

Application of discrete wavelet transform in the analysis of nonlinear chemical system

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Oscillations of species concentration are phenomena accompanying several types of electrochemical and purely chemical processes. Importance of analyzing of such processes results from both scientific and practical reasons. In the paper the authors deal with investigation of time dependent spectra of various stages of Belousov-Zhabotinsky type chemical oscillations. As the analytical tool the discrete wavelet transform is proposed.

KEY WORDS: Belousov-Zhabotinsky reaction, homogenous oscillatory reactions, wavelet transform

AMS subject classification: 92E20

1. Introduction

It was found that there exist chemical systems which exhibit highly nonlinear and complicated dynamic behavior. The best known and studied Belousov-Zhabotinsky (BZ) reaction is an example of chemical process which, depending on the conditions in which it is conducted, performs oscillations of different form: periodic, mixed-mode and even chaotic [1]. The BZ reaction consists in the oxidation of organic substrate (usually malonic acid) by bromate in strong acidic conditions [2]. The mechanism of BZ reaction has been extensively studied and well described in the form of, so called, FKN mechanism and then mathematically modeled as an Oregonator [3]. But the complex mechanism of BZ reaction has not been revealed and great number of publications, devoted to the problem of kinetics and dynamics of that reaction, is published every year.

The interpretation and identification of complex chemical systems is usually performed on the basis of time series analysis. Majority of different methods of time series analysis has been developed in order to investigate and

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describe the dynamics of nonlinear chemical systems. Among them analysis of phase portraits, Poincare sections and maps methods [4], attractor reconstruction, Lyapunov exponent analysis should be mentioned [5]. The analysis of signal evolution in the direct space of representation is classically complemented by the examination of an equivalent representation in the Fourier domain. In order to distinguish between periodic, quasiperiodic and chaotic regimes in BZ oscillations the power spectra can be determined [6]. In general, power spectral density describes the frequency and the energy distribution of the analyzed signal [7]. It is the unquestionable advantage of classical Fourier transform. Unfortunately the Fourier transform has its limitations. It gives proper results in case of stationary signals. Moreover, by switching to the Fourier domain, a mathematically equivalent representation is obtained but all the explicit temporal descriptions of the signal are lost. Most of chemical oscillations are non-stationary signals and their spectral composition cannot be properly analyzed using Fourier transform.

In recent years several novel representations allying time and frequency or time and scale of analysis have been introduced in literature. In case of nonlinear, nonstationary signal the time-frequency analysis provides revealing its simultaneous energy and frequency distribution in time domain [8–10]. The applications of short time Fourier transform (STFT) and some functions from Cohen's class distributions to the joint time and frequency analysis of chemical oscillations have been described elsewhere [11,12]. The aim of the current paper is to present possible applications of wavelets in the characterization of complex chemical signals.

2. Experimental

The reagents KBrO_3 , H_2SO_4 , $\text{CH}_2(\text{COOH})_2$, $\text{Ce}(\text{SO}_2)\cdot 4\text{H}_2\text{O}$ were of analytical grade. All the solutions were prepared using triply distilled water. The oscillatory BZ reaction was conducted in the reactor with perfect mixing, which was thermostatically maintained at 25°C in water bath. Appropriate volumes of KBrO_3 , H_2SO_4 , $\text{CH}_2(\text{COOH})_2$, $\text{Ce}(\text{SO}_2)\cdot 4\text{H}_2\text{O}$ 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, bromide selective and platinum electrode were used. Changes of potentials of the electrodes 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 amplification. The potential fluctuations of the electrodes were registered with sampling frequency 10 Hz.

2.1. Method of analysis

Significant information concerning the character of complex chemical process may be delivered by applying spectral analysis. A classic approach to the above problem is based on application of Fourier analysis. When analyzing discrete records, the discrete Fourier transformation [7] is used, defined by formula:

$$X(n) = \sum_0^{N-1} x(k) \exp\left(\frac{-2\pi ink}{N}\right) \quad (1)$$

where $X(n)$, usually complex-valued Fourier transform of signal $x(k)$, N , length of analyzed record, k , index of discrete time, n , index of discrete frequency. In order to present the signal energy distribution in the domain of frequency, a power spectral density estimator $PSD(n)$ is introduced of dimension (in the case of a dependent variable of potential dimension) V^2/Hz :

$$PSD(n) = \frac{2|F\{x(k)\}|^2}{N} \quad (2)$$

Independence of time is an important feature of the Fourier transform presented in relation (1). In the case of a discrete Fourier transformation, the analyzed signal is presented in the form of finite trigonometric series, the terms of which correspond to sinusoid functions of a given frequency. Analysis of signals applied in electrochemical investigation is primarily reduced to investigations of amplitude characteristics, delivering required information on the signal energy distribution.

