Polish J. Chem., **78**, 575–582 (2004)

Frequency Distribution of Chemical Oscillations in the Closed Belousov-Zhabotinsky Reaction

by K. Darowicki[*] and W. Felisiak

Department of Electrochemistry, Corrosion & Materials Engineering, Chemical Faculty,
Gdańsk University of Technology, 80-952 Gdańsk, Narutowicza 11/12, Poland

(Received September 1st, 2003; revised manuscript January 12th, 2004)

The potential registers of chemical oscillations, generated in the closed Belousov-Zhabotinsky reaction, have been submitted to detail spectral analysis using two algorithms based on the Fourier transform. It has been found that for selected stationary fragments of this signal the FFT algorithm distinctly reflects the strength of the spectral components contained in an exemplary potential register of BZ reaction. The temporal localization of these components is hidden in the phase of the spectrum, what makes the drawing of correct conclusions about the process investigated impossible. The cone-shape distribution, belonging to the group of joint time-frequency transformations, has been proposed as a proper method of nonstationary signals analysis. Spectrograms obtained by the above method have been presented, showing frequency evolution of chemical oscillations in time domain and their energy distribution simultaneously. Good reproducibility of spectrograms for potential registers of different time courses has been found. On the basis of harmonic components analysis the linear dependency between the frequency of harmonics and the composition of BZ reacting mixture has been noticed.

Key words: Belousov-Zhabotinsky reaction, chemical oscillations, spectral analysis of chemical oscillations, time-frequency analysis

Oscillating chemical reactions have been extensively studied phenomena since couple of decades. Among them the most thoroughly studied and known is Belousov-Zhabotinsky reaction, consisting in oxidation of organic reagents by bromate in acidic solutions in the presence of catalytic amounts of metal ions. The mechanism of complex dynamics of BZ reaction was proposed by Field, Körös and Noyes [1] and presented in the form of Oregonator mathematical model. Since that moment, the majority of experimental and theoretical analyses have been conducted on BZ reaction. Physical and chemical conditions, like concentration of reagents, speed of agitation, kind of reactor, temperature *etc.* have substantial influence on the dynamics of BZ reaction [2,3,4]. In general the variations of concentration of oscillating species (Br^-, $HBrO_2$, HOBr, Br_2, $BrO\cdot$, Ce^{+4}/Ce^{+3}) manifest themselves in the form of periodic and chaotic oscillations, multistability, excitability and the formation of chemical waves as well as spatial patterns.

The frequency of oscillations is a very important parameter, characterizing the kinetics of BZ reaction. Fourier transform is commonly used to evaluate the frequency

---

[*] Author for correspondence; Kazimierz Darowicki: zak@chem.pg.gda.pl

of signals. Recently, Marchettini and Rustici using the Fourier transform have presented the systematic frequency analysis of oscillations in unstirred BZ reaction for different concentrations of polyethylene-glycol [5]. In the next paper of the same authors studied the effect of temperature in a closed unstirred BZ system using FT algorithm also [6]. The Fourier transform is correct for the analysis of stationary signals. The record of electrode potential variations in BZ reaction, conducted in a closed reactor, is a typical example of nonstationary signal. In order to provide the stationarity of the signal, the investigated spectrophotometric records in cited works had to be divided into several intervals. The procedure of determining the subrecords of correct length is troublesome [7] and results obtained in such analysis are always mean. Due to this fact, the interpretation of results is ambiguous and difficult. This problem was widely discussed earlier on the example of electrochemical oscillations by Darowicki and coworkers [8].

The main purpose of this paper is to propose a suitable method of frequency analysis of chemical oscillations, generated in the BZ reaction in a closed reactor. The approach presented here is based on the application of novel spectral method of nonstationary signal analysis, so called joint time-frequency analysis. It allows decomposition of the analysed signal in joint time and frequency domain simultaneously with additional possibility to observe the energy distribution of it. Properly selected algorithms of time-frequency representations should provide correct results of analysis of periodic chemical oscillations, generated in the closed Belousov-Zhabotinsky reaction. In this approach, the frequency and the energy of oscillations in any moment of reaction progress is closely related to the kinetics of BZ reaction. The energy distribution of the potential signal, associated with chemical oscillations, provides much information on the nature of analysed process. That is why the selection of proper method of spectral analysis of potential registers of BZ reaction is very important. The application of Short Time Fourier Transformation in the analysis of BZ reaction in a closed system has already been studied by Darowicki and others [9]. It has been shown, that joint time and frequency analysis gives accces to the parameters, which are normally hidden in the analysis in time domain. In this work we focus on the comparison of two common methods of spectral analysis of signals – the FFT algorithm and the one of the members of Cohen's class time and frequency representations, the cone-shape distribution.

