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Time-Frequency Characteristics of Chemical Oscillations. Experimental and Model Studies*

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Chemical oscillations exhibit nonlinear, and nonstationary features and their complete characterization cannot be accomplished *via* classical Fourier transform. That is why there is a need for another analysis framework in joint time-frequency domain. In this paper the authors propose a proper methodology of spectral analysis of Belousov-Zhabotinsky (BZ) reaction. The short time Fourier transformation (STFT) has been applied to the analysis of potential registers of BZ reaction in a batch reactor. The method allowed finding the frequency and energy distribution of chemical oscillations in the function of time. The similarities and the differences between the spectrograms generated for the experimental data and simulated time series, based on the modified Oregonator model, are briefly discussed.

Key words: chemical oscillations, Belousov-Zhabotinsky reaction, joint time-frequency analysis, short time Fourier transformation (STFT)

Studies on nonlinear dynamics are a part of rapidly developing interdisciplinary research field. In recent years investigations of chemical oscillations have become an important part of this field. The highly nonlinear Belousov-Zhabotinsky (BZ) reaction is the most widely studied phenomenon among all of homogeneous chemical oscillators [1]. There are numerous evidences of complicated dynamical behavior of this system. During the oxidation of organic reagents by bromate, catalyzed by metal ions various concentration oscillations have been observed so far. Complex oscillations and chaotic behavior have been observed experimentally and explained theoretically using appropriate chemical models in BZ system when conducted in a continuous-flow stirred reactor (CSTR) [2–5] and batch reactor [6–10].

Nonlinear dynamics of chemical oscillations is very often analyzed in the domain of frequency. A common way of signals analysis is to decompose them into a number of waves, each having its own rate and frequency of oscillation. The Fourier transform is usually utilized to analyze spectral composition of signals. The large number of publications concerning Fourier analysis confirms its high suitability in investigation of chemical oscillations [5,11–12]. However, there are some limitations of this

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* Dedicated to Prof. Dr. Z. Galus on the occasion of his 70th birthday.

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method, because the reliability of obtained results strongly depends on the stationarity of analyzed signal. Stationarity is treated as a constancy of statistic values: the mean value and variance in the whole range of the time recording [13]. In case of stationary signal its autocorrelation function is independent on time and depends only on the displacement value, implying constancy of the frequency composition of the signal. Experiments conducted on the BZ reaction show that the amplitude as well as the frequency of oscillations vary with time. It means that their character is highly nonstationary and application of regular Fourier transformation strongly depends on the time interval of analyzed record. Lack of stationarity results in variability of the power spectral density as a function of time. The FT applied to a nonstationary signal (*i.e*. BZ reaction record) gives always averaged results in the form of spectrum being the composition of time dependent spectra.

Due to the inherent nonstationarity of BZ reaction records and the limitations of classical approach there is a need for simultaneous analysis of nonstationary chemical oscillations in time and frequency domains. The purpose of this paper is to present the main concepts of a method of signal analysis, called time-frequency representations (TFR), which characterize the temporal and spectral signal components on a joint basis. TFRs were designed for the analysis of nonstationary signals. The method has been broadly utilized as a perfect tool for exploratory analysis as well as for filtering of different oscillatory signals, which frequency and amplitude varies with time [14]. In recent papers Darowicki and others have focused on the theoretical introduction to the analysis of chemical oscillations using time-frequency representations. Different methods of joint time-frequency analysis, among them short time Fourier transform (STFT) and Cohen's class distributions, have been discussed in terms of common criteria, namely: the precision or resolution of the decomposition, the form and ease of interpretation of results and the complexity of computation [15].

In this approach experimental potential registers of chemical oscillations generated in a BZ reaction will be submitted to detailed analysis using the STFT algorithm. The results of analysis will be qualitatively compared with the simulated data created on the basis of the available mathematical models of BZ reaction. A new technique of ridge extraction from time-frequency spectrograms will be demonstrated as a method for ideal visualization of spectral composition of chemical oscillations.

