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# Determination of gases (NO, CO, Cl<sub>2</sub>) using mixed-mode regimes in the Belousov–Zhabotinskii oscillating chemical reaction

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## Abstract

We show a principle possibility of the determination of gases concentrations (NO, CO, Cl<sub>2</sub>) by their affect on mixed-mode oscillations in the Belousov–Zhabotinskii (BZ) oscillating chemical reaction. These oscillations are characterized by single large amplitude oscillation followed by a number of small amplitude oscillations. The method of the determination is based on a construction of a calibration plot given by the dependence of the number of small amplitude oscillations on gas concentration. © 2000 Elsevier Science B.V. All rights reserved.

**Keywords:** Analytical chemistry; Gas determination; Chemical oscillations

## 1. Introduction

Kinetic methods of analysis are useful for determination of low concentrations of chemical compounds in solutions [1–3]. These methods are based on an ability of a substance to change kinetics of chemical reaction. The choice of a reaction suitable for the determination of a given compound is primarily governed by dynamic regime of chemical process. Chemical reactions may exhibit various dynamic regimes, for example, monotonic, oscillatory, quasi-periodic, mixed-

mode oscillations, chaotic etc. [4]. Among them only monotonic regimes have been widely applied in kinetic methods for trace analysis. In this case a signal obtained in experiment usually reflects reaction rate, which depends on the concentration of a compound to be determined. The determination procedure is based on the measurement of instrumental signal and its comparison with the calibration plot.

The first paper concerning possible application of regular chemical oscillations for determination of trace amounts of chemical compounds was published in 1978 [5]. The authors of this publication have shown that oscillation period may be applied as useful attribute for the determination of trace amounts of ruthenium(III). After that

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Table 1  
Purity of the gases used in experiments

Ar		NO		CO		Cl <sub>2</sub>	
Compound	Concentration (v/v %)	Compound	Concentration (v/v %)	Compound	Concentration (v/v %)	Compound	Concentration (v/v %)
Ar	>99.99	NO	>99	CO	>99.99	Cl <sub>2</sub>	>99.99
O <sub>2</sub>	$7 \times 10^{-4}$	NO <sub>2</sub>	$1 \times 10^{-3}$	CO <sub>2</sub>	$9 \times 10^{-4}$	HCl	$< 8 \times 10^{-4}$
N <sub>2</sub>	$5 \times 10^{-3}$	N <sub>2</sub> O	$8 \times 10^{-2}$	CH <sub>2</sub> O	$1 \times 10^{-3}$	O <sub>2</sub>	$< 8 \times 10^{-4}$
H <sub>2</sub>	$< 1 \times 10^{-3}$	N <sub>2</sub>	$5 \times 10^{-2}$	H <sub>2</sub> O	$1 \times 10^{-3}$	H <sub>2</sub> O	$1 \times 10^{-3}$
H <sub>2</sub> O	$9 \times 10^{-4}$	H <sub>2</sub> O	$1 \times 10^{-3}$				

several studies have been performed illustrating possibility of analytical applications of regular chemical oscillations [6–8]. Particularly, it was reported recently a procedure to determine various compounds using copper(II) catalyzed oscillating chemical reaction between hydrogen peroxide and sodium thiocyanate in alkaline medium [9–11].

There are also few publications revealing that trace amounts of chemical compounds may change complex dynamics (i.e. not simple regular oscillations) of nonlinear chemical reaction in a qualitative [12] or quantitative manner [13–16]. Qualitative changes are associated with changes of the positions of the bifurcation points. Position of the bifurcation point defines the critical value of the control parameter (concentration, temperature, stirring rate etc.) at which dynamic regime changes qualitatively, for example, steady state loses its stability and oscillations occur. Quantitative changes express the dependence of oscillations attributes (period, amplitude, Fourier spectrum, the largest Lyapunov exponent, etc.) on the concentration of chemical compound to be determined.

Most of kinetic methods of analysis are oriented on the determination of chemical compounds in water solutions. There are no methods for the determination of gaseous compounds using their effect on complex dynamics in nonlinear chemical reactions. Development of these methods is especially important for the determination of biologically active gases, such as nitric oxide (NO) and carbon monoxide (CO) [17,18]. Nitric oxide is a neurotransmitter in the central and

peripheral nervous systems and a key regulator of diverse physiological processes that include vasoregulation, platelet and neutrophil adherence, and immune defense [17]. CO has been implicated in neurotransmission [18]. Moreover, NO, CO,

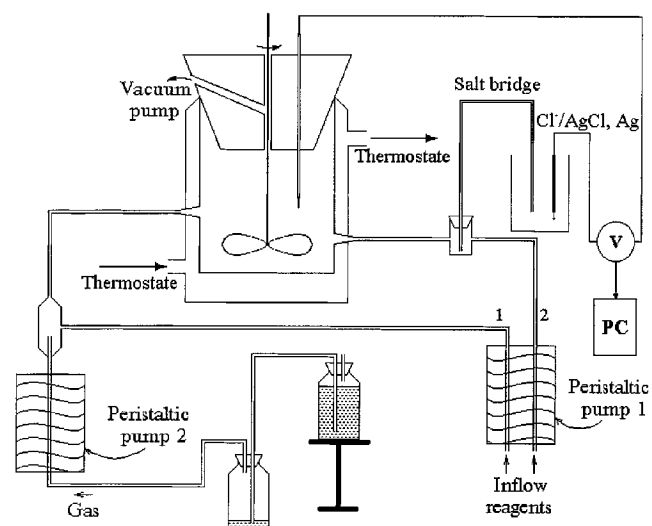


Fig. 1. Schematic diagram of the experimental set-up.