Real-world oscillations recordings take the form of complicated structures of a large variety of shapes dependent on the physicochemistry of respective reactions. Determination of the energy distribution can be a 'fingerprint' of an appropriate oscillation structure.

Figure 1a presents a single oscillatory structure. In figure 1b the corresponding power spectral density function has been presented. The PSD in the discussed case can be the proper fingerprint of the described signal. Figure 1c illustrates a situation where another structure occurs, separated from the first one with an arbitrarily chosen time interval. In figure 1d the respective power spectral density function has been presented for the described case. A different power is visible in the domain of frequency. It is caused by lack of time localization of Fourier series terms describing the analyzed recording. Approximation of the described signal with a system of sinusoidal functions should take into account components responsible for pulses, as well as the drop of the instantaneous signal value occurring between them. Hence, the described PSD is not a multiple of the fingerprint of single oscillation but one of a new function composed of two pulses separated by a given distance.

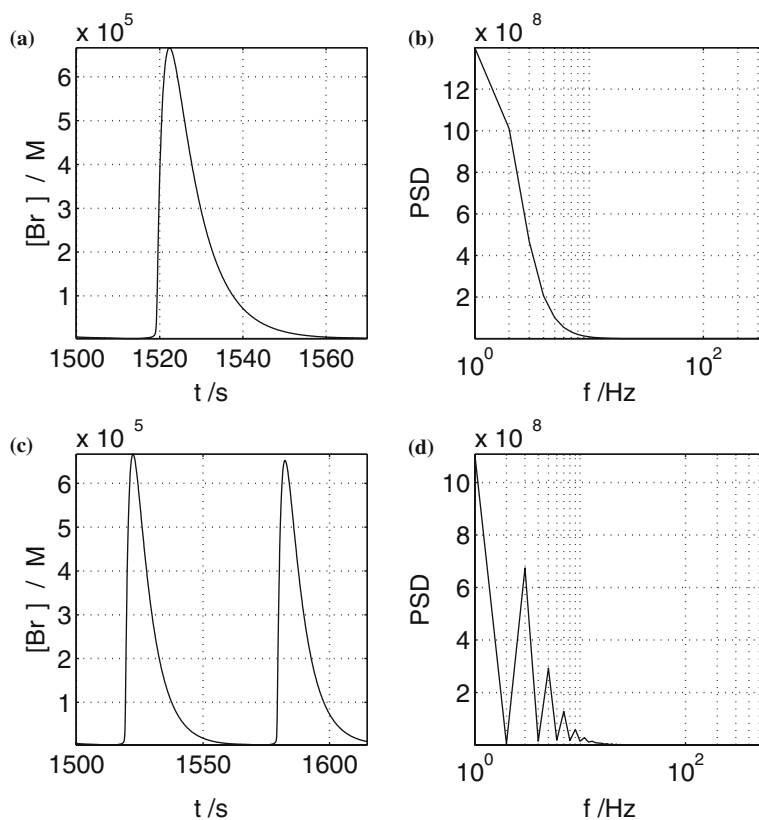


Figure 1. Simulated time series of the BZ reaction (single oscillation (a) and two successive oscillations (c) with corresponding PSD spectra (b) and (d). Time series calculated on the basis of the scheme of modified Oregonator model [13].

Application of joint analysis in the domain of time and frequency is proposed as an alternative to Fourier analysis. This problem was discussed by Darowicki et al. [14,15]. In this paper the possibility of application of one of the time-frequency analysis techniques, namely wavelet transformation, in electrochemical oscillation investigations has been presented.

