%. Good results were also obtained with catechol [11], tyrosine [12], alizarin red S [13], phenyl-phosphate [14], sodium aminosalicylate [15], or gentisic acid [16]. Gao *et al.* [17] found that changes in B-Z oscillation period and amplitude were linearly proportional to the -log[L-tryptophan] from 6.44×10^{-7} - 2.55×10^{-4} M, with a lower detection limit of 6.5×10^{-8} M. For D-tryptophan the range was 4.9×10^{-5} - 8.24×10^{-4} M (Fig. 2). Because the optimum conditions for determination of L- and D-tryptophan are not the same, a small amount of D-tryptophan does not affect the determination of L-tryptophan. Satisfactory results were obtained for L- and D-methionine [18]. Liu *et al.* [19] reported that L-cysteine decreased the tris(2,2'-bipyridine) ruthenium(II)-catalyzed B-Z oscillating chemiluminescence and the period and induction time were prolonged. L-cysteine can reduce $Ru(bpy)_3^{3+}$ to $Ru(bpy)_3^{2+}$ directly without light emission. The induction period was used as the analytical parameter. Under optimum conditions, the changes in induction period were linearly proportional to [L-cysteine] from 8.0×10^{-7} to 5.0×10^{-5} M (r=0.997) with a detection limit of 4.3×10^{-7} M.

Because of the consumption of reactants, it is impossible to continue injection of samples in a closed system, so some substances were analyzed in the CSTR open system. Several APP determinations of organic compounds have been reported in the last six years. Gao *et al.* [20] found that when furfural was injected into the Mn(II)-catalyzed B-Z system, the change in amplitude and/or period was linearly proportional to log[furfural] from 3×10^{-8} - 1×10^{-5} M, with a detection limit of 3×10^{-9} M under optimum conditions, and 8 samples could be determined per hour. In addition, Yang *et al.* [21] proposed using sequential perturbation caused by different amounts of α-naphthol on the Cu(II)-catalyzed oscillating reaction between alkaline hydrogen peroxide and sodium thiocyanate in a CSTR. The method relied on the linear relationship between changes in oscillation amplitude and the α-naphthol concentration from 0.034 - 530 uM (r=0.9991). The applications of oscillating chemical reactions to organic compound determinations are summarized in Table 1.

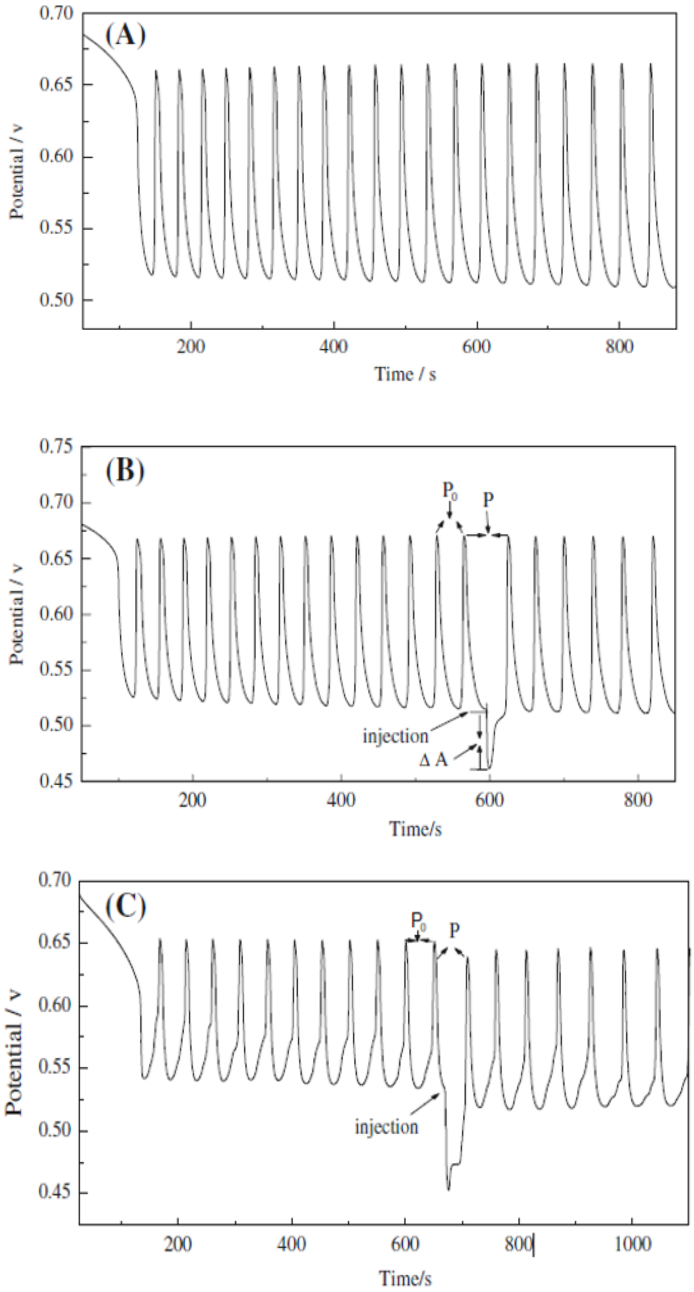

Figure 2. (A) Without tryptophan, (B) [L-tryptophan]=8.359×10^{-6} M. Common conditions: [$KBrO_3$] = 0.055 M, [$CH_2(COOH)_2$] = 0.168 M, [Ce(IV)] = 0.0018 M, [H_2SO_4] = 0.7 M. (C) Profile of potential oscillation at 6.679×10^{-5} M D-tryptophan. Common conditions: [$KBrO_3$] = 0.065 M, [$CH_2(COOH)_2$] = 0.163 M, [Ce(IV)] = 0.0020 M, [H_2SO_4] = 0.8 M. (Adapted from [17]).