Table 2  
Dependence of  $N_s$  on the flow rate (conditions are the same as in Fig. 2)

$f_0$ (min <sup>-1</sup> )	$N_s$
0.12	1.5
0.16	4.6
0.20	7.5
0.26	13.1
0.33	17.6
0.43	29.8
0.54	51.3

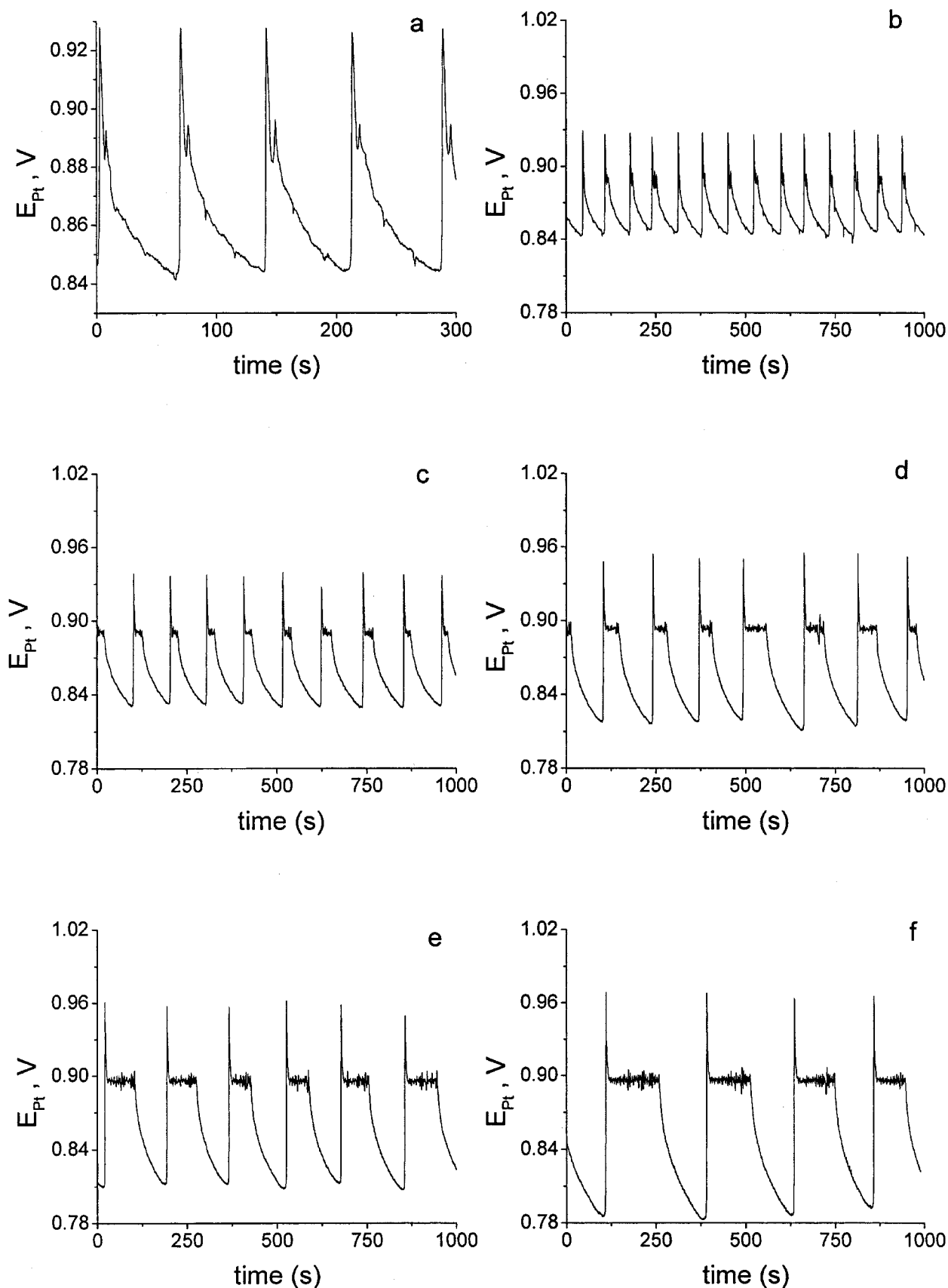


Fig. 2. Time dependencies for the Pt-electrode potential at different flow rates ( $T = 295.5$  K; inflow concentrations,  $[\text{KBrO}_3]_0 = 0.15$  M;  $[\text{H}_2\text{SO}_4]_0 = 0.32$  M;  $[\text{MA}]_0 = 0.24$  M;  $[\text{ferroin}]_0 = 1.7 \times 10^{-3}$  M), a,  $f_0 = 0.112 \text{ min}^{-1}$ ; b,  $f_0 = 0.12 \text{ min}^{-1}$ ; c,  $f_0 = 0.16 \text{ min}^{-1}$ ; d,  $f_0 = 0.26 \text{ min}^{-1}$ ; e,  $f_0 = 0.33 \text{ min}^{-1}$ ; f,  $f_0 = 0.43 \text{ min}^{-1}$ .