EXPERIMENTAL

The reagents $KBrO_3$, H_2SO_4, $CH_2(COOH)_2$, $Ce(SO_4)_2 \cdot 4H_2O$ were of analytical grade. All the solutions were prepared using triply distilled water. The oscillatory Belousov-Zhabotinsky reaction was conducted in the reactor with perfect mixing, which was thermostatically maintained at 25°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 platinum selective electrode was used. Changes of potentials of Pt electrode were registered *versus* calomel reference electrode, connected with reacting mixture *via* salt bridge. The volume of reacting mixture was 220 ml and the volume of reactor 250 ml.

Data acquisition system consisted of a DAQ 16-XE50 card, 4-channel SCXI-1121 isolation amplifier and antialiasing SCXI-1141 filter. The system allowed collection of data in two-channel mode, at high level of accuracy and with necessary (5 times) amplification. The potential fluctuations of Pt electrode were registered with sampling frequency 10 Hz.

RESULTS AND DISCUSSION

Figure 1 presents the exemplary records of Belousov-Zhabotinsky reaction conducted in the batch reactor. It is demonstrated that, depending on the set of initial concentrations of the reagents, BZ reaction may exhibit different, even very complex dynamic behavior. In each of the experiments there is a short (about 10 minutes) induction period after which oscillations occur. Fig. 1(a) shows simple periodic oscillations. In this case the amplitude and period of individual oscillations vary only slightly from that of the previous event. The time evolution of reaction depicted in Fig. 1(b) is more irregular. The transition between periodic oscillations and mixed mode oscillations is evident. The most complex behavior of BZ reaction is shown in Fig. 1(c). After regular oscillatory phase, which lasts over one hour, the course of the reaction changes substantially and the following oscillations of different amplitude and frequency appear unpredictably.

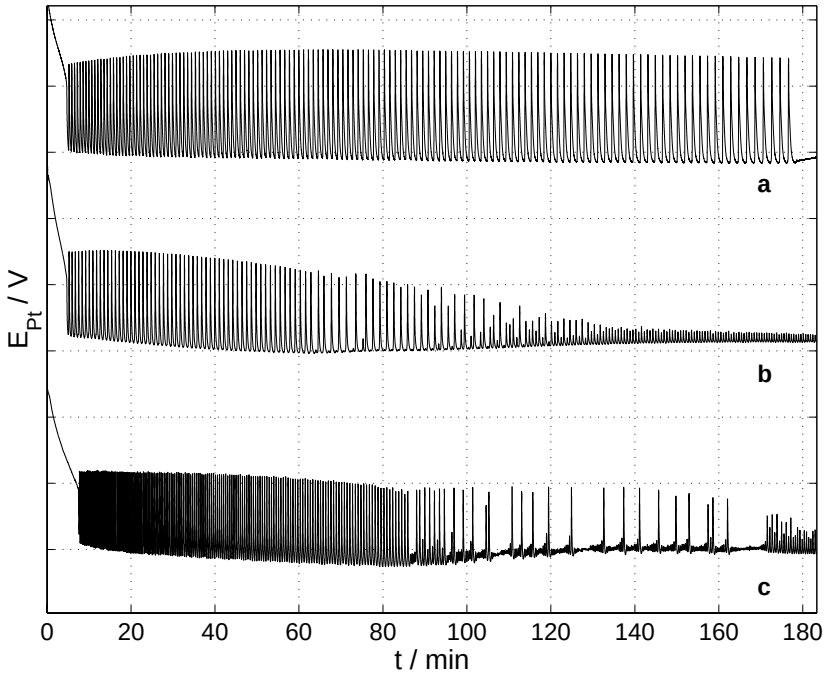

Figure 1. Exemplary time records of Pt electrode potential fluctuations during the Belousov-Zhabotinsky reaction. The reagent concentrations are as follows: (a) $[KBrO_3]$ = 0.07 M, $[CH_2(COOH)_2]$ = 0.2 M, $[Ce(SO_4)_2]$ = 0.001 M, $[H_2SO_4]$ = 1 M, (b) $[KBrO_3]$ = 0.03 M, $[CH_2(COOH)_2]$ = 0.2 M, $[Ce(SO_4)_2]$ = 0.001 M, $[H_2SO_4]$ = 1 M, (c) $[KBrO_3]$ = 0.055 M, $[CH_2(COOH)_2]$ = 0.3 M, $[Ce(SO_4)_2]$ = 0.001 M, $[H_2SO_4]$ = 1 M.