2.2. Use of regular oscillations in pharmaceutical analysis

Biological oscillation originates in chemical reactions, and the most numerous and important chemical oscillators are found in living systems. The similarities between chemical and biological phenomena can be striking, and similar behavior can certainly arise from similar causes. To gain insight into biological oscillators many researchers study chemical systems by investigating the effects of a pharmaceutical on a chemical oscillator and examine the mechanism. Gao *et al*. reported the determination of several pharmaceutical samples by this method [29-31]. For example, they found that penicillin reduced the free Mn^{2+} concentration leading to the changes in both oscillation period and amplitude. These were linearly proportional to –log[penicillin] from

Table 1. Use of regular oscillation in organic determinations.

Analyte	Oscillating chemical system	Dynamic linear range (M)	Detection limit (M)	Ref.
Pyrogallol	$NaBrO_3$-H_2SO_4-malic acid-$[CuL](ClO_4)_2$(B)	$\Delta A:1.5\times10^{-6}-1\times10^{-4}$	1.34×10^{-6}	[10]
Catechol	$NaBrO_3$-H_2SO_4-malic acid-$[CuL](ClO_4)_2$(B)	$\Delta A:2.1\times10^{-6}-2.1\times10^{-4}$	1.37×10^{-6}	[11]
Tyrosine	$NaBrO_3$-H_2SO_4-malic acid-$[CuL](ClO_4)_2$(B)	$\Delta A:1.2\times10^{-6}-2.7\times10^{-4}$ $\Delta T:7.4\times10^{-7}-4.5\times10^{-4}$		[12]
Alizarin red S	$NaBrO_3$-H_2SO_4-malic acid-$[CuL](ClO_4)_2$(B)	$\Delta A:1.5\times10^{-7}-1\times10^{-3}$		[13]
Phenyl-phosphate	$NaBrO_3$-H_2SO_4-malic acid-$[CuL](ClO_4)_2$(B)	$\Delta A:2.0\times10^{-6}-6.0\times10^{-4}$		[14]
Sodium aminosalicylate	$NaBrO_3$-H_2SO_4-malic acid-$[CuL](ClO_4)_2$(B)	$\Delta A:4.97\times10^{-7}-1.96\times10^{-4}$	1.96×10^{-7}	[15]
Gentisic acid	$NaBrO_3$-H_2SO_4-malic acid-$[CuL](ClO_4)_2$(B)	$\Delta A:1.25\times10^{-6}-1\times10^{-4}$	8.5×10^{-7}	[16]
L-tryptophan	$KBrO_3$-MA- Ce(IV) -H_2SO_4(B)	$\Delta A:6.44\times10^{-7}-2.55\times10^{-4}$	6.5×10^{-8}	[17]
D-tryptophan	$KBrO_3$-MA- Ce(IV) -H_2SO_4(B)	$\Delta P:4.97\times10^{-5}-8.24\times10^{-4}$		[17]
L-cysteine	H_2SO_4-$Ru(bpy)_3^{2+}$-$KBrO_3$ MA(B)	$\Delta T_{in}:8.0\times10^{-7}-5.0\times10^{-5}$	4.3×10^{-7}	[18]
L-methionine	Glucose-acetone- BrO_3^--Mn^{2+} -H_2SO_4(B)	$\Delta T: 7.5\times10^{-7}-1.0\times10^{-5}$		[19]
D-methionine	Glucose-acetone- BrO_3^--Mn^{2+} -H_2SO_4(B)	$\Delta T: 4.0\times10^{-6}-2.3\times10^{-5}$		[19]
L-phenylalanine	NaOH-NaCl-H_2O_2-NaSCN-Cu(II) (B)	$\Delta A:1.86\times10^{-6}-1.80\times10^{-4}$	2.61×10^{-7}	[22]
D-phenylalanine	NaOH-NaCl-H_2O_2-NaSCN-Cu(II) (B)	$\Delta T:1.80\times10^{-9}-1.40\times10^{-4}$	2.69×10^{-11}	[22]
1-naphthylamine	$KBrO_3$-MA- Ce(IV) -H_2SO_4(B)	$\Delta T:7.08\times10^{-6}-7.08\times10^{-5}$ $\Delta A:1.0\times10^{-6}-7.08\times10^{-5}$	5.64×10^{-9}	[23]
Hydrazine	$KBrO_3$-MA- Ce(IV) -H_2SO_4(B)	$\Delta A:1\times10^{-6}-1\times10^{-3}$	1×10^{-6}	[24]
Sulfanilamide	acetone-BrO_3^--Mn^{2+} -H_2SO_4(B)	$\Delta A:9.33\times10^{-8}-3.02\times10^{-6}$ $\Delta T:4.27\times10^{-8}-7.41\times10^{-4}$	6.03×10^{-8} 2.69×10^{-8}	[25]
Guanine	MA-BrO_3^--Mn^{2+} -H_2SO_4(B)	$\Delta T:2.5\times10^{-8}-1.4\times10^{-4}$	2.5×10^{-9}	[26]
Furfural	Mn(II)-BrO_3^- -diacetone-H_2SO_4(O)	$\Delta A:3\times10^{-8}-1\times10^{-5}$	3×10^{-9}	[20]
Alpha-naphthol	NaOH-NaCl-H_2O_2-NaSCN-Cu(II) (O)	$\Delta A:3.4\times10^{-8}-5.3\times10^{-4}$		[21]
Uric acid	lactic acid-acetone-BrO_3^--Mn^{2+} -H_2SO_4(O)	$\Delta T: 2.0\times10^{-5}-5.0\times10^{-4}$	3.28×10^{-6}	[27]
Taurine	$KBrO_3$-MA- Ce(IV) -H_2SO_4(B)	$\Delta A:4\times10^{-6}-4\times10^{-1}$	10^{-6}	[28]