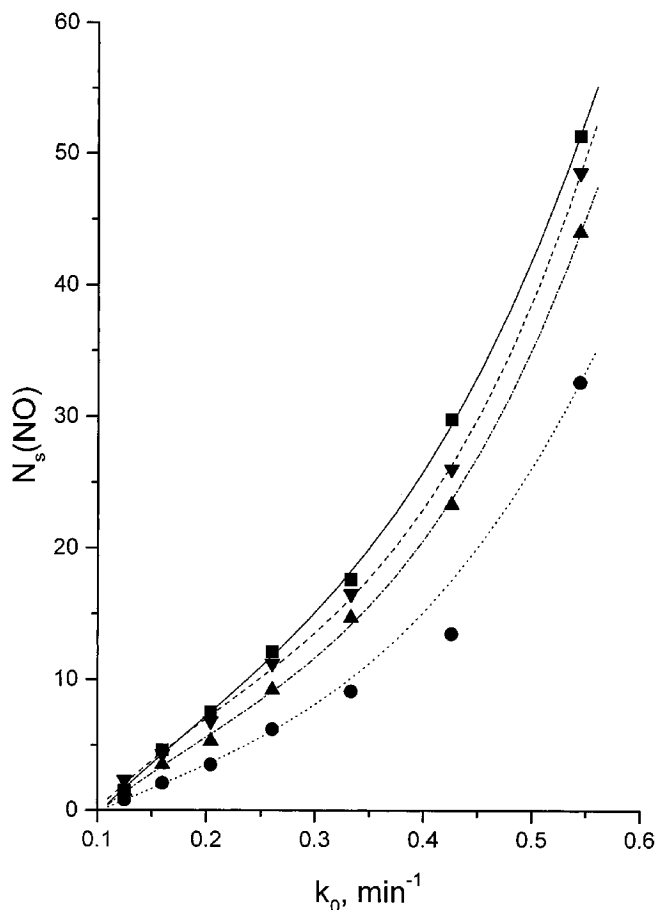


Fig. 3. Dependencies of  $N_s$  on the flow rate at various NO concentrations in its mixture with Ar (other conditions are the same as in Fig. 2), ■,  $p_{\text{NO}} = 0\%$  (v/v); ▼,  $p_{\text{NO}} = 25\%$  (v/v); ▲,  $p_{\text{NO}} = 50\%$  (v/v); ●,  $p_{\text{NO}} = 100\%$  (v/v).

and  $\text{Cl}_2$  are known as biological poisons. They are produced in various combustion processes [19–22].

In the present paper, we develop a new method for determination of gases concentrations ( $\text{NO}$ ,  $\text{CO}$ ,  $\text{Cl}_2$ ) by their affect on mixed-mode oscillations in the Belousov–Zhabotinskii (BZ) oscillating chemical reaction. These oscillations consist of single large amplitude oscillation (L) followed by a number ( $n$ ) of small-amplitude oscillation (S). They may be attributed by the symbol  $\text{LS}^n$ . We have found that  $\text{NO}$ ,  $\text{CO}$ , and  $\text{Cl}_2$  change a number of small amplitude oscillations. This property is used to construct calibration plots.

## 2. Experimental

### 2.1. Reagents

All reagents were analytical grade (Reakhim, Russia). Stock solutions of 0.3 M  $\text{KBrO}_3$ , 4 M malonic acid (MA), 6 M  $\text{H}_2\text{SO}_4$ , and  $2.5 \times 10^{-2}$  M ferroin were prepared using double distilled water.

Aqueous ferroin solution was prepared using standard method [23].

Argon was used without additional purification.

Nitric monoxide was prepared by treating copper with 32 wt.% aqueous solution of nitric acid [24]. The gas was passed through a water trap to remove nitrogen dioxide and nitric acid.

Carbon monoxide was prepared by adding formic acid dropwise to concentrated sulfuric acid at  $80^\circ\text{C}$ . The liberated gas was passed through a trap containing 10 wt.% potassium hydroxide solution, and a U-tube containing potassium hydroxide pellets [24].

Chlorine was prepared using Scheele reaction by adding saturated hydrochloric acid dropwise to manganese dioxide. To remove hydrochloric acid, the gas was passed over manganese dioxide [24].

All gases ( $\text{NO}$ ,  $\text{CO}$ ,  $\text{Cl}_2$ ) were passed through a U-tube containing a pure aluminum oxide to remove moisture.

The purity of the gases ( $\text{Ar}$ ,  $\text{NO}$ ,  $\text{CO}$ ,  $\text{Cl}_2$ ) and amounts of possible impurities were verified by gas chromatography. The results presented in Table 1 indicate that the purity of the gases was not worse than 99% (v/v).

### 2.2. Apparatus

All studies were conducted using experimental setup which is shown schematically in Fig. 1. The continuously stirred flow tank reactor (CSTR), inflow solutions and examined gas mixture were thermostated at the constant temperature  $T = 295.5 \pm 0.1$  K. Stirring rate was  $1000 \pm 30$  rpm in all experiments. State of the system was monitored by measuring the platinum electrode potential using a silver/silver chloride electrode as a reference. The impedance-matched electrode signals were fed via a Data Translation A/D converter board into a personal computer. Signals

were recorded as a function of time with time step 0.1 s.

Previously, we have used similar conditions of the BZ reaction for the development of the procedure for the manganese determination [13]. It is worth noting that the experimental setup reported here is different from those used in [13]. The manganese determination was based on a sensitivity of transient chaos observed in batch reactor. The optimal temperature was 294.2 K. In the present paper, we show that asymptotic mixed-mode regimes observed in a CSTR may be used for NO, CO, and Cl<sub>2</sub> determination. We have found that optimal temperature is 295.5 K with an error of 0.1 K. This value of error indicates that variations of temperature in the CSTR has been < 0.1 K, whereas error of temperature mentioned in [13] has indicated the temperature uncertainty of the thermostat.

For monitoring the state of the system, we have used a signal of the Pt electrode potential. Another signals may be also used for the procedure reported here. For example, one may record a potential of the bromide-selective electrode, carbon–glass electrode, optical density of the solution, etc. Our experiments have shown that the results of these measurements are the same, because it exists one-to-one correspondence between all these signals. It means that oscillation period, numbers of small and large amplitude oscillations and their sequences are the same.