EXPERIMENTAL

The reagents $KBrO_3$, H_2SO_4, $CH_2(COOH)_2$, $Ce(SO_4)\cdot 4H_2O$ were of analytical grade. All the solutions were prepared using triply distilled water. The oscillatory Belousov-Zhabotinsky reaction was conducted in a closed reactor with perfect mixing, which was thermostatically maintained at 30°C in water bath. Appropriate volumes of $KBrO_3$, $CH_2(COOH)_2$, H_2SO_4, $Ce(SO_4)_2\cdot 4H_2O$ solutions were poured in this order into the reactor and then mixed. Stirring was initiated during addition of the reagents. In order to register the oscillations a Ag/AgBr electrode was used. Bromide selective electrode was placed at the bottom of a rotating teflon collar. Changes of potentials of Ag/AgBr electrode were registered *versus* Ag/AgBr reference electrode, connected with reacting mixture *via* a salt bridge. The reference electrode was placed outside the reactor in order to avoid the possibility of Br^- ions migration into the reacting mixture. The volume of reacting mixture was 220 ml and the volume of reactor 250 ml. The potential fluctuations of Ag/AgBr electrode were registered using a National Instruments 16-XE50 card. Sampling frequency was 10 Hz. Processing of the signals was carried out with the JTFA (Joint Time Frequency Analysis) application from LabView software and some applications from MatLab.

RESULTS AND DISCUSSION

Three exemplary records for bromide selective electrode in the Belousov-Zhabotinsky reactions conducted in the closed system for the selected substrates concentrations are presented in Fig. 1. Belousov-Zhabotinsky reaction is known for its sensitivity to the initial conditions of temperature, reagent concentration and mixing. All the reactions were carried out in the same conditions in the same reactor, accordingly to the experimental details described in the previous section. The experimental setup guaranteed the same conditions for all the measurements. However, the stock solutions were not deaerated before reaction. It might have some influence on the reaction progress, due to different amount of oxygene in the reacting mixtures. In Fig. 1 it is evident that the time of so called induction period (before oscillations occur) and the time of oscillation period is comparable for all the registers. However, the shape of records, the amplitude and the potential range are quite different. The amplitude of the register, depicted in Fig. 1(a), increases constantly, until the end of the oscillations, that is when the reaction reaches the thermodynamical equilibrium.

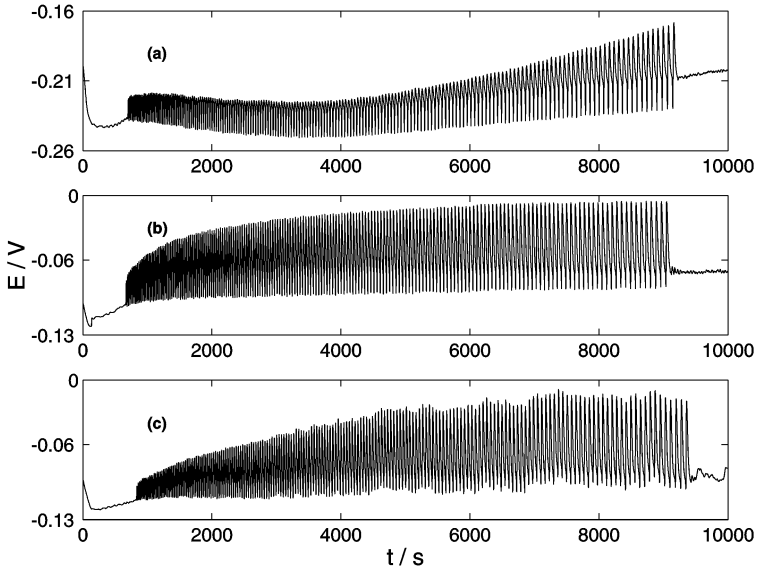

Figure 1. Determined experimentally time traces of potential of an electrode specific to bromide ion. The concentrations of the various constituents are: $[KBrO_3] = 0.07$ M, $[Ce(IV)] = 0.001$ M, $[H_2SO_4] = 1$ M, $[CH_2(COOH)_2] = 0.2$ M.