Where B stands for batch system and O is CSTR system.

2.97×10^{-7} to 5.50×10^{-5} M or 2.97×10^{-6} - 5.50×10^{-5} M, with respective regression coefficients of 0.9981 and 0.9985. The detection limit was 5.94×10^{-8} M and 15 samples could be analyzed per hour. Fan *et al.* [32] described a method for determining ascorbic acid from 5.7×10^{-4} - 8.5×10^{-2} M. Ascorbic acid in fruit juice [33] and cabbage [34] was determined by this method. In the last five years, vitamin B1 [35], vitamins B1, B2, and B6 [36], Levodopa [37], ampicillin [38] and Acetamiprid [39] were also satisfactorily determined (Table 2).

Oscillating chemical reactions have also recently have been applied to analyze Chinese medicines qualitatively. Wang et al. [40] observeded that salvia miltiorrhiza added to the oxalic acid-acetone- $KBrO_3$-Mn^{2+}-H_2SO_4 oscillating system changed the system behavior. This phenomenon was called the salvia miltiorrhiza fingerprint. Wang *et al.* [41] studied the effect of lighiyellow sophora root on the acetone- $KBrO_3$-Mn^{2+}-H_2SO_4 oscillating system and the same result was obtained. The effect of the Chinese medicinal herb Chuanxiong on the acetone-$KBrO_3$-Mn^{2+}-H_2SO_4 oscillating system was also studied by Zhao *et al.* [42]. This may represent a new trend in analytical applications.

2.3. Use of regular oscillations in metal ion determinations

The first analytical use of oscillating chemical reactions was for metal ions [4]. Hu *et al.* [43] proposed a new approach to Ag^+ determination by its perturbations on the B-Z oscillating system catalyzed by an unsaturated

Table 2. Use of regular oscillation in medicine analysis.

Analyte	Oscillating chemical system	Dynamic linear range (M)	Detection limit (M)	Ref.
Ascorbic acid	$CH_2(COOH)_2$-BrO_3^--Mn^{2+}- H_2SO_4 (B)	ΔA: 5.7×10^{-4}-8.5×10^{-2}		[32]
Vitamin C (in juice)	$KBrO_3$-MA- Ce(IV) -H_2SO_4 (B)	ΔA: 0.1-20 mg/L		[33]
Vitamin C (in cabbage)	$KBrO_3$-MA- Ce(IV) -H_2SO_4 (B)	ΔA: 0.1-20 mg/L		[34]
Vitamin B1	$KBrO_3$-MA- Ce(III) -H_2SO_4 (B)	ΔT: 7×10^{-4}-1.5×10^{-3}		[35]
Vitamin B1	$KBrO_3$-MA- Ce(IV) -H_2SO_4 (B)	ΔA:9.10×10^{-5}-3.26×10^{-4}		[36]
Vitamin B2	$KBrO_3$-MA- Ce(IV) -H_2SO_4 (B)	ΔA:4.65×10^{-6}-2.40×10^{-4}		[36]
Vitamin B6	$KBrO_3$-MA- Ce(IV) -H_2SO_4 (B)	ΔA:7.30×10^{-6}-1.50×10^{-4}		[36]
Levodopa	$NaBrO_3$-H_2SO_4-malic acid-$[CuL](ClO_4)_2$ (B)	ΔA:9.90×10^{-6}-2.44×10^{-4}		[37]
Ampicilin	$KBrO_3$-MA- Ce(IV) -H_2SO_4 (B)	ΔA: 5.0×10^{-9}- 1.0×10^{-7}	3.3×10^{-11}	[38]
Ribavirin	H_2SO_4- $KBrO_3$- $MnSO_4$ -MA (B)	ΔA: 1.5×10^{-7}-6.3×10^{-5}	3.2×10^{-8}	[31]
Penicillin	Lactic acid-acetone- $KBrO_3$-Mn^{2+} -H_2SO_4 (O)	ΔA:2.97×10^{-7}-5.00×10^{-5} ΔT: 2.9×10^{-6}- 5.50×10^{-5}	5.94×10^{-8}	[29]
Dopamine	$KBrO_3$-MA- Ce(IV) -H_2SO_4 (O)	ΔA: 2.4×10^{-7}-4.9×10^{-5}	9.8×10^{-8}	[30]
Acetamiprid	$KBrO_3$-MA- Ce(IV) -H_2SO_4 (O)	ΔT: 4.80×10^{-5}-2.00×10^{-4}	5.0×10^{-7}	[39]