The complex mechanism of BZ reaction has been deeply studied earlier. Now universally accepted is the FKN mechanism [16]. One of the modifications of mathematical model of the FKN, called Oregonator, with the elementary reactions and rate constants is summarized in Table 1. It explains the mutual interactions between the major species in BZ system. Accordingly the frequency of oscillations is determined by the rate of turning on the appropriate reactions on and off at proper time. In general the variations of concentration of the oscillating species (Br^-, $HBrO_2$, HOBr, Br_2, BrO•, Ce^{4+}/Ce^{3+}) manifest themselves in the form of different kinds of oscillations. The potential of platinum electrode, E_{Pt}, corresponds to the oscillations in the ratio of $[Ce^{4+}]/[Ce^{3+}]$ as well as other oscillating species and describes the time evolution of the whole investigated system. It is of crucial importance that the trace of Pt or Br^--ion specific electrode can be clearly resolved into repeating periods corresponding to the elementary chemical processes. Therefore the frequency of the processes of formation and decay of cerium (forms Ce^{3+} or Ce^{4+}) and bromide ions alternately is an important parameter related to the kinetics of BZ reaction. Tracking the period changes is a key to better understanding of the mechanism of chemical oscillations.

In the subsequent part of the paper the method for the extraction of frequency information from the selected register of the BZ reaction will be demonstrated. The register depicted in Fig. 1(a) will be submitted to a detailed analysis in joint time and frequency domain using the STFT algorithm. The reason for the selection of the register depicted in Fig. 1(a) is that it represents the most regular form from all the presented registers, has the smallest deviation from the stationarity and it may be reconstructed using numerical methods on the basis of modified Oregonator model.

Spectral techniques allow decomposition of the signals presenting complicated multifrequency courses as the sum of simple harmonic components. Application of Fourier transform makes it possible to recognize the regions of concentration of oscillations energy and connect them with the parameters of kinetics of analyzed system. Unfortunately classical Fourier analysis gives averaged results in case of the signals which frequency and amplitude can undergo significant changes during relatively short periods of time. This problem in case of chemical oscillations has been widely discussed by the authors elsewhere [17]. The investigated register of BZ reaction is a typical example of nonstationary signal. It has been proved that its statistical properties evidently vary with time [18]. The proper method of the analysis of such systems is spectral analysis in joint time and frequency domain. Application of short time Fourier transformation (STFT) allows observation of oscillatory-type reactions where the intensity of main and harmonic components tends to form patters in the time-frequency plane. The general formula of STFT is [13]:

$$STFT(t,\omega) = \int s(\tau)\gamma^*_{t,\omega}(\tau)d\tau = \int s(\tau)\gamma^*(\tau - t)e^{-j\omega\tau}d\tau \tag{1}$$

where $s(t)$ is time signal, $\gamma(t)$ is elementary function localized in time and frequency domain simultaneously, called *window function.* According to the formula the procedure of computing STFT of a time signal $s(t)$ is as follows: the signal $s(t)$ is multiplied by the function $\gamma(t)$ and then the Fourier transform of the product $s(\tau)\gamma^*(\tau - t)$ is computed. Because the window function $\gamma(t)$ has short time duration, the Fourier transform of $s(\tau)\gamma^*(\tau - t)$ reflects the signal's local frequency properties. By moving the $\gamma(t)$ and repeating the same procedure the idea of how the signal's frequency evolves over time can be obtained.

