

A novel method of spectral analysis of oscillatory Belousov–Zhabotinsky reaction

Kazimierz Darowicki *, Waldemar Felisiak and Artur Zieliński

Department of Anticorrosion Technology, Gdansk University of Technology, 11/12 G. Narutowicza St., 80-952 Gdansk, Poland

Received 18 December 2002

This paper is a preliminary study of time–frequency behavior of homogenous Belousov–Zhabotinsky reaction in a batch reactor. A series of measurements performed for a variable concentration of the reaction substrates led to the conclusion that there exists time-dependency of an instantaneous frequency of fundamental frequency and harmonics and of electrode potential fluctuations generated during the process discussed. The Short Time Fourier Transformation (STFT) was proposed for analyzing electrode potential registers. On the basis of STFT analysis a decrease in frequency of oscillations of exponential character has been postulated.

KEY WORDS: Belousov–Zhabotinsky reaction, homogenous oscillatory reactions, short time Fourier transformation

1. Introduction

Belousov–Zhabotinsky (BZ) reaction belongs to the group of homogenous oscillatory reactions [1–5]. Classical Belousov–Zhabotinsky reaction consists in a catalytic oxidation of malonic acid using bromate (V) BrO_3^- in acidic environment in the presence of Ce(IV)/Ce(III) redox system. Oscillatory character of the reagents concentration variation in a reactor can be registered in many ways: potentiometrically, spectrophotometrically or by recording temperature changes of the system [6]. A mechanism of BZ reaction is very complex and still not entirely explained [7]. The research on this reaction is still of great scientists concern.

The conditions in which BZ reaction is carried out have a decisive influence on its proceeding. In the closed system periodic oscillations are observed, which become attenuated monotonically till complete attenuation, that is till the system achieves thermodynamic equilibrium. Duration and frequency of the oscillations depend on initial concentration of the reagents, temperature and speed of agitation [8]. Depending on an initial composition of the reacting mixture the reactions lasting from several minutes to several hours and additionally characterized by different induction periods can be obtained [9]. So far the investigations on BZ reaction in the closed reactor

* Corresponding author. E-mail: zak@chem.pg.gda.pl

were used to study kinetics mainly and they utilized the potentiometric measurements already mentioned. But statistical frequency analysis of the oscillations has not been performed yet.

The aim of this paper is to present a novel method of the STFT (Short Time Fourier Transformation) spectral analysis [10] for investigation of the oscillations in BZ reaction inside the closed reactor for selected range of reagents concentration. The STFT, also called Gabor transformation, allows a frequency decomposition of the signal analyzed, in this particular case of chemical oscillations and simultaneous observation of intensity variation of these oscillations with time. Such time–frequency analysis of BZ reaction performed for a wide spectrum of the reagents concentration can be the source of very interesting information concerning the nature of oscillatory reactions in general. The STFT transform was not used in an investigation of chemical oscillations earlier. And approach presented here is completely new. A detailed analysis on the applicability of Gabor transform in the investigation similar case of electrochemical oscillations was however presented by Darowicki et al. [11]. Uselessness of classical Fourier transform in the analysis of non-stationary signals was also indicated. In [12] a comparison of several spectral methods for simultaneous analysis of the oscillations associated with the electrochemical processes occurring on the electrodes was presented. A theoretical background of the STFT method, its advantages and drawbacks will be given in the next section.

2. STFT transformation – theoretical background

Application of discrete Fourier transformation enables to decompose a signal on the frequency components represented by the successive multiples of a fundamental frequency. The analysis in such case is based on application of an analyzing function having the shape of one period of a complex sine function and the successive harmonic components of this function. The system defined in such a way allows correct amplitude spectrum or power spectral density to be obtained only in certain cases. As each of the analyzing sine functions is defined in the range equal to the total length of the record subjected to the analysis, it is not possible to give a precise time localization of instantaneous fluctuations of the frequency composition appearing in certain moments of time. These fluctuations become assigned to the total length of the signal instead and they can be erroneously interpreted as additional frequency components of the signal analyzed. Apart from instantaneous, short-lasting variations of the frequency composition one may also expect to have the components in the record, which frequencies are not constant but undergo monotonic changes with time. The examples of that kind of situation are the “chirp” signals, the analysis of which is widely discussed in the literature [13,14].