Where B stands for batch system and O is CSTR system.

macrocyclic Cu(II) complex, $[CuL](ClO_4)_2$. The relationship between the change in period and log[Ag^+] was linear from 1.00×10^{-7} - 6.25×10^{-5} M with an RSD of 0.8%. They also detected calcium pantothenate based on the same reaction [44]. The change in amplitude was linearly proportional to [calcium pantothenate] from 5×10^{-6} - 2.5×10^{-3} M while the change in period was a second-order polynomial proportional to [calcium pantothenate] from 1.5×10^{-5} - 2.5×10^{-3} M with a detection limit of 2.5×10^{-6} M and RSD of 0.3%. The method was suitable for practical analysis. The determination of aqueous indium (it increases the bromide concentration and perturbs the period) was performed by Gao *et al.* [45]. The change in period is linearly proportional to [In^{+3}] from 4.98×10^{-7} - 3.85×10^{-6} M, with a correlation coefficient of 0.9984 and a detection limit of 4.96×10^{-7} M under the optimum conditions.

Gao *et al.* [46] modified the B-Z oscillating system with Na_2S. As adding Ag^+, Bi^{3+}, Cd^{2+}, Cu^{2+}, Hg^{2+} or Pb^{2+} decreases the effective S^{2-}concentration by insoluble sulfide formation, these metals were detected. The method exhibited much higher sensitivity than the classical B–Z system (detection limit of 10^{-12} M). In addition, they also found that the B-Z system modified with oxalic acid was very sensitive and highly selective towards Eu^{3+} [47]. Yang *et al.* [48] developed a brand-new double substrate system by adding malic acid to the classical B-Z system which could be used to determine cobalt ion with high sensitivity. The limit of detection was 5.20×10^{-13} M, the highest metal ion sensitivity yet found using oscillating chemical reactions. The surprising selectivity and sensitivity for Co^{2+} is due to the moderate Co^{2+}-malic acid complex stability. The method has been successfully used to determine cobalt in vitamin B12 injections.

Simplicity, convenience, rapidity, and reproducibility characterize the oscillating reaction analytical technique. It can be used in genuinely routine analysis. Compared with modern instrumental methods, the sensitivity is not high except for thallium [49].

3. Non-equilibrium stationary state in analytical determinations

In 1999 Vukojevic′ *et al.* first described a novel quantitative method that builds on non-linear systems far from thermodynamic equilibrium [7] (Table 4). When a control parameter such as temperature, flow rate, or inflow concentration is varied, bifurcation and transition from one dynamic structure to another occurs, establishing a non-equilibrium stationary state. For example, transition from sustained oscillations to a stable stationary state occurred at a critical temperature in the B-L system. The bifurcation point was found by linear extrapolation of a plot of the square of the amplitude of the limit cycle oscillations *vs.* temperature. They also pointed out [8] that a bifurcation point is in the vicinity of two nearby attractors. This creates an extremely fragile balance, susceptible to perturbation. Even very small changes in intermediate concentrations caused by analyte addition may disturb this balance and induce detectable changes in the dynamic pattern. The non-equilibrium stationary state must be close to the

Table 3. Use of regular oscillation in metal ion determination.

Analyte	Oscillating chemical system	Dynamic linear range (M)	Detection limit (M)	Ref.
Ag^+	$NaBrO_3$-H_2SO_4-malic acid-[CuL] $(ClO_4)_2$(B)	ΔT :1.00×10^{-7} to 6.25×10^{-5}		[43]
Calcium pantothenate	$NaBrO_3$-H_2SO_4-malic acid-[CuL] $(ClO_4)_2$(B)	ΔA: 5×10^{-6}- 2.5×10^{-3}	2.5×10^{-6}	[44]
Indium ion	$KBrO_3$-MA-Ce(IV)-H_2SO_4(B)	ΔT:4.98×10^{-7}-3.85×10^{-6}	4.96×10^{-7}	[45]
Transition metal ions	Na_2S-$KBrO_3$-MA- Ce(IV) -H_2SO_4(B)	Ag^+: 8.11×10^{-12}-8.11×10^{-10} Bi^{3+}: 3.16×10^{-11}-1.10×10^{-10} Cd^{2+}:8.76×10^{-12}-3.47×10^{-10} Cu^{2+}:8.91×10^{-12}-8.91×10^{-10} Hg^{2+}:8.13×10^{-12}-8.13×10^{-10} Pb^{2+}:1.74×10^{-12}-8.70×10^{-9}	10^{-12}	[47]
Europium ion	oxalic acid-acetone- $KBrO_3$- Ce(IV)-H_2SO_4(B)	ΔT: 1.41×10^{-8}- 1.41×10^{-4}	1.04×10^{-9}	[48]
Cobalt ion	malic acid-malonic acid- BrO_3^-- Ce(IV)-H_2SO_4(B)	ΔT:5.37×10^{-12}- 5.27×10^{-8}	5.20×10^{-13}	[49]
Cr(IV) ion	Glucose-actone-$KBrO_3$- Ce(IV)-H_2SO_4(B)	ΔT_{in}: 3.5×10^{-6}- 6.0×10^{-4}	7.0×10^{-7}	[50]