### 2.3. Procedures

The BZ reaction catalyzed by ferroin was studied in a CSTR at various flow rates. Flow rate ( $f_0$ , min<sup>-1</sup>) is determined by dividing the total

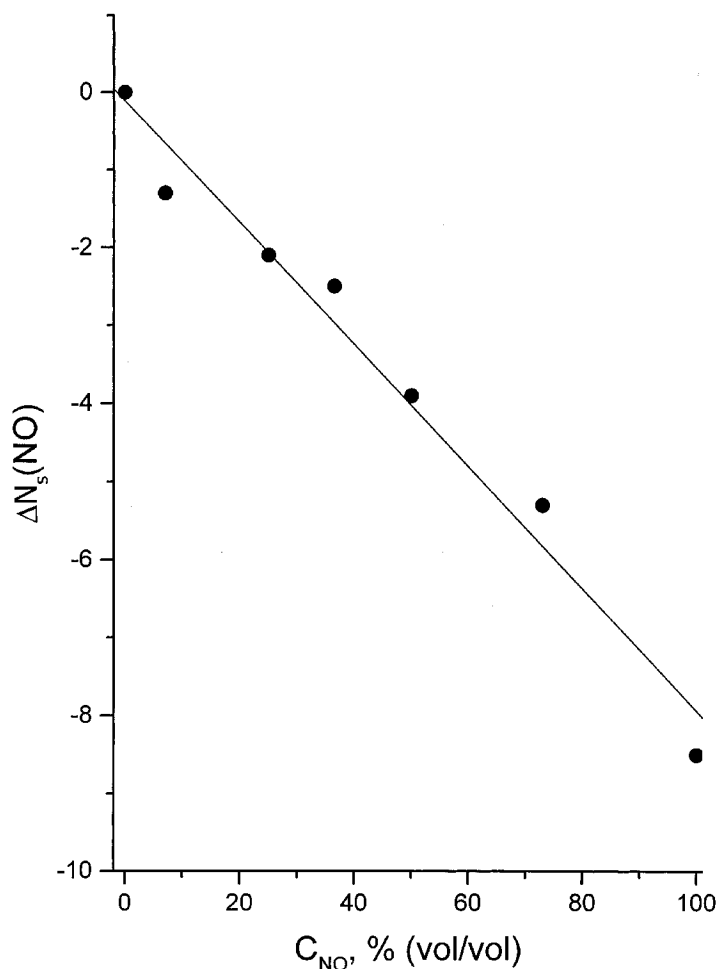


Fig. 4. Calibration plot for the NO determination at  $f_0 = 0.33 \text{ min}^{-1}$  (other conditions are the same as in Fig. 2).

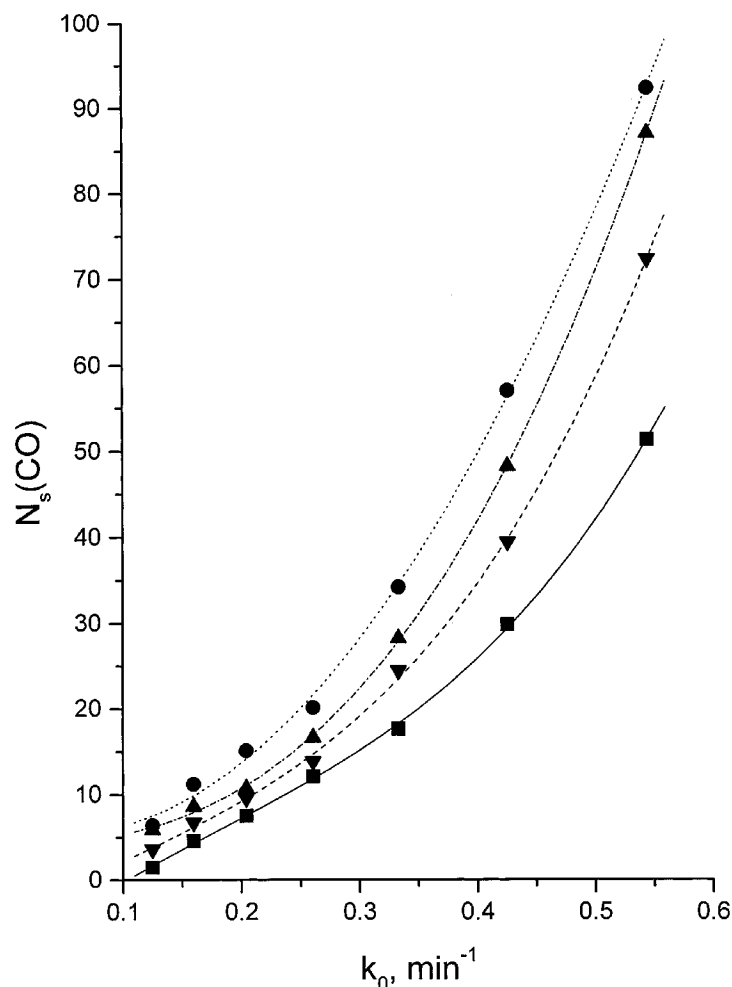


Fig. 5. Dependencies of  $N_s$  on the flow rate at various CO concentrations in its mixture with Ar (other conditions are the same as in Fig. 2), ■,  $p_{\text{CO}} = 0\%$  (v/v); ▼,  $p_{\text{CO}} = 45\%$  (v/v); ▲,  $p_{\text{CO}} = 81\%$  (v/v); ●,  $p_{\text{CO}} = 100\%$  (v/v).

rate of inflow liquid reagents ( $w$ ,  $\text{ml min}^{-1}$ ) by volume of a CSTR ( $V$ , ml),

$$f_0 = \frac{w}{V}.$$

Solutions of inflow reagents were flowed into reactor by peristaltic pump through two channels. Solution 1 containing 0.48 M MA, 0.64 M  $\text{H}_2\text{SO}_4$  and  $3.4 \times 10^{-3}$  M ferroin was pumped through the first channel, and solution 2 of 0.3 M  $\text{KBrO}_3$  was pumped through the second channel. As shown in Fig. 1, gas mixture was always pumped to a chamber located in the first channel at constant rate of  $0.35 \pm 0.01 \text{ ml min}^{-1}$  by second peristaltic pump. The Pt electrode potential corresponding to asymptotic oscillating mixed-mode regime was recorded after transient regime ( $\neq$

1500 s). The calibration plot was obtained as a dependence of the average number of small amplitude oscillations on gas concentration. Mixture of argon and a gas at a given concentration was prepared before conducting experiments by dilution of pure gas by argon using a pair of aspirator bottles, i.e. argon from the aspirator bottle was flowed into the second aspirator bottle contained a given gas above a locking solution [24]. Volumes of mixed gases were controlled by the volumes of the locking solutions. The saturated water solution of sodium chloride was used as the locking solution. The gas mixture used in experiments was stored in the aspirator bottle under locking solution. Another aspirator bottle contained locking solution was situated above it at height 15–20 cm as shown in Fig. 1. The total pressure of gas mixture was 101 kPa.