To detect and observe the frequency composition fluctuation inside a given time record, the short-time Fourier transformation method is used [10]. The basic concept of this technique is implementation of a sliding time window. It allows to select a fragment of the record analyzed. Window translation describes time localization, so the squared modulus of Fourier transform taken for the fragment selected is an approximation of

instantaneous frequency energy distribution. In a digital analysis the following form of the equation is utilized:

$$STFT(m, n) = \sum_{k=0}^{L-1} s(m)\gamma(k-m)W_L^{-nk}, \quad (1)$$

where $STFT(k, n)$ is the short-time Fourier transform for a given (k, n) knot of a discrete time–frequency grid, $s(k)$ is the signal under investigation, W_L^{-nk} is the conjugated n th harmonic of a complex sinusoid of period L , $\gamma(k)$ is the sliding time window of a given shape, variable k denotes the instant translation of the window.

Equation (1) is the basic formula of the short-time Fourier transformation. Similar to a classical analysis based on Fourier series, a scalar product of signal and analyzing function is also present in this case. The modification in form of a time-dependent γ function (window) is of great significance for the results obtained and has an influence on the shape of a dual window employed in a reconstruction of the signal s from the set of the STFT coefficients defined by the formula (1). This problem is more broadly discussed in [10].

Computation of the discrete STFT is usually performed according to the following algorithm.

W samples of the input signal are read into a local buffer:

$$s_m(k) = s(k-mT), \quad k = -W_h, -W_h+1, \dots, W_h-1, W_h, \quad m = 0, \dots, M-1, \quad (2)$$

where s_m is called the m th frame of the input signal and $W_h = 1/2(W-1)$ assuming that the register W is odd. The time advance T (in samples) from one frame to the next is called the hop size. T determines the resolution of the transform in the time domain.

Obtained sequence of results (data frame) is modified by pointwise multiplying by selected spectrum analysis window $h(k)$. In this way we can achieve m th windowed data frame:

$$\tilde{s}_m(k) = s_m(k)h(k), \quad k = -W_h, \dots, W_h. \quad (3)$$

Extending the signal with zeros on both sides of the $\tilde{s}_m(k)$ is performed to obtain the zero-padded windowed data frame and simultaneously better resolution in the frequency domain:

$$\tilde{s}'_m(k) = \begin{cases} \tilde{s}_m(k), & |k| \leq W_h, \\ 0, & W_h < k < \frac{N}{2} - 1, \\ 0, & -\frac{N}{2} \leq k < -W_h, \end{cases} \quad (4)$$

where N is the FFT size, chosen to be a power of two larger than W .

In the last step the modified register is subjected to N -pointed FFT giving the transform STFT at time m :

$$S(n, m) = \sum_{k=-N/2}^{N/2} \tilde{x}'(k) \exp\left(\frac{-j2\pi nk}{N}\right). \quad (5)$$

For the sake of the properties of symmetry of Fourier transform each of the analysed signal is represented by matrix $N/2M$ of so-called factors. Squared modulus of factors determine the square representation of signal – STFT spectrogram also called Gabor spectrogram.

Depending on the particular needs the analyzing windows of different shape can be utilized. In this work Hanning window [15, pp. 106, 109], one of the most universal ones, was used. Application of the analyzing window introduces an additional limitation originating from a time–frequency variant of the uncertainty principle [16, pp. 24–36]. Due to the above it is impossible to obtain ideal localization of a given signal in the time and frequency domain simultaneously. Narrowing the analyzing window meaning higher accuracy of the time localization deteriorates resolution in the frequency domain and vice versa. This forces a compromise between these quantities being dependent on the particular purpose of the analysis [10].