Continuous wavelet transformation of signal $s(t)$ is defined as:

$$W(a, \tau) = |a|^{-1/2} \int_{-\infty}^{\infty} s(t) w^* \left(\frac{t - \tau}{a} \right) dt \quad (3)$$

where t variable denotes the time shift and a represents dilation of so-called mother wavelet $w(t)$, asterisk represents the complex conjugation.

The set of wavelet functions is obtained by shifting and dilating of prototypic mother wavelet $w(t)$ at unit scale $a = 1$ and position $t = 0$:

$$W(a, \tau) = |a|^{-1/2} w\left(\frac{t - \tau}{a}\right) \quad (4)$$

Factor $|a|^{-1/2}$ introduces equality of energy of rescaled wavelets.

The continuous wavelet transform is redundant. In practical implementations it is sufficient to use discrete version of transform. In order to obtain this form of signal presentation continuous parameters a and t can be represented as:

$$a = a_0^k, \quad \tau = \tau_0 j a^k, \quad j, k \in Z \quad (5)$$

Such an operation leads to the new form of formula of dilating and shifting mother wavelet:

$$w_{k,j}(t) = |a_0|^{-k/2} w(a_0^{-k} t - \tau_0 j) \quad (6)$$

In the case of $a_0 = 2$ and $\tau_0 = 1$ set of wavelets derived in this way forms dyadic, orthonormal basis in the L^2 space [16,17]. Signal is then represented by the sum of following wavelet series:

$$s(t) = \sum_{k,j} b_{k,j} w_{k,j}(t) \quad (7)$$

where $b_{k,j}$, coefficients of wavelet expansion of the signal $s(t)$, $w_{k,j}(t)$, wavelets. The set of coefficients $b_{k,j}$ is determined by the correlation degree of function $s(t)$ with the wavelet of frequency and time localization given by k and j , respectively. As the square of continuous or discrete wavelet transform modulus can be taken as the measure of the signal energy, application of the wavelet transformation allows obtaining the time-dependent signal energy distribution.

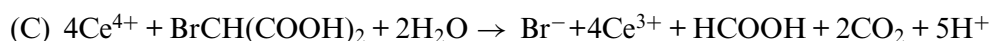
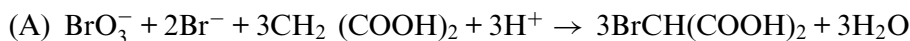
A number of wavelet families are used in practical applications. Their extensive review with principles of their formation and determination of required properties can be found in [16]. Introduction the tree algorithm by Mallat [17,18] led to application of digital filter banks in the process of obtaining wavelet expansion coefficients (transform) from sampled signal $s(t)$. The set of vectors $b_{k,j}$ of coefficients is obtained by filtering performed by a set of filters associated with a given wavelet [16]. After the filtering, decimation of the resultant vector proceeds. The vector resulting from high-pass filtering is treated as the vector of wavelet coefficients, whereas set of low-pass coefficients is the input vector for the next level of filter bank. The signal filtering and decimation operation is repeated by iteration on consecutive levels of the filter bank leading to separation of the signal into frequency bands (analysis levels) which correspond to the scale variable k . Coefficients obtained on consecutive analysis levels can be processed in

order to expose or remove signal properties disclosed at a given level. It should be noticed that as the transform expressed in the form of coefficients depends on time then isolation is possible of a group of coefficients responsible for local signal properties occurring at given moments of time and frequency ranges.

The set of coefficients, obtained as the result of application of a set of analyzing filters, submitted to processing is the basis of signal reconstruction. When the orthogonal wavelet is applied, it is a reversal of the analysis procedure, i.e., interpolation of coefficient vectors with filtering by filters being mirror reflections of analyzing filters. Reconstruction of the signal is performed separately in consecutive levels of synthesizing filter sets, giving a set of courses specified as approximation and details or crystals [19], determining signal properties characterizing it on a given level of analysis (frequency band).

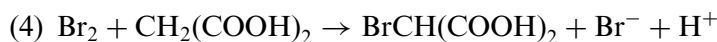
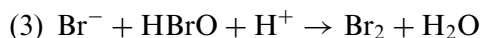
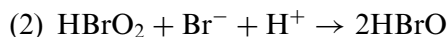
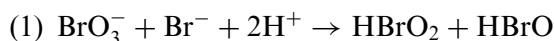
3. Results and discussion

Figure 2a presents the exemplary transient of BZ reaction in the closed system. The trace of bromide-selective electrode, consisting of dozens of oscillations can be clearly resolved into repeating periods corresponding to the elementary chemical processes well described in a FKN mechanism. According to the FKN mechanism an interpretation of the chemistry in BZ system involves three, overall summary reactions.