Where B stands for batch system and O is CSTR system.

Table 4. Use of non-equilibrium species analysis.

Analyte	Oscillating chemical system	Dynamic linear range (M)	Detection limit (M)	Ref.
Cl^-	KIO_3-H_2SO_4 -H_2O_2	1.3×10^{-6}- 1.6×10^{-4}	1.3×10^{-6}	[7]
Br^-	KIO_3-H_2SO_4 -H_2O_2	1.0×10^{-6}-8.3×10^{-5}	1.0×10^{-6}	[7]
I^-	KIO_3-H_2SO_4 -H_2O_2	2.0×10^{-6}-1.0×10^{-4}	2.0×10^{-6}	[7]
Mn^{2+}	KIO_3-H_2SO_4 -H_2O_2	8.4×10^{-7}-8.3×10^{-5}	8.4×10^{-7}	[7]
MA	KIO_3-H_2SO_4 -H_2O_2	3.8×10^{-7}-2.1×10^{-5}	3.8×10^{-7}	[7]
Quercetin	KIO_3-H_2SO_4 -H_2O_2	1.5×10^{-8}-3.7×10^{-5}	1.5×10^{-8}	[7]
Hesperidin	KIO_3-H_2SO_4-H_2O_2	7.5-599.4 μg mL^{-1}	0.65 μg mL^{-1}	[51]
Morphine	KIO_3-H_2SO_4-H_2O_2	4.0×10^{-9}- 1.8×10^{-7}	1×10^{-9}	[52]
Paracetamol	KIO_3-H_2SO_4-H_2O_2	8.5×10^{-9}- 1.5×10^{-6}	2.7×10^{-9}	[53]
Ascorbic acid	KIO_3-H_2SO_4-H_2O_2	1.0×10^{-8}- 1.0×10^{-6}	9×10^{-9}	[54]
Sudan I	$KBrO_3$-MA-Ce(IV)-H_2SO_4	6.17×10^{-10}- 3.24×10^{-6}	9.55×10^{-11}	[55]
p-nitroaniline	tartrate-acetone-Mn^{2+}-$KBrO_3$-H_2SO_4	2.50×10^{-7}- 3.75×10^{-5}	2.50×10^{-8}	[56]
p-phenylenediamine	$KBrO_3$-MA-H_2SO_4-$Fe(phen)_3$	4.68×10^{-7}- 1.95×10^{-5}	9.50×10^{-8}	[57]
Hg^{2+}(in soil)	acetone-Mn^{2+}-$KBrO_3$-H_2SO_4-S^{2-}	8.02×10^{-10}- 6.51×10^{-7}	2.12×10^{-11}	[58]
INAH	$KBrO_3$-MA-Ce(IV)-H_2SO_4	8.60×10^{-8}- 5.00×10^{-5}	6.76×10^{-9}	[59]
Uric acid	p-HBA- $KBrO_3$ -H_2SO_4	3.73×10^{-8}- 7.48×10^{-4}	7.45×10^{-9}	[60]
Epinephrine	KIO_3-MA-Mn(II)-H_2O_2-H_2SO_4	5.2×10^{-9}- 1.1×10^{-7}	6.8×10^{-10}	[61]

bifurcation point to preserve this sensitivity. On the other hand, it must also be sufficiently far from it that small spontaneous perturbations will not induce transitions to the oscillatory side of the bifurcation. They detected hesperidin [51] in the B-L system by this method and found a linear relationship between maximum potential shift and log[hesperidin] between 7.5 - 599.4 μg mL^{-1}. The limit of detection was 0.65 μg mL^{-1}. Morphine was determined based on the linear relationship between maximum potential shift and the logarithm of the added morphine from 0.004-0.18 μmol [52]. In addition to high sensitivity (the limit of detection was 0.001 μmol), the method exhibited good precision (RSD=1.6%) and excellent sample throughput (45 samples h^{-1}). Paracetamol in pure and pharmaceutical dosage forms [53] and ascorbic acid in pharmaceutical dosage forms and in urine [54] were also determined with the B-L reaction using the pulse perturbation technique. This method has also been applied to the classical B-Z reaction. For Sudan I Gao *et al.* [55] found the range was 6.17×10^{-10}- 3.24×10^{-6} M. The limit of detection was 9.55×10^{-11} M. The main benefits are high sensitivity