3. Experimental

Belousov–Zhabotinsky reaction was conducted in 250-ml closed reactor with perfect stirring. The reactor was kept in a water bath at constant temperature of 30°C. The speed of agitation was the same for all the measurements. The total volume of a reacting mixture was equal to 220 ml. In the investigation pfa reagents were used. They were prepared with triple distilled water. Chemical reagents in the experiment KBrO_3 , $\text{CH}_2(\text{COOH})_2$, H_2SO_4 , $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ were prepared without previous purification except KBrO_3 , which was subjected to recrystallization after hot dissolution to remove Br^- ions. The reagents were added to the reactor in the following order: water, KBrO_3 , $\text{CH}_2(\text{COOH})_2$, H_2SO_4 , $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, stirring was initiated during addition of the reagents. Several reactions for different reagents concentrations were carried out.

In order to register the variation of bromide ions and Ce(III)/Ce(IV) concentration silver/silver bromide (Ag/AgBr) electrode and platinum electrode were placed inside the reactor. Silver/silver bromide electrode immersed in 0.01M KBr solution constituted a reference electrode. To eliminate the possibility of Br^- ion migration to the reacting mixture the reference electrode was placed outside the reactor and connected with it via an electrolytic key. 10% solution of KNO_3 served as an electrolyte.

The reaction was registered in a two-channel mode using a National Instruments 16-XE50 card and obtaining the records of Pt electrode and Ag/AgBr electrode potential fluctuations simultaneously. Sampling frequency was equal to 10 Hz. Processing of the signals was carried out with the JTFA (Joint Time Frequency Analysis) application from LabView software by the National Instruments and some applications from MatLab software.

4. Results and discussion

STFT analysis was applied to the set of several registers of BZ reactions. In every case similar results were obtained, therefore the discussion presented below is

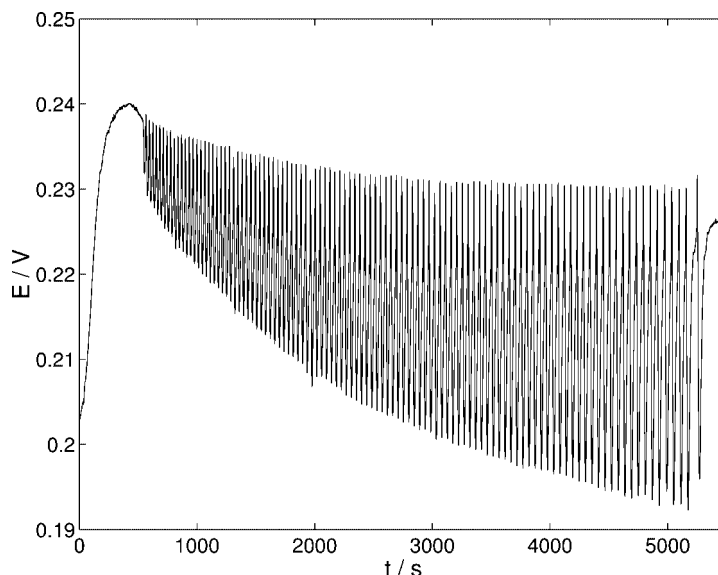


Figure 1. An exemplary time record of Ag/AgBr electrode potential fluctuations during oscillatory Belousov-Zhabotinsky reaction. Reaction reagents concentrations are: $[\text{KBrO}_3] = 0.07 \text{ M}$, $[\text{CH}_2(\text{COOH})_2] = 0.2 \text{ M}$, $[\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}] = 0.001 \text{ M}$, $[\text{H}_2\text{SO}_4] = 0.6 \text{ M}$. Potential oscillations sampled at frequency 10 Hz.

related to one, particular reaction register. The reagents concentrations of this reaction were: $[\text{KBrO}_3] = 0.07 \text{ M}$, $[\text{CH}_2(\text{COOH})_2] = 0.2 \text{ M}$, $[\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}] = 0.001 \text{ M}$, $[\text{H}_2\text{SO}_4] = 0.6 \text{ M}$.