The reactions depicted in Fig. 1(b) and Fig. 1(c) are of different course. Their amplitudes change slightly, but one can observe the substantial change of potential range of oscillations in comparison with the register depicted in Fig. 1(a). In addition, the course of time record presented in Fig. 1(c) is disturbed.

Different courses of obtained registers may lead to the conclusion that the reproducibility of such reactions is poor. Nevertheless, the ultimate confirmation of such conclusion cannot be stated without the exact analysis of spectral composition of oscillations. Moreover, some authors suspect common features of different signals using analysis in the domain of frequency.

The most common method of signal analysis in the frequency domain is the fast Fourier transform (FFT) [10]. The advantage of FFT algorithm is the possibility of determination of the instantaneous spectra. The FFT algorithm gives proper results for stationary signals. In the case of nonstationary ones, the interpretation of such spectra may be difficult and ambiguous, because of the weak legibility of spectra resulting from the superposition of frequency bands. The FFT spectrum of bromide selective electrode register, as presented in Fig. 1, will not reflect its spectral composition properly. The results will be averaged. In this case, the analysis using FFT is suitable only for specified width of time register, when the condition of stationarity of signal is fulfilled. The FFT spectra for cut out fragments of the same register give correct results, however, the frequency distribution of harmonics will differ, depending on the specified time of investigated signal. One may expect shifts in the frequency and energy values of successive harmonics on the spectra. Thus, the time parameter is of great importance and should be taken into account in the analysis, in order to obtain correct and useful results.

The conclusions described above became an inspiration to present the proper method of spectral analysis of potential records in Belousov-Zhabotinsky reaction in the closed reactor. In the following section, the joint time and frequency method of signal analysis and its possible application will be demonstrated.

The time-frequency analysis is a modern branch of harmonic analysis, which is a form of local Fourier analysis, that treats time and frequency simultaneously and symmetrically [11]. Most time-frequency transformations (TFRs) transform one-dimensional signal $s(t)$, into two-dimensional function of time and frequency, $T_{s}(t,f)$ [12]. The TFRs represent a surface above time-frequency plane, that gives an indication, which spectral components of the signal are present at a given time and their relative amplitude. In other words, joint time-frequency transformations offer the possibility of observing frequency composition evolution of a signal and simultaneously its time location and energy distribution. Such transformations are useful for the analysis, visualization, modification and synthesis of different nonstationary signals of complex spectral content. The application of time and frequency representations in the analysis of electrochemical oscillations and noise has been widely studied earlier by Darowicki and coworkers [13,14]. The majority of time-frequency functions have been developed so far. In the case of BZ reaction analysis, the short time Fourier transform (STFT) method is promising [9]. The next studies on the utilization of Cohen's class quadratic time-frequency representation provided even better results – high resolution of time-frequency bands has been achieved. In this approach, we will focus on the applications of one of the member of the Cohen's class of bilinear time-frequency distribution, so called cone-shape distribution. The general formula describing Cohen's class distribution is [15]:

$$C(t,\varpi)=\frac{1}{2\pi}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}AF(\vartheta,\tau)\Phi(\vartheta,\tau)\exp\{(j(\vartheta t-\omega\tau)\}\,d\vartheta d\tau \tag{1}$$

where $AF(\vartheta,\tau)$ is the symmetric ambiguity function defined by:

$$AF_s=\int_{-\infty}^{\infty}s(t+\frac{\tau}{2})s(t-\frac{\tau}{2})\exp\{-j\vartheta t\}\,dt \tag{2}$$

where $\Phi(\vartheta,\tau)$ is called the kernel function, s – analysed signal, t – time, τ – time shift, ϖ – frequency, ϑ – frequency shift. The kernel function in the formula (1) is introduced in order to minimize the effect of unwanted cross-terms interference and to preserve true auto-terms. In other words, kernel function is a kind of filter, whose proper selection guarantees obtaining the spectrogram of the best properties. The characteristics of different kernel functions and ambiguity function are described in [16] in more detail. In this study, a mentioned above, cone-shape kernel will be used. In general the cone-shape kernel can be expressed as:

$$\Phi(\vartheta,\tau)=g(\tau)\int_{-\tau/2}^{\tau/2}\exp\{-j\vartheta t\}\,dt=2g(\tau)\frac{\sin(\vartheta\tau/2)}{\vartheta} \tag{3}$$

The kernel function applied to calculations is defined by:

$$\Phi(t,\tau)=\begin{cases}\exp(-\dfrac{\alpha\tau^2}{500}) & \mathit{for}\quad t<|\tau| \\ 0 & \mathit{otherwise}\end{cases} \tag{4}$$

The parameter α controls the degree of suppression and the larger α, the more cross-terms are suppressed at the expense of more disturbed auto-terms. It is of substantial importance, that the cone-shape kernel distribution is able to attenuate effectively the cross-terms created by two functions that have the same time center. In the process of calculating the spectrograms kernel parameter α was chosen to be 1.