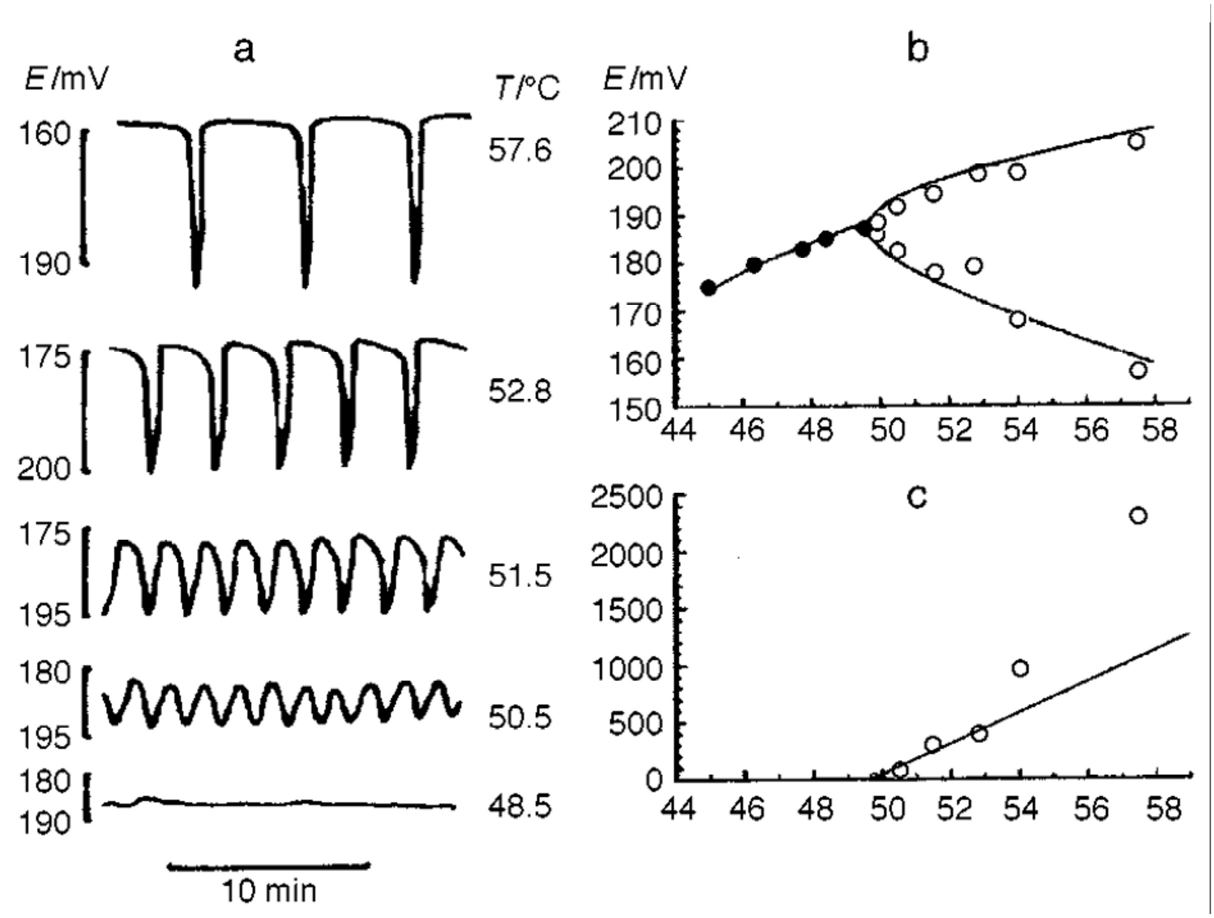

Figure 3. (a) Time series showing stable dynamic structures observed in the BL reaction at different temperatures, under the following experimental conditions: $[KIO_3]_0 = 5.9\times10^{-2}$ M, $[H_2SO_4]_0 = 5.5\times10^{-2}$ M and $[H_2O_2]_0 = 2.0\times10^{-1}$ M, specific flow rate $j_0 = 2.96\times10^{-2}$ min^{-1} and stirring rate = 900 rpm. The temperature was controlled within ±0.2 K. (b) Bifurcation diagram showing transition from sustained periodic oscillations (open circles) to a stable stationary state (solid circles) for decreasing temperature. (c) Plot of the square of the oscillation amplitudes (top to bottom) as a function of temperature. (Adapted from [7]).

and wide dynamic range. This method can be used for routine *p*-nitroaniline determination in wastewater with a recovery of 97.5% - 102.7% [56].

4. Conclusion

Oscillating chemical reactions have aroused interest both in the context of kinetic methods of analysis and their applications to analytical determinations. Over the last few years many studies have shown the potential of these reactions. The following conclusions can be drawn: (1) oscillating chemical reactions can be made extremely sensitive (*ca.* 10^{-8}-10^{-12} M, sometimes down to 10^{-13} M) to some species by modifying the system or determination in the non-equilibrium stationary state after bifurcation, providing new analytical methods. (2) Increasing numbers of species can be determined by oscillating chemical reactions. Although applications are not yet wide suggestions are beginning to emerge.