Figure 1 presents an exemplary record of bromide electrode potential fluctuation during the oscillatory reaction. There are changes of both amplitude and frequency of particular oscillations visible that are exhibited as gradual “departure” of the successive fluctuations of electrode potential. A result of the spectral analysis in form of the PSD spectrum is shown in figure 2. Strong band existing near the frequency of 0.02 Hz was subjected to a detailed analysis. Two additional power spectra were determined (figure 3) – the first engulfed (figure 3(a)) a sub-record being the first half of the signal analyzed, depicted in figure 1. The second subrecord (figure 3(b)) corresponded to the second half of the signal under investigation. A frequency analysis of the band discussed revealed a shift in its localization from 23.6 mHz to 18.9 mHz. Frequency fluctuation of one of the bands suggested application of the short-time Fourier transformation. Figures 4 and 5 present the spectrograms (square of the STFT modulus) of the oscillations for the case described. Changes in the frequency of the band previously analyzed and of the rest of harmonic components are evident and confirm the need of the STFT application. There are given the spectrograms for different length of the analyzing window – 256 and 64 points. Broadening of the bands associated with an implementation of the narrower analyzing window is visible. It is a direct result of the time-frequency uncertainty principle described earlier. Because of much better accuracy in

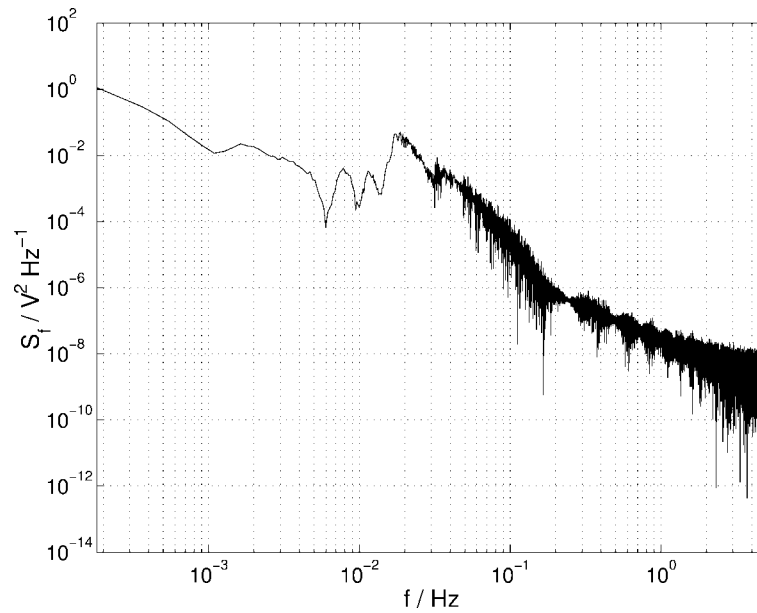


Figure 2. Power spectral density of the record presented in figure 1.