### 3. Results and discussion

Depending on flow rate ( $f_0$ ), the BZ reaction exhibits different mixed-mode oscillations as shown in Fig. 2. Fig. 2a gives the  $LS^1$  mixed-mode regime. Increase of flow rate causes the consequent increase of the number of small amplitude oscillations as illustrated in Fig. 2b–f. The data presented in Fig. 2 indicate that only compositions of  $LS^i$  mixed-mode oscillations with various numbers of small amplitude oscillations ( $i$ ) are observed at high flow rates. For example, Fig. 2b gives mixed-mode oscillations, which consist of  $LS^0$ ,  $LS^1$  and  $LS^2$  basic patterns. Therefore, each time series is characterized by average number of small amplitude oscillations per one large amplitude oscillation

$$N_s = \frac{\text{number of small amplitude oscillations}}{\text{number of large amplitude oscillations}}$$

For example, for the  $LS^{34}LS^{27}LS^{28}LS^{20}$  oscillations shown in Fig. 2f one estimates that  $N_s = (34 + 27 + 28 + 20)/4 = 27.25$ . Table 2 gives the values of  $N_s$  at various flow rates.

To verify a possibility of analytical application of mixed-mode oscillations, we studied an effect of three gases (NO, CO,  $Cl_2$ ) on these regimes. We have found that a number of small amplitude oscillations depend monotonically on concentration of these gases. Therefore, the value of  $N_s$  is useful for a construction of a calibration plot. Another characteristics of mixed-mode oscillations, such as average amplitudes of large amplitude oscillations or averaged time intervals between large amplitude oscillations, also depend on gas concentration. However, dependencies of these characteristics on flow rate or concentration of gases are not monotonic. Therefore, they can not be used for a construction of a calibration plot.

Fig. 3 shows the dependence of  $N_s$  on the flow rate at different NO concentrations in its mixture with argon. Increasing the NO concentration decreases the number of small amplitude oscillations. Therefore, increasing the NO concentration forces the BZ reaction to change the mixed-mode regime from  $LS^n$  to  $LS^{n-m}$  initiating a transition  $LS^n \rightarrow LS^{n-m}$ . The effect is more pronounced at high flow rates, i.e. for mixed-mode oscillations with large numbers of small amplitude oscillations. The dependence of  $N_s$  on the NO concentration allows one to suggest the following value to construct a calibration plot

$$\Delta N_s(\text{NO}) = N_s(\text{NO}) - N_s(\text{Ar})$$

where  $N_s(\text{NO})$  gives the average number of small amplitude oscillations for a given NO concentration in its mixture with Ar, and  $N_s(\text{Ar})$  is the corresponding number if only Ar is flowed. Fig. 4 illustrates that  $\Delta N_s(\text{NO})$  depends linearly on the NO concentration. This figure gives the linear calibration plot for the NO determination.

An increase of a number of small amplitude oscillations is caused by those reactions between NO and intermediates of the BZ reaction that are responsible for the transition  $LS^n \rightarrow LS^{n-m}$ . Only

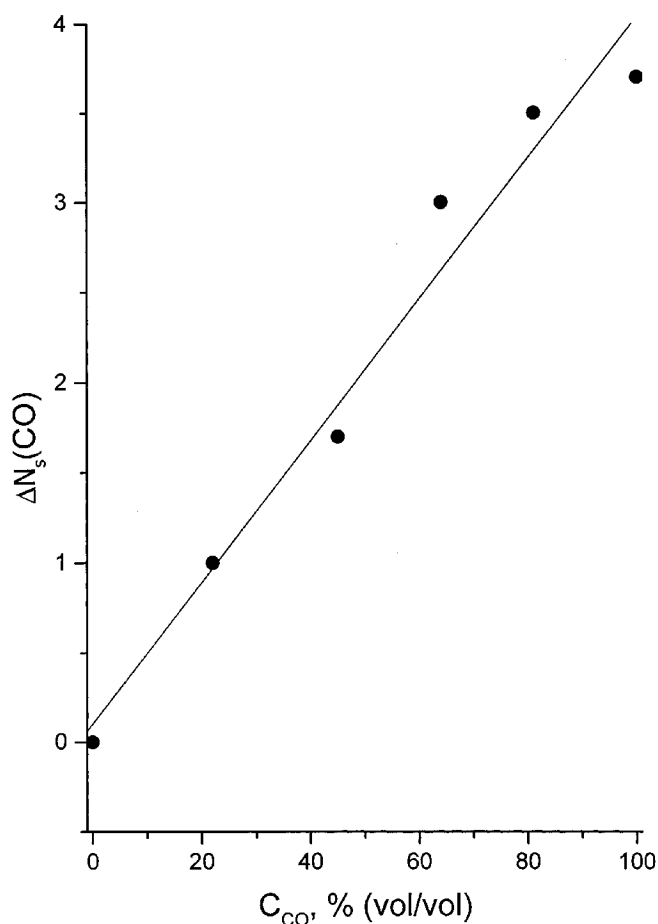


Fig. 6. Calibration plot for the CO determination at  $f_0 = 0.26 \text{ min}^{-1}$  (other conditions are the same as in Fig. 2).