According to the formula (1) the analyzed signal $s(t)$ is a potential register E_{Pt} in our case. The results of STFT computations of the signal can be represented in the form of two or three-dimensional spectrograms containing the time, frequency and the energy axes. Fig. 2 is a STFT spectrogram of the fragment of the selected BZ reaction register. The distinct harmonic components show the evolution of the frequency of chemical oscillations during the reaction progress. It can be seen that the frequency of oscillations decreases exponentially with time. The obtained spectrogram contains information about the energy of signal also. The change in the energy of signal is direct reflection of the variations in the frequency of peak occurrences as well as the amplitude of particular peaks.

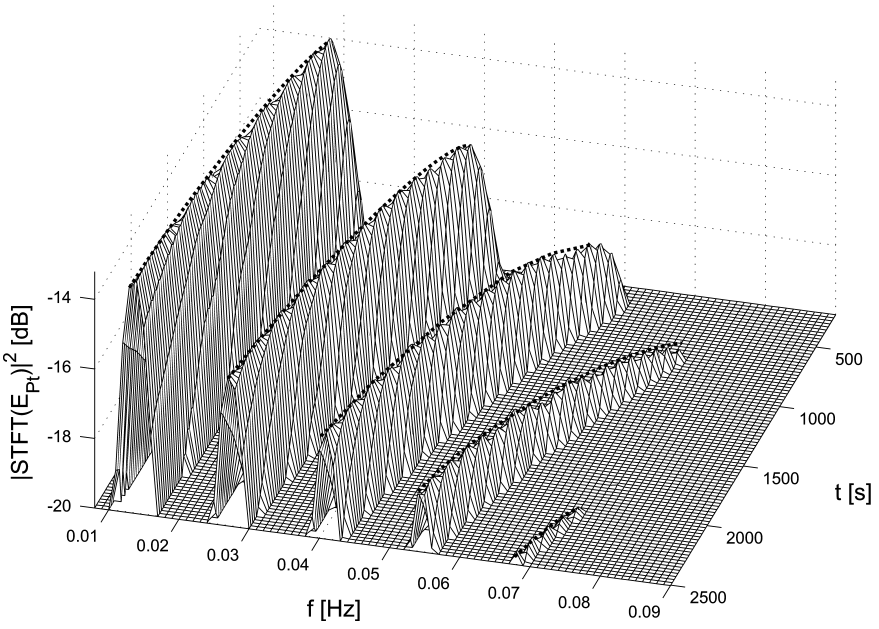

Figure 2. A fragment of STFT spectrogram of Pt electrode potential register, presented in Fig. 1(a).

Unfortunately, due to the connection between time resolution and frequency selectivity of such spectrograms it is not possible to obtain ideal localization of energy maxima in both domains simultaneously. The trade off between the time and frequency resolution is clearly visible. The applied Hanning type window, of length 512 points, provided satisfactory resolution in the frequency domain, however the time resolution is slightly deteriorated. In order to obtain the best results of signal decomposition in time and frequency domain simultaneously one may use some other available time-frequency algorithms (*i.e*. cone-shape distribution from the Cohen's class) or digitally process the STFT spectrogram. The dotted lines over the harmonic components in Fig. 2 indicate that the instantaneous energy of oscillations tend to concentrate in particular regions of time-frequency plane, called ridges. In other words, ridges are the collection of frequencies corresponding to the local maxima in the STFT spectrogram. Fig. 3(b) displays the extracted ridges from the STFT spectrogram presented in Fig. 3(a). Extraction of ridge coordinates provides the pinpoint estimate of the instantaneous frequency of the oscillating system.