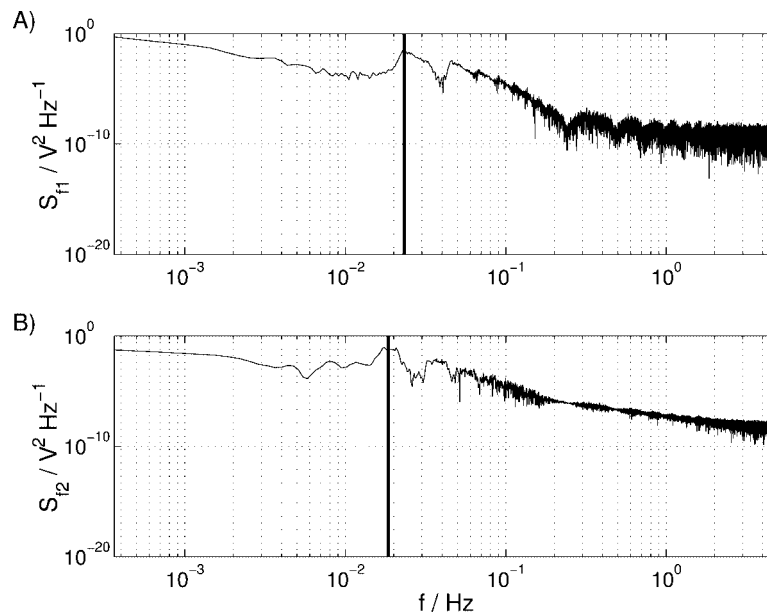


Figure 3. Change of a center frequency of the selected band during oscillations. (a) the PSD of a subrecord taken as the first half of total oscillations lifetime; (b) the PSD for the second half, respectively.

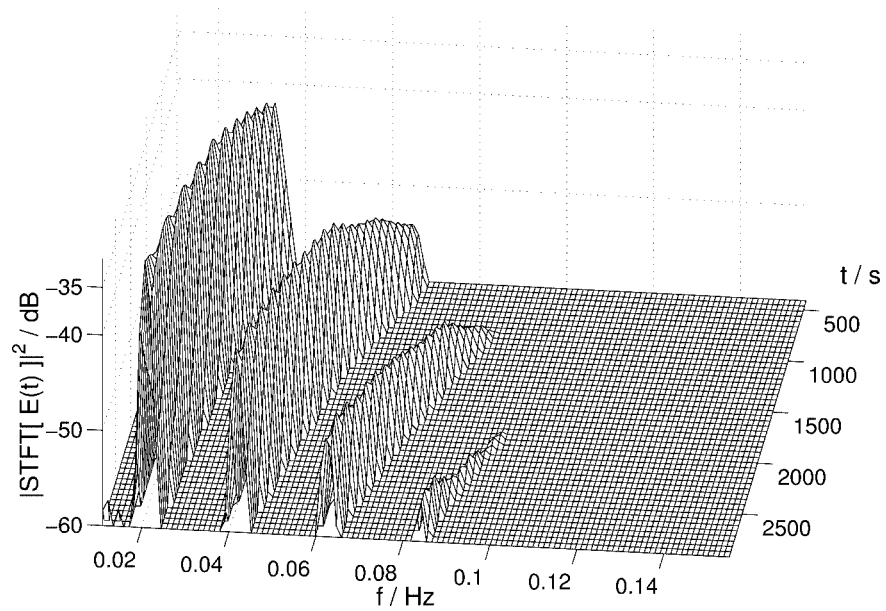


Figure 4. A fragment of the spectrogram of Ag/AgBr electrode potential oscillations, presented in figure 1. Hanning window of length 256 points was applied.