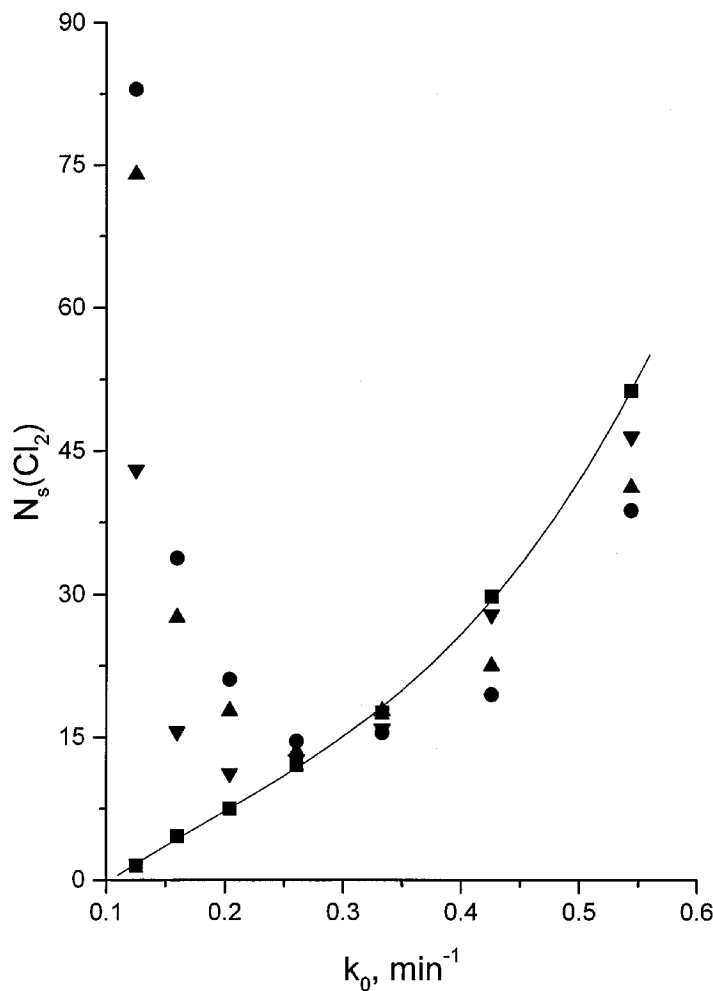
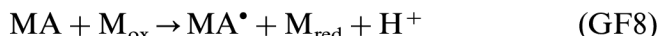
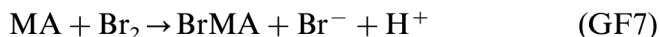
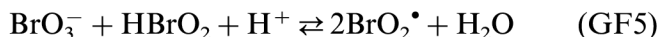
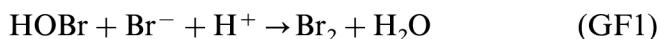


Fig. 7. Dependencies of  $N_s$  on the flow rate at various  $\text{Cl}_2$  concentrations in its mixture with Ar (other conditions are the same as in Fig. 2), ■,  $p_{\text{Cl}_2} = 0\%$  (v/v); ▼,  $p_{\text{Cl}_2} = 39\%$  (v/v); ▲,  $p_{\text{Cl}_2} = 80\%$  (v/v); ●,  $p_{\text{Cl}_2} = 100\%$  (v/v).

recently has a chemically-sound model for the BZ reaction been derived that reproduces the observed mixed-mode regimes [25]. The model can be written as,



Using steady state assumption this nine-variable model may be reduced to the four-species scheme that involves autocatalytic compound  $\text{HBrO}_2$ , control compound  $\text{Br}^-$ , catalyst (M), and bromomalononic acid (BrMA) as source of  $\text{Br}^-$  [25,26]. The autocatalysis appears as the sequence of reversible steps GF5 and GF6, limited by step GF5. The accumulation of bromomalononic acid and its consuming are represented correspondingly by steps GF7 and GF9. The steps GF1–GF6 provide for a classic clock reaction. The clock resetting is modeled by steps GF7–GF11. Concentration of  $\text{Br}^-$  governs the competition between these steps. For the BZ reaction cata-

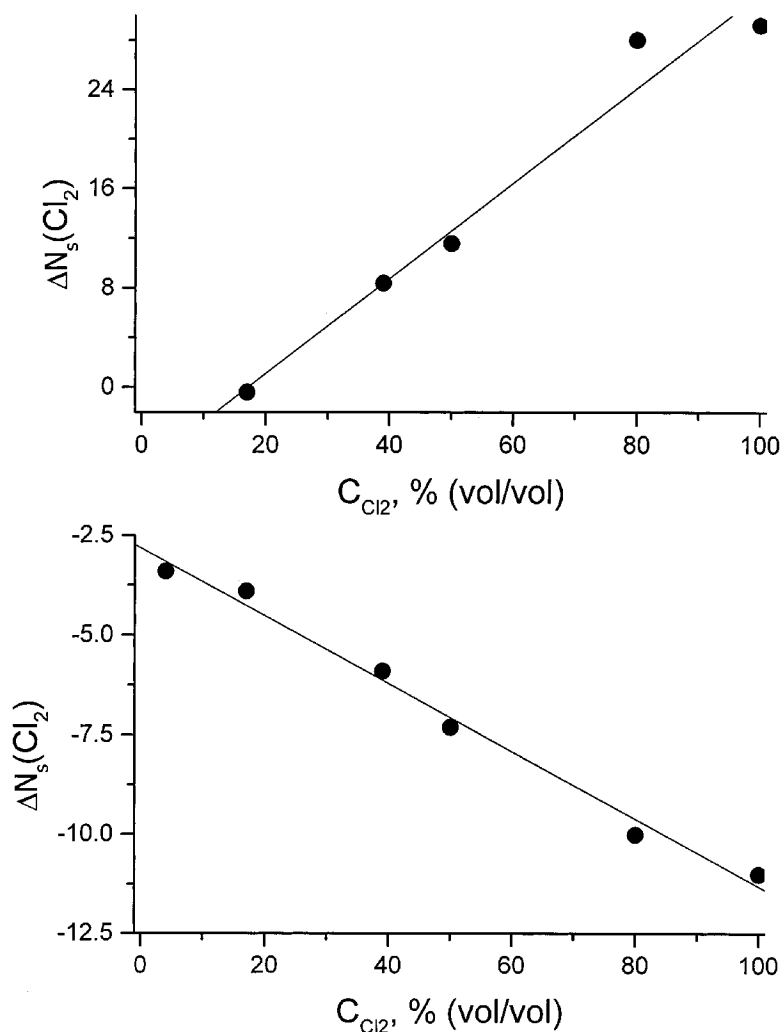


Fig. 8. Calibration plot for the  $\text{Cl}_2$  determination at  $f_0 = 0.16 \text{ min}^{-1}$  (a) and  $f_0 = 0.43 \text{ min}^{-1}$  (b) (other conditions are the same as in Fig. 2).