Fig. 2 presents the cone-shape distribution of the record depicted in Fig. 1(a). The obtained spectrogram reflects the time spectrum and the energy of potential registers of Belousov-Zhabotinsky reaction. The decrease in frequency of oscillations as a function of time is evident. The instantaneous frequency of oscillations can be estimated for any moment of reaction progress. Basing on the spectrograms for all three records depicted in Fig. 1(a), (b) and (c), we have evaluated the frequency values of three harmonics corresponding to emergence and dying out of oscillations.

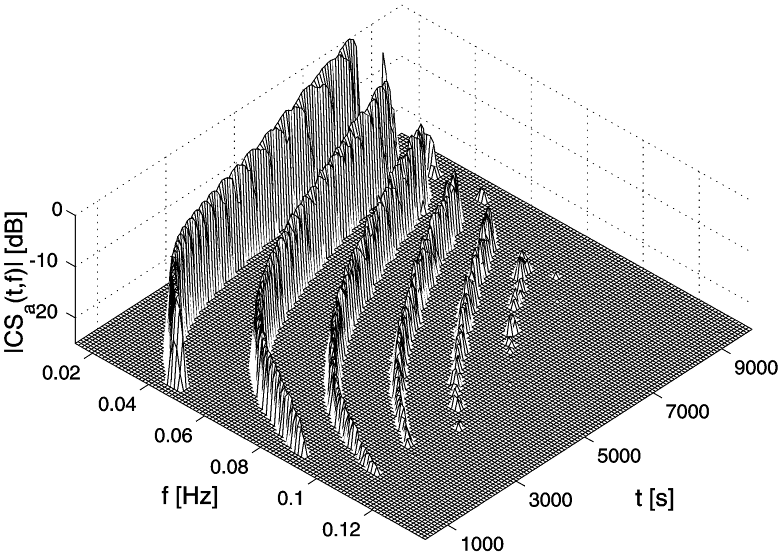

Figure 2. The spectrogram obtained by applying the cone-shape distribution algorithm to the potential register depicted in Fig. 1(a).

The results of simple analysis are collected in Tab. 1. The identitical values of frequency indicate, that the spectral composition of all three reactions is the same and may be related to the conditions, in which the reaction is conducted.

Table 1. The values of frequency of emergence and decay of the three harmonic components on the cone shape spectrograms of registers depicted in Fig. 1(a), (b) and (c).

Symbol of reaction	No. of harmonic component	Frequency [Hz] At the beginning of oscillations	Frequency [Hz] At the end of oscillations
a, b and c	1	0.057	0.012
	2	0.093	0.027
	3	0.120	0.037

It has become a motivation to carry out a series of reactions for different reagents concentrations, in order to observe the influence of composition of reacting mixture on the frequency evolution of oscillations. Five reactions were conducted in the wide range of $KBrO_3$ concentrations from 0.04 M to 1.5 M. The concentrations of the remaining substrates were constant and equal to: $[H_2SO_4] = 1$ M, $[CH_2(COOH)_2] = 0.2$ M, $[Ce(SO_4)_2 \cdot 4H_2O] = 0.001$ M. The dependency between the frequency of the appearance of the first harmonic component and the concentration of $KBrO_3$ is shown in Fig. 3. A linear increase in frequency as a function of increasing $KBrO_3$ concentration has been found.