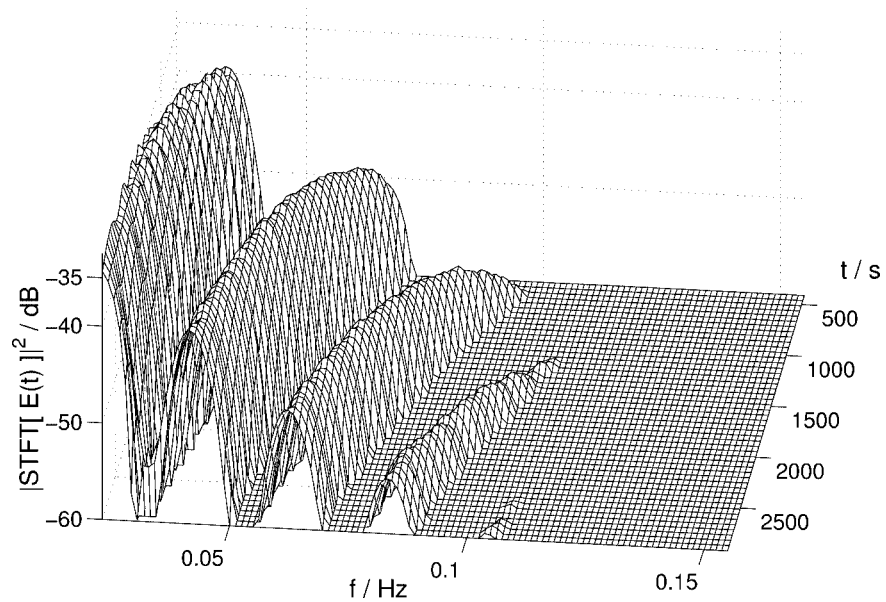


Figure 5. A fragment of the spectrogram of Ag/AgBr electrode potential oscillations, presented in figure 1. Hanning window of length 64 points was applied.

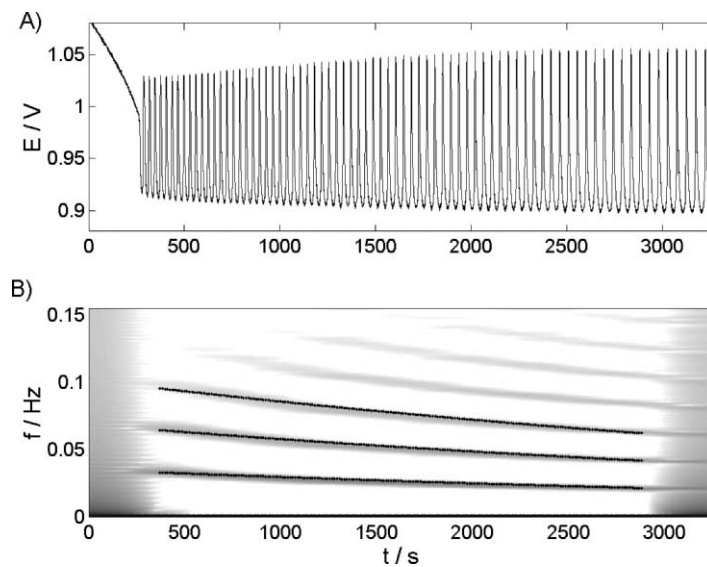


Figure 6. Oscillations of Pt electrode potential (a) and corresponding spectrogram with the results of an exponential fit marked by solid line (b). Reaction reagents concentrations are: $[KBrO_3] = 0.07$ M, $[CH_2(COOH)_2] = 0.2$ M, $[Ce(SO_4)_2 \cdot 4H_2O] = 0.001$ M, $[H_2SO_4] = 0.6$ M. Sampling frequency of signal: 10 Hz.

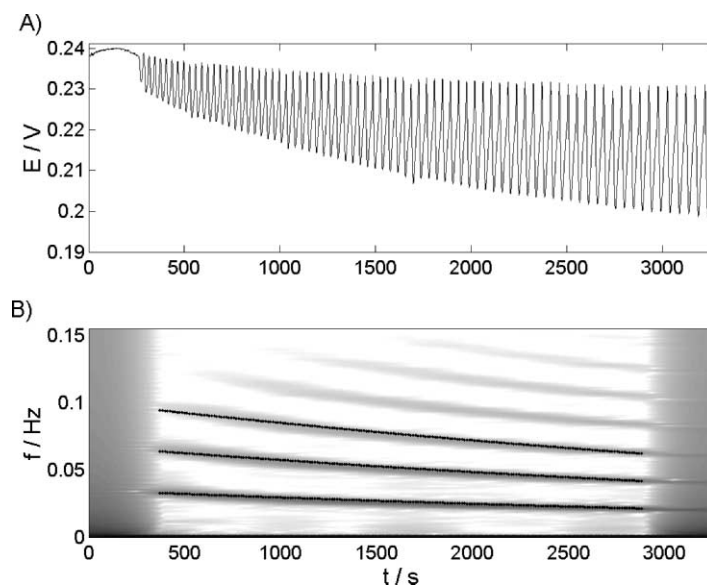


Figure 7. Oscillations of Ag/AgBr electrode potential (a) and corresponding spectrogram with the results of an exponential fit marked by solid line (b). Reaction reagents concentrations are: $[KBrO_3] = 0.07$ M, $[CH_2(COOH)_2] = 0.2$ M, $[Ce(SO_4)_2 \cdot 4H_2O] = 0.001$ M, $[H_2SO_4] = 0.6$ M. Sampling frequency of signal: 10 Hz.