lyzed by ferroin, we have proposed recently a chemical model that describes mixed modes by

taking into account 13 chemical species [27]. We have found that a transition  $\text{LS}^n \rightarrow \text{LS}^{n-1}$  may be

Table 3

Sensitivity ( $\pi$ ) and detection limit ( $C_L$ ) for the determination NO, CO, or  $\text{Cl}_2$  at various flow rates ( $f_0$ )

$f_0$ ( $\text{min}^{-1}$ )	NO		CO		$\text{Cl}_2$	
	$(\pi \pm \delta\pi) \times 100$	$C_L$ (% v/v)	$(\pi \pm \delta\pi) \times 100$	$C_L$ (% v/v)	$(\pi \pm \delta\pi) \times 100$	$C_L$ (% v/v)
0.12	$-1.1 \pm 0.3$	14	$2.9 \pm 0.6$	14	$85.1 \pm 17.3$	19
0.16	$-2.2 \pm 0.3$	18	$4.6 \pm 0.7$	5	$38.3 \pm 4.2$	7
0.20	$-3.6 \pm 0.5$	5	$4.4 \pm 0.5$	18	$13.6 \pm 2.7$	12
0.26	$-5.0 \pm 0.9$	4	$3.9 \pm 0.3$	1	$9.4 \pm 2.4$	10
0.33	$-7.8 \pm 1.2$	2	$8.5 \pm 2.4$	10	$5.3 \pm 1.32$	16
0.43	$-11.9 \pm 1.9$	15	$8.3 \pm 2.0$	12	$-8.5 \pm 0.5$	5
0.54	$-25.1 \pm 8.9$	21	$20.9 \pm 6.4$	10	$-2.8 \pm 2.3$	6

Table 4

Determination of different gases in their mixtures with argon

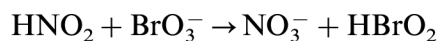
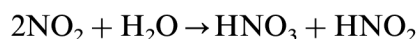
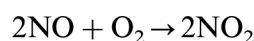
Gas, conditions	Added (% v/v)	Recovered (% v/v)	Relative error (%)
NO, $f_0 = 0.33 \text{ min}^{-1}$	25.0	25.4	1.6
	50.0	49.4	−1.2
	50.0	49.0	−2.0
	50.0	50.2	0.4
	73.0	66.3	−9.2
CO, $f_0 = 0.26 \text{ min}^{-1}$	45.0	40.6	−9.8
	45.0	43.5	−3.3
	45.0	42.8	−4.9
	64.0	66.8	4.4
	81.1	86.3	6.4
Cl <sub>2</sub> , $f_0 = 0.16 \text{ min}^{-1}$	39.0	39.0	0.0
	39.0	39.2	0.5
	39.0	40.1	2.8
	50.0	48.9	2.2
	80.0	90.2	12.8
Cl <sub>2</sub> , $f_0 = 0.43 \text{ min}^{-1}$	17.0	12.8	−24.7
	39.0	38.1	−2.3
	50.0	52.0	4.0
	50.0	51.5	3.0
	50.0	52.9	5.8

Table 5

Tolerance levels of foreign compounds in the determination of 73% (v/v) nitric oxide, 45% (v/v) carbon monoxide, and 39% (v/v) chlorine

Foreign compounds	Tolerated concentration (v/v%)		
	NO ( $f_0 = 0.33 \text{ min}^{-1}$ )	CO ( $f_0 = 0.26 \text{ min}^{-1}$ )	Cl <sub>2</sub> ( $f_0 = 0.16 \text{ min}^{-1}$ )
O <sub>2</sub>	9	8	8
N <sub>2</sub>	27	55	61
H <sub>2</sub>	2	1	3
NO <sub>2</sub>	2	Not tested	Not tested
N <sub>2</sub> O	4	Not tested	Not tested
CO <sub>2</sub>	Not tested	7	Not tested
CH <sub>2</sub> O	Not tested	2	Not tested
HCl	Not tested	Not tested	4

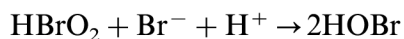
caused by an increase of the rate of autocatalytic steps in the BZ reaction. For example, this may be caused by an increase of the HBrO<sub>2</sub> production rate. Therefore, increasing the NO concentration results in an increase of this rate. It may be described by the following chemical reactions,



After oxidation of NO by oxygen, nitrogen dioxide produces nitric acid which reacts with bromate ions releasing additional amount of HBrO<sub>2</sub>. Finally, the rate of the autocatalytic steps GF5 and GF6 increases.

Contrary to the effect of NO, adding CO increases a number of small amplitude oscillations as it follows from the data presented in Fig. 5. Increasing the CO concentration produces the transition  $LS^n \rightarrow LS^{n+m}$ . The effect also is more pronounced at high flow rates. The calibration plot for the CO determination is also linear as shown in Fig. 6.

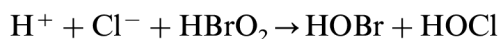
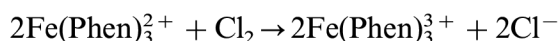
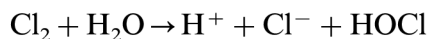
The effect of CO is caused by decreasing consumption rate of  $HBrO_2$ . It may be accounted for by the following chemical reactions



The bromination of CO produces species that release  $Br^-$ . An increase of  $Br^-$  concentration results in decreasing  $HBrO_2$  concentration according to the third reaction.