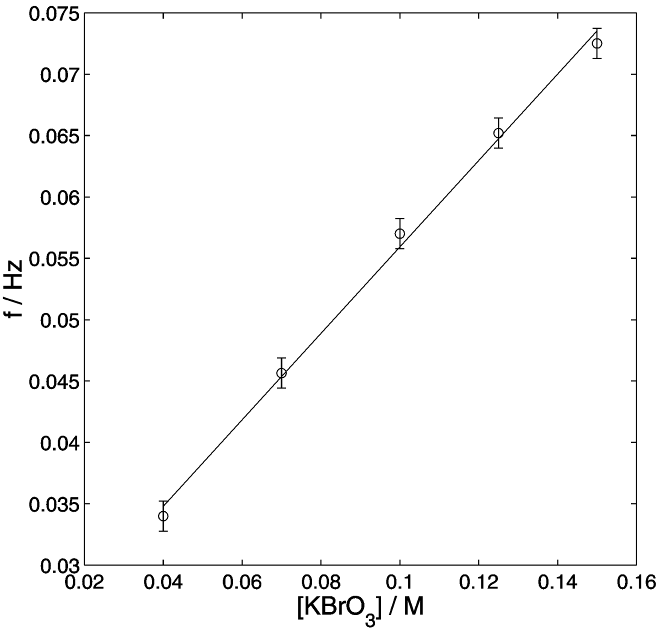

Figure 3. Frequency of the emergence of the first harmonic component on the spectrograms *versus* the concentration of $KBrO_3$ in reacting mixture. The concentrations are: $[KBrO_3]_1$ = 0.04 M, $[KBrO_3]_2$ = 0.07 M, $[KBrO_3]_3$ = 0.1 M, $[KBrO_3]_4$ = 0.125 M, $[KBrO_3]_5$ = 0.15 M, and [Ce(IV)] = 0.001 M, $[H_2SO_4]$ = 1 M, $[CH_2(COOH)_2]$ = 0.2 M.

It was proved that the FFT algorithm cannot provide satisfactory results in the case of analysis of oscillations generated in the closed Belousov-Zhabotinsky reaction. The reason is the nonstationary nature of the investigated potential registers. The FFT method may be correctly used for the analysis of short time intervals of potential registers. For longer blocks of signal, the interpretation of FFT spectra may lead to incorrect conclusions, because spectral composition of oscillations significantly varies with time. The proper and suitable version of spectral analysis, belonging to the group of joint time-frequency analysis, has been proposed. The cone-shape distribution allows observation of the change of energy of the signal, being the register of chemical oscillations and the frequency evolution in the full extent of time. Obtained spectrograms reveal the decrease in frequency of oscillations. The instantaneous values of frequency of emergence and the decay of harmonic components are deterministic parameters, which depend on the reaction composition. The linear dependency between the potassium bromate concentration and the frequency of oscillations was determined. This unquestionable fact suggests the possibility of the existence of a close relationship between the change of frequency of chemical species oscillations in the Belousov-Zhabotinsky reaction and the experimental conditions. Further studies should be undertaken in order to confirm above results and to use time-frequency representations in the study of the kinetics of the BZ reaction.

REFERENCES

1. Field R.J., Körös E. and Noyes R.M, *J. Am. Chem. Soc.*, **94**, 25 (1972).
2. Strizhak P. and Menzinger M., *J. Chem. Educ.*, **73**, 9 (1996).
3. Wang J., Sørensen P.G. and Hynne F., *Z. Phys. Chem.*, **192** (1995).
4. Johnson B.R., Scott S.K. and Thompson B.W., *Chaos*, **7**, 2 (1997).
5. Marchettini N. and Rustici M., *Chem. Phys. Lett.*, **317** (2000).
6. Masia M., Marchettini N., Zambrano V. and Rustici M., *Chem. Phys. Lett.*, **341** (2001).
7. Rustici M., Caravati C., Petretto E., Branca M. and Marchettini N., *J. Phys. Chem. A*, **103** (1999).
8. Darowicki K., Krakowiak A. and Zieliński A., *Electrochem. Comm.*, **4** (2002).
9. Darowicki K., Felisiak W. and Zieliński A., *J. Math. Chem.*, **33**, 3–4 (2003).
10. Ramirez R.W., The FFT fundamentals and concepts, Prentice Hall PTR, Englewood Cliffs, New Jersey 1985, p. 124.
11. Gröchening K., Foundations of time-frequency analysis, Birkhäuser, Boston 2001, p. 23.
12. Poularikas, The Transforms and Applications Handbook: Second Edition, CRC Press LLC, Inc, Boca Raton 2000, p. 3.
13. Darowicki K., Krakowiak A. and Zieliński A., *J. Electrochem. Soc.,* **148**, 5 (2001).
14. Darowicki K. and Zieliński A., *J. Electroanal. Chem.*, **504** (2001).
15. Qian S. and Chen D., Joint time-frequency analysis, methods and applications, Prentice Hall PTR, Upper Saddle River, New Jersey 1996, p. 146.
16. Mecklenbräuker W. and Hlawatsch F., The Wigner distribution, Elsevier, Amsterdam 1997, p. 7.