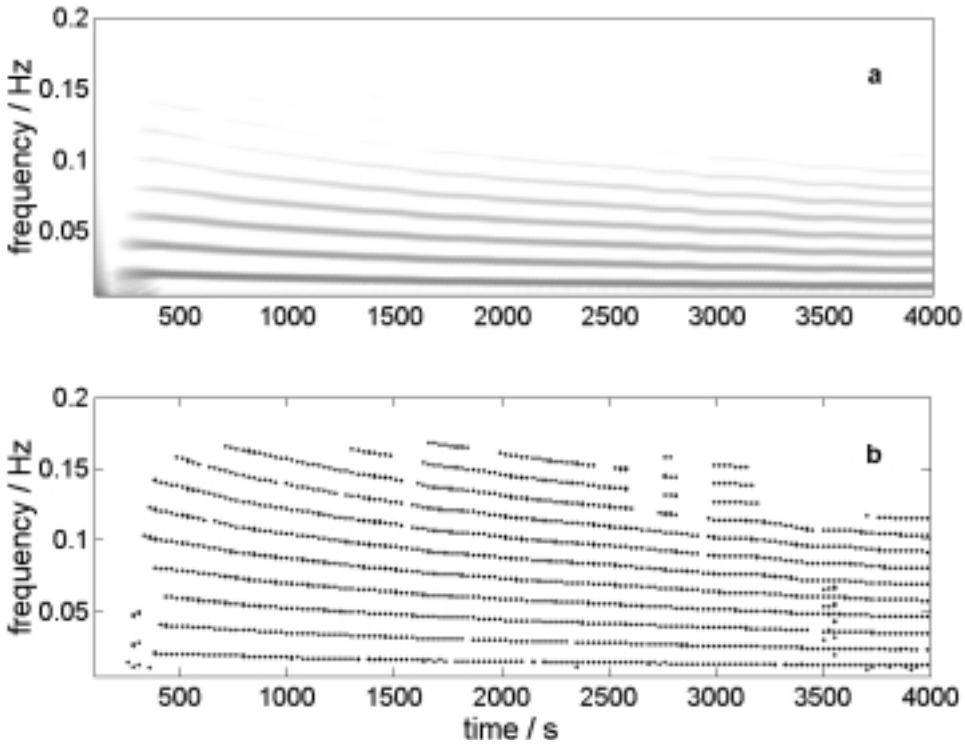

Figure 3. STFT spectrogram (a) of oscillations presented in Fig. 1(a) with the extracted ridges (b).

Table 1. Modified Oregonator used for simulating the Belousov-Zhabotinsky reaction with rate constants.

No.	Reaction	Rate constant k_n
1	$BrO_3^- + Br^- + 2H^+ \rightarrow HBrO_2 + BrMA$	$2\ M^{-3}\ s^{-1}$
2	$HBrO_2 + Br^- + H^+ \rightarrow 2BrMA$	$3 \cdot 10^6\ M^{-2}\ s^{-1}$
3	$2HBrO_2 \rightarrow BrO_3^- + BrMA + H^+$	$3 \cdot 10^3\ M^{-1}\ s^{-1}$
4	$BrO_3^- + HBrO_2 + H^+ \rightarrow 2HBrO_2 + 2Ce^{4+}$	$42\ M^{-2}\ s^{-1}$
5	$Ce^{4+} + BrMA \rightarrow BrMA\bullet$	$30\ M^{-1}\ s^{-1}$
6	$Ce^{4+} + MA \rightarrow MA\bullet$	$0.3\ M^{-1}\ s^{-1}$
7	$2\ MA\bullet \rightarrow MA + P$	$3.2 \cdot 10^9\ M^{-1}\ s^{-1}$
8	$MA\bullet + BrMA\bullet \rightarrow Br^-$	$1 \cdot 10^9\ M^{-1}\ s^{-1}$
9	$2\ BrMA\bullet \rightarrow Br^- + BrMA$	$1 \cdot 10^8\ M^{-1}\ s^{-1}$
10	$BrMA\bullet \rightarrow Br^-$	$7\ s^{-1}$
11	$BrMA \rightarrow P$	$4 \cdot 10^{-4}\ s^{-1}$