The effects of some medicines on oscillating reactions suggest their effects on the complex metabolic processes of the body (3).

In summary, oscillating chemical reactions have significant applications in analytical chemistry and medicinal chemistry.

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References

[1] I.R. Epstein, J.A. Pojman, An introduction to nonlinear chemical dynamics: Oscillations, waves, patterns and chaos (Oxford University press, New York, 1998)

[2] I. Ferino, E. Rombi, Catalysis Today, 52, 291 (1999)

[3] A.F. Taylor, Prog.React. Kinet.&Mech. 27, 247 (2002)

[4] L.P. Tikhonova, L.N. Zakrevskaya, K.B. Yasimirskii, J. Anal. Chem. 33, 1991 (1978)

[5] R. Jimenez-Prieto, M.Silva, D. Perez-Bendito, Anal. Chem. 67, 729 (1995)

[6] R. Jimenez-Prieto, M.Silva, D. Perez-Bendito, Analyst 123, 1R (1998)

[7] V.B. Vukojevic′, N.D. Pejic′, D.R. Stanisavljev, S.R. Anic′, L.Z. Kolar-Anic′, Analyst 124, 147 (1999)

[8] V.B. Vukojevic′, S. Anić, Lj. Kolar-Anić, J. Phys. Chem. A 104, 10731 (2000)

[9] J.Z. Gao, Paki. J. Bio. Sci. 8(4), 512 (2005)

[10] G. Hu, P.P. Chen, W. Wang, L. Hu, J.M. Song, L.G. Qiu, J. Song, Electrochim. Acta. 52, 7996 (2007)

[11] P.P. Chen, G. Hu, W. Wang, J.M. Song, L.G. Qiu, H.L. Wang, L.L. Chen, J.F. Zhang, L. Hu, J.Appl. Elctrochem. 38, 1779 (2008)

[12] H. Shen, Z.D. Zhang, G. Hu, J.Uni.Sci.&Tech.Chin. 40(7), 686 (2010) (in Chinese)

[13] G. Hu, L.L. Chen, J.F. Zhang, P.P. Chen, W. Wang, J.M. Song, L.G. Qiu, J. Song, L. Hu, Cent. Eur. J. Chem. 7(3), 291 (2009)

[14] H.Y. Liu, G. Hu, L. Hu, J. Anhui Uni. (Nat. Sci.) 35(1), 85 (2011) (in Chinese)

[15] M. Meng, M.M. Guo, G. Hu, Q. Wang, Huaxue Shiji 34(5), 429 (2012) (in Chinese)

[16] Q. Wang, G. Hu, M. Meng, J. Anhui Uni. (Nat. Sci.) 36(2), 79 (2012) (in Chinese)

[17] J.Z. Gao, J. Qu, W. Yang, X.X. Wei, H.X. Dai, D.Y. Lv, J. Ren, H. Chen, Amino Acid 36, 391 (2009)

[18] J.Z. Gao, Y.J. Liu, X.L. Zhang, M. Li, J. Northwest Normal Uni. (Nat. Sci.) 47(3), 49 (2011) (in Chinese)

[19] H.M. Liu, H.Y. Han, Luminescence 24, 300 (2009)

[20] J.Z. Gao, H.X. Dai, W. Yang, Anal.& Bioanal. Chem. 384(6), 438 (2006)

[21] W. Yang, K.J. Sun, W.L. Lv, L.L. Bo, X.Y. He, N. Suo, J.Z. Gao, Anal. Chim. Acta. 554, 218 (2005)

[22] J. Ren, L.L. Ji, J.Z. Gao, Y.J. Liu, W. Yang, J. Instrum. Anal. 30(11), 1311 (2011) (in Chinese)

[23] J.Z. Gao, X.X. Wei, W. Yang, D.Y. Lv, J. Qu, H. Chen, H.X. Dai, J. Hazard. Mater. 144, 67 (2007)

[24] J. Raoof, R. Ojani, A. Kiani, Bull. Chem. Soc. Jpn. 78, 258 (2005)

[25] J.Z. Gao, D.Y. Lv, W. Yang, X.X. Wei, J. Qu, H. Chen, H.X. Dai, J. Ren, Cent. Eur. J. Chem. 5(2), 581 (2007)

[26] J.Z. Gao, X.L. Zhang, J. Ren, J. Northwest Normal Uni. (Nat. Sci.) 47(1), 53 (2011) (in Chinese)

[27] J. Wang, S.T. Yang, R.X. Cai, Z.X. Lin, Z.H. Liu, Talanta 65, 799 (2005)

[28] L. Wang, W.L. Hao, Q.F. Zhang, D.Z. Sun, J. Liaocheng Uni. (Nat. Sci.) 25(1), 52 (2012) (in Chinese)

[29] J.Z. Gao, J. Qu, X.X. Wei, M. Guo, J. Ren, W. Yang, Chin. J. Anal. Chem. 36(6), 735 (2008)

[30] J.Z. Gao, G.H. Zhao, Z.X. Zhang, J. Zhao, W. Yang, Microchim. Acta 157, 35 (2007)