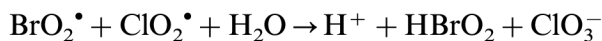
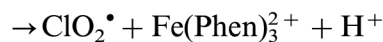
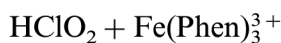
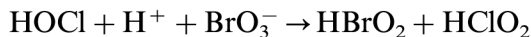
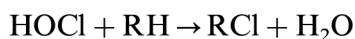
The effect of  $Cl_2$  is more complicated comparing with NO or CO. Fig. 7 gives the dependence of  $N_s$  on the flow rate at different  $Cl_2$  concentrations. The effect of  $Cl_2$  depends strongly on the flow rate. At high flow rates, an increase of the  $Cl_2$  concentration decreases the number of small amplitude oscillations, i.e. induces  $LS^n \rightarrow LS^{n-m}$  transition which is similar to the effect of NO. At low flow rates the effect of  $Cl_2$  is similar to the effect of CO, i.e. increasing the  $Cl_2$  concentration induces the  $LS^n \rightarrow LS^{n+m}$  transition. However, in both cases the dependence of  $N_s$  on the  $Cl_2$  concentration is linear. Fig. 8 gives two calibration plots which differ by the slope signs.

An increase of the number of small amplitude oscillations caused by an increase of the  $Cl_2$  concentration may be accounted for by the following chemical reactions



This subset of reactions is dominant at low flow rates. The  $HBrO_2$  concentration decreases due to the third reaction resulting in a decrease of the rate of the autocatalytic steps GF5 and GF6. At high flow rates, the total concentration of organic

species and organic radicals is higher than at low flow rates [25,28,29], and the following reactions will be dominant [30]



This subset of reactions for  $Cl_2$  illustrates that at high flow rates adding  $Cl_2$  leads to the growth of the  $HBrO_2$  concentration increasing the rate of the autocatalytic step.

Our experimental results indicate that it exists a linear dependence of  $\Delta N_s$  on the gas concentration  $C$

$$\Delta N_s = a + \pi C,$$

where  $\pi$  gives the value of the sensitivity. Each dependence is also characterized by the value of the detection limit defined by  $C_L$ , which corresponds to loss of linearity between  $\Delta N_s$  and  $C$ .

Changing flow rate may result in obtaining the most suitable calibration plot. Table 3 presents the values of sensitivities, their errors, and detection limits obtained from the dependencies of  $\Delta N_s$  on the gas concentration for at different  $f_0$ . An increase of  $f_0$  increases the sensitivity of the NO and CO determination. However, the error of determination increases as well. Detection limit has minimal values at intermediate values of  $f_0$ . Therefore, the optimal calibration plot is obtained at intermediate values of  $f_0$ . Figs. 4 and 6 give the optimal calibrations for NO and CO determination. Thus, using data presented in Table 3, one may conclude, that detection limits for the NO determination is 2% (v/v), and for the CO determination is 1% (v/v).

The data presented in Table 3 indicate that for chlorine an increase of flow rate causes a decrease of a sensitivity. Moreover, at high flow rates sensitivity of mixed-mode regimes to  $Cl_2$  changes the sign. Two optimal calibration plots exist for chlorine determination at  $f_0 = 0.16$  and  $0.43 \text{ min}^{-1}$ . The calibrations are presented in Fig. 8a and b. Detection limits are equal to 7 and 5% (v/v), respectively.

Our study of the effect of NO, CO, and Cl<sub>2</sub> on mixed-mode oscillations in the BZ reaction shows a possibility to obtain calibration plots for these gases determination. The calibration plots are presented in Figs. 4, 6 and 8. Table 4 gives the results of gases determination and their reproducibility. Relative error ranges from  $-9.2$  to  $+1.6\%$  for the nitric oxide determination, from  $-9.8$  to  $+6.4\%$  for the carbon monoxide determination, and from  $-24.7$  to  $12.8\%$  for chlorine determination. Presented results show satisfactory reproducibility of gas determination.

We have also studied the tolerance limits to some compounds for the determination of 73% (v/v) nitric oxide, 45% (v/v) carbon monoxide, and 39% (v/v) chlorine. The tolerance level of each potentially interfering compound was tested and, if interference occurred, the ratio was reduced until it ceased. The tolerance level was defined as the amount of foreign species producing an error not exceeding  $\pm 5\%$  in the determination of nitric oxide, carbon monoxide or chlorine. The results are given in Table 5. The compounds, that are not involved in redox reactions with intermediates of the BZ reaction, do not interfere with the determination, even if they are presented in large excess. Comparison of the data presented in Table 5 and concentrations of impurities in gases (see Table 1) indicates that impurities in gases do not affect on the determination procedure.

Our results shows a principal possibility of application of mixed-mode oscillations observed in nonlinear chemical reactions for the determination of gases. We have found that bubbling of different gases into inflow solutions of the BZ reaction leads to qualitative changes of LS<sup>*n*</sup> oscillations depending on the gas concentration. Adding CO produces the LS<sup>*n*</sup> → LS<sup>*n+m*</sup> transition where *m* increases with the increase of the gas concentration. Adding NO produces the LS<sup>*n*</sup> → LS<sup>*n-m*</sup> transition and *m* also increases with increasing gas concentration. The effect of Cl<sub>2</sub> depends strongly on the flow rate. At high flow rates, adding Cl<sub>2</sub> induces the LS<sup>*n*</sup> → LS<sup>*n-m*</sup> transition whereas at low flow rates adding Cl<sub>2</sub> induces the LS<sup>*n*</sup> → LS<sup>*n+m*</sup> transition. The value of *m* also increases with the increasing gas concentration.

The effect of these three gases on the BZ reaction is determined by their abilities to accumulate or to consume HBrO<sub>2</sub>, changing the autocatalytic rate. Decrease of the autocatalytic rate leads to the LS<sup>*n*</sup> → LS<sup>*n+m*</sup> transition, whereas its increase induces the LS<sup>*n*</sup> → LS<sup>*n-m*</sup> transition.

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