In the study of BZ reaction a lot of attention is paid to the reconstruction of experimental time series using appropriate mathematical models. It is extremely important in order to understand the mechanistic features of the reaction. We have tried to reproduce experimentally observed time series by the model shown in Table 1. This modification of Oregonator was used by Wang and others for simulation of the effect of oxygen in the BZ reaction [19]. In our laboratory the reaction was carried out in the batch reactor, in aerobic conditions, that is why we expected to achieve the best results of qualitative reconstruction of experimental data using the mentioned model. In this approach we followed the procedures of the BZ reaction simulation described in the paper [19]. There are seven dynamical variables in the model, the concentration of (Ce^{4+}), bromate (BrO_3^-), bromous acid ($HBrO_2$), bromide (Br^-), bromomalonic acid (BrMA), bromomalonic acid radical (BrMA•), and malonic radical (MA•); P represents inactive products such as CO_2. The time evolution is obtained by numerical integration of the system of rate equations obtained from the model (Table 1) with the seven dynamical variables described above. The initial concentrations of malonic acid (MA) and sulfuric acid H_2SO_4 in the experiments are much bigger than that of BrO_3^-; these concentrations are held constant in the model. Fig. 4 shows the result of simulations of the BZ reaction for two rate constants different than in the original modified Oregonator. The initial conditions of reagents concentrations were exactly the same like in the experiment. The values of adjustable parameters of reaction 6 and 11 have the decisive influence on the course of the simulated curves. For the certain values of parameters the time series for the $\log[Ce^{4+}]$ depicted in Fig. 4(b) gives the best reconstruction of the trajectory of experimental potential register presented in Fig. 4(a). The length of oscillations and amplitude of these two signals are comparable. To detect and to observe the frequency composition fluctuations of simulated time series the STFT spectrogram was performed. Fig. 5 presents result of application of this method to the discussed data with extracted ridges of instantaneous frequency maxima. In general the spectrogram reflects several high energy harmonic components, which frequencies of occurrence correspond to the same values in the spectrogram

presented in Fig. 2 and Fig. 3. However, the energy distribution and the frequency evolution in the whole time span is slightly different that in case of STFT analysis of experimental data. Although the exponential character of diminishing of oscillations frequency is evident, the dynamics of that process is different – the frequency of oscillations in case of simulated process decreased faster.

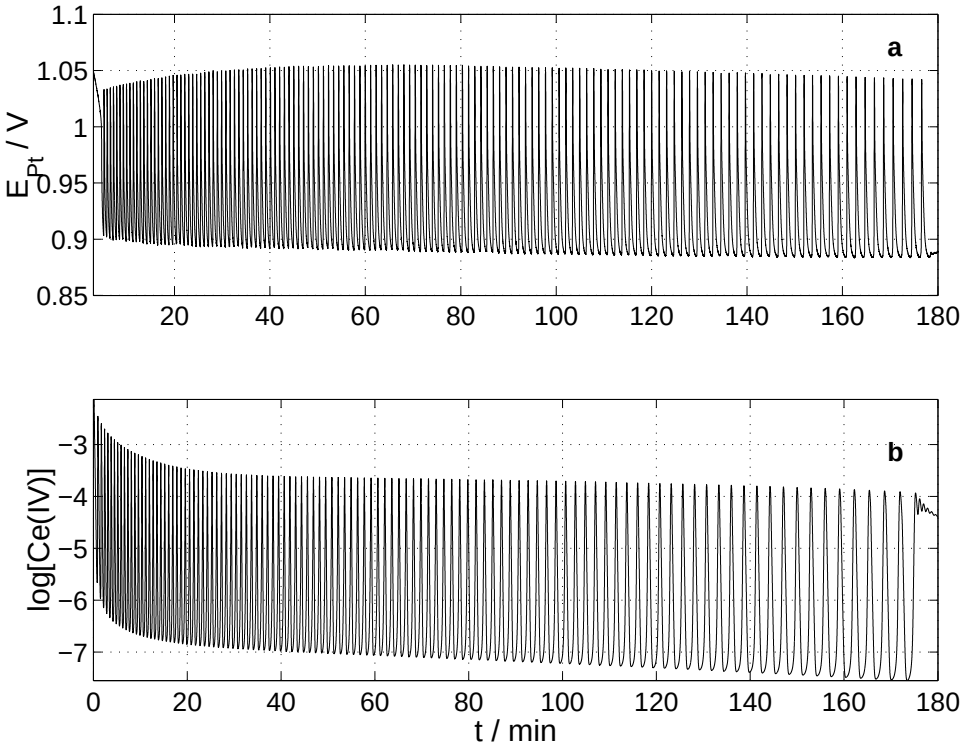

Figure 4. Experimental potential register (a) and simulated time series of the BZ reaction (b), calculated on the basis of the scheme of Oregonator model presented in Table 1. Initial concentrations of reagent for experimental and simulated reactions were: $[KBrO_3] = 0.07$ M, $[CH_2(COOH)_2] = 0.2$ M, $[Ce(SO_4)_2] = 0.001$ M, $[H_2SO_4] = 1$ M, the rate constants are as follows $k_6 = 0.5$, $k_{11} = 0.0007$. All other constants are as in Table 1.