[31] J.Z. Gao, H.X. Dai, H. Chen, J. Chil. Chem. Soc. 52(2), 1150 (2007)

[32] W.Q. Fan, Y.H. Wang, J. Dalian Jiaotong Uni. 30(3), 66 (2009)

[33] L.L. Wang, J.H. Liu, Det.&Anal. 10(3), 41 (2007) (in Chinese)

[34] Y. Wang, J. Anhui Agri. Sci. 37(8), 3360 (2009) (in Chinese)

[35] X.Q. Bai, Y.X. Xie, H.F. Liu, X.S. Shen, J. Anhui. Agri. Sci. 37(9), 3880 (2009) (in Chinese)

[36] J.L. Wang, L.P. Long, W.X. Li, Huaxue Shiji 33(2), 138 (2011) (in Chinese)

[37] M.M. Guo, H.Y. Liu, G. Hu, J. Huainan Normal Uni. 12(3), 14 (2010) (in Chinese)

[38] Y.J. Dong, K. Gai, Mendeleev Commun. 15(6), 256 (2005)

[39] Y.S. Li, G.H. Zhao, J. Zhao, X. Li, H.B. Zhang, J.Gansu Agri. Uni. 44(6), 107 (2009) (in Chinese)

[40] X.H. Wang, Chem. Eng. 23(7), 9 (2009)

[41] X.H. Wang, Z.H. Fei, Chem.&Bioeng. 26(7), 58 (2009) (in Chinese)

[42] W.W. Zhao, Z.X. Li, Chem.& Bioeng. 27(5), 66 (2010) (in Chinese)

[43] L. Hu, G. Hu, H.Q. Xu, J. Anal. Chem. 61, 1021 (2006)

[44] L.L. Chen, G. Hu, J.F. Zhang, L. Hu, Mendeleev Commun. 19, 224 (2009)

[45] J.Z. Gao, L. Wang, W. Yang, J. Braz. Chem. Soc. 17(3), 458 (2006)

[46] P.E. Strizhak, O.Z. Didenko, T.S. Ivashchenko, Anal. Chim. Acta. 428, 15 (2001)

[47] J.Z. Gao, H. Chen, H.X. Dai, D.Y. Lv, J. Ren,

L. Wang, W. Yang, Anal. Chim. Acta 571, 150 (2006)
[48] J.Z. Gao, Y.Y. Zhang, J. Ren, M. Li, W. Yang, Cent. Eur. J. Chem. 8(3), 602 (2010)
[49] J. Wang, W. Yang, J. Ren, M. Guo, X.D. Chen, W.B. Wang, J.Z. Gao, Chin. Chem. Lett. 19,1103 (2008)
[50] J.L. Wang, L.P. Long, W.Y. Li, G.Q. Xiao, L. Li, Y. Chen, H. Tan, F.Y. Zeng, Z. Huang, Z.G. Tang, Chin. J. App. Chem. 26(2), 214 (2009) (in Chinese)
[51] N.D. Pejic′, S.M. Blagojevic′, S.R. Anic′, V.B. Vukojevic′, L.Z. Kolar-Anic′, Anal.Bioanal. Chem. 381, 775 (2005)
[52] N.D. Pejic′, S.M. Blagojevic′, S.R. Anic′, V.BVukojevic′, M.D. Mijatovic′, J.S. C′iric′, Z.S. Markovic′, S.D. Markovic′, L.Z. Kolar-Anic′, Anal. Chim. Acta. 582, 367 (2007)
[53] N.D. Pejic′, L.Z. Kolar-Anic′, S.R. Anic′, D.R. Stanisavljev, J. Pharma. Biomed. Anal. 41, 610 (2006)
[54] N.D. Pejic′, S. Blagojevic′, S.R. Anic′, Anal. & Bioanal.Chem. 389(6), 2009 (2007)
[55] J.Z. Gao, X.D. Chen, J. Ren, Y.Y. Zhang, X.X.Wei, M.Guo, W.B.Wang, J.Wang, W.Yang, Chin. J. Anal. Chem. 10, 1354 (2008) (in Chinese)
[56] J.Z. Gao, J. Liu, J. Ren, X.L. Niu, Y.Y. Zhang, W. Yang, Cent. Eur. J. Chem. 7, 298 (2009)
[57] J.Z. Gao, X.D. Chen, J. Ren, W.Yang, J. Braz. Chem. Soc. 1 (2011)
[58] W. Yang, M. Li, J. Ren, J. Northwest Normal Uni. (Nat.Sci.) 47(2), 55 (2011) (in Chinese)
[59] J. Ren, L.L. Ji, M.Q. Wang, J.Z. Gao, W. Yang, Chin. J. Anal. Lab. 31(1), 35 (2012) (in Chinese)
[60] J. Ren, W. Yang, X.L. Niu, J.Z. Gao, Chin. J. Chem. 30, 288 (2012)
[61] J.Z. Gao, Y.J. Liu, J. Ren, X.L. Zhang, M. Li, W. Yang, J. Serb. Chem. Soc. 77(1), 95 (2012)