the frequency domain, the window of length 256 points was selected as the analyzing one.

In order to find some regularity in the instantaneous frequency variations of the oscillatory system three frequency bands corresponding to the lowest frequencies were subjected to the analysis. A linear characteristic of the frequency bands discussed, displayed in a semi-logarithmic scale, suggests the possibility of a simple model application to each of them:

$$f_i = f_{i0} \exp(b_i t), \quad (6)$$

where: f_i ($i = 1, \dots, 3$) is the instantaneous frequency of the successive band, f_{i0} , b_i are the constants of an exponential model of frequency attenuation of the successive components of the oscillatory bands. The examples of the least square method fits for potential oscillation of Ag/AgBr and platinum electrodes are shown in figures 6 and 7, respectively. High correlation coefficients of 98% order indicate a correct model selection.

5. Conclusions

The results of the analysis of Belousov–Zhabotinsky oscillatory reaction have been presented. Variations with time of the amplitude and frequency of electrode potential have been found. This fact suggested the necessity of the short-time Fourier transform application in order to visualize temporal fluctuations of a frequency composition of the process investigated. A series of measurements performed for different concentration of the reaction substrates revealed the possibility of fitting an exponential model of frequency decrease of the successive harmonics in the oscillatory process. The paper presents the preliminary investigations, which ultimate aim will be to connect the parameters of instantaneous frequency–time relation with kinetic parameters of chemical oscillatory process.

Acknowledgement

This work was financed by KBN grant number 8T10C05215.

References

- [1] B.P. Belousov, Ref. Radiats. Med. 145 (1958) 1959.
- [2] G. Nicolis and J. Portnow, Chem. Rev. 73(4) (1973) 365–384.
- [3] R. Epstein, Physica D 7 (1983) 47–56.
- [4] H.L. Swinney, Physica D 7 (1983) 3–15.
- [5] J.L. Hudson, M. Hart and D. Marinko, J. Chem. Phys. 71 (1981) 1601.
- [6] S. Fujieda and W. Zhang, Thermochim. Acta 267 (1995) 95–106.
- [7] R.J. Field, E. Körös and R.M. Noyes, J. Am. Chem. Soc. 94(25) (1972) 8649–8664.

- [8] V.K. Vanag and D.P. Melikhov, *J. Phys. Chem.* 99 (1995) 17372.
- [9] J.C. Roux, A. Rossi, S. Bachelart and C. Vidal, *J. Phys. Lett.* 42 (1981) L271.
- [10] S. Qian and D. Chen, in: *Joint Time–Frequency Analysis, Methods and Applications* (Prentice Hall, New York, 1996) pp. 45–73.
- [11] K. Darowicki, A. Krakowiak and A. Zieliński, *J. Electrochem. Soc.* 148(5) (2001) E233–E236.
- [12] K. Darowicki, A. Krakowiak and A. Zieliński, *Electrochem. Comm.* 4 (2002) 158–162.
- [13] S. Kayhan, *Signal Processing* 66 (1998) 111.
- [14] N. Ma, D. Vray, P. Delachartre and G. Gimenez, *Signal Processing* 56 (1997) 149.
- [15] R. Carmona, W.-L. Hwang and B. Torresani, *Practical Time–Frequency Analysis* (Academic Press, 1998).
- [16] K. Grochenig, *Foundations of Time–Frequency Analysis* (Birkhauser, Boston, 2001).