CONCLUSIONS

The objective of signal processing is often to describe data from different perspectives (time domain, frequency domain, amplitude domain *etc.*). In this paper we discuss the advantages of specific time-frequency representations in case of analysis of chemical oscillations. The highly nonlinear chemical oscillatory reaction, namely Belousov-Zhabotinsky reaction, has been submitted to detailed spectral analysis us-

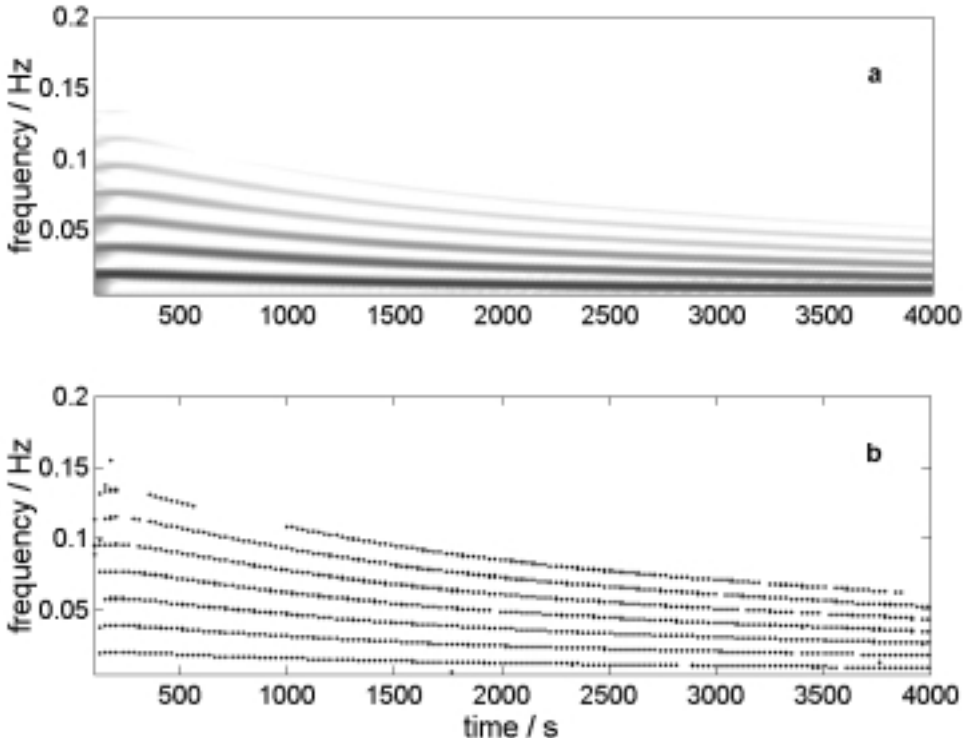

Figure 5. STFT spectrogram (a) of simulated time-series presented in Fig. 4(b) with the extracted ridges (b).

ing the simplest method, called short time Fourier transformation. The detailed investigation of STFT spectrograms of potential registers of Belousov-Zhabotinsky reaction in the batch reactor has been conducted. By this method it is possible to perform the frequency decomposition of investigated signals, simultaneously observing changes of their intensity in the function of time. It has been demonstrated that thanks to the application of STFT algorithm, it is possible to perform the comparison of experimental and simulated time series of BZ reaction in joint time and frequency domains. Such analysis gives new possibilities of studies of nonstationary chemical oscillations concerning their frequency and amplitude distribution in time.

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