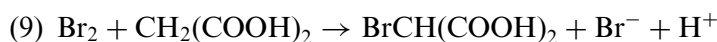
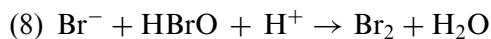
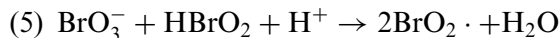


The processes A, B and C consist of several steps.

Process (A):



Process (B):



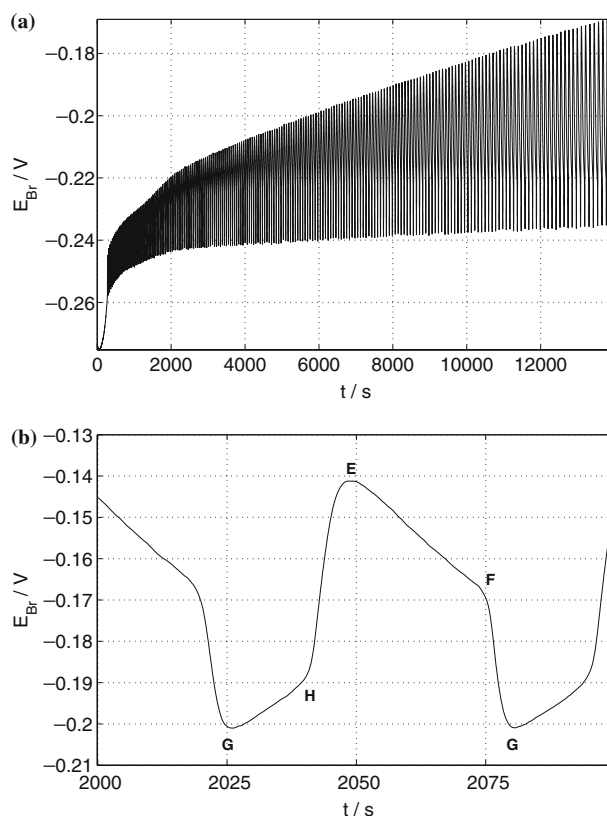


Figure 2. Exemplary time record of bromide selective electrode potential oscillations during the BZ reaction figure 2a. The reagent concentrations are as follows: $[KBrO_3] = 0.07$ M, $[CH_2(COOH)_2] = 0.4$ M, $[Ce(SO_4)_2] = 0.001$ M, $[H_2SO_4] = 1$ M. Figure 2b shows a fragment of potentiometric trace exhibiting characteristic periods of BZ reaction. The reagent concentrations are the same like in figure 1a except $[CH_2(COOH)_2] = 0.4$ M.

For the sake of simplicity the full version of FKN mechanism will not be discussed here, because it was widely described in the literature [20]. Generally speaking two sets of essentially noninteracting reactions, nonradical process A and radical process B, are coupled by the third process C. Bromide ion is the critical intermediate which concentration determines whether process A (of high Br^- concentration) or process B (of low Br^- concentration) is in control. Process C inhibits process B by the production of Br^- from products of process B what returns control to process A.

The single oscillation, presented in the figure 2b, consists of subsequent sections corresponding to the elementary chemical reactions. The subsequent periods are: period GH called ‘slow bromide production period’ is characteristic for reactions of process B, section HE, called ‘rapid bromide production’ during

which oxidation of malonic acid by bromate is proceeding quite rapidly whereas concentration of Br^- is very low and $\text{Ce}^{3+}/\text{Ce}^{4+}$ remains at relatively constant value. Reactions of process A are characteristic for the next section EF called 'slow bromide consumption'. At point F, the bromide concentration has reached critical value and the onset of process B starts until the point G. The steep slope FG is called 'rapid bromide consumption'.

The FKN was presented to explain the mutual interactions between major species in BZ system. According to this the rate of oscillations, as well as the shape of single oscillation, is determined by the rate of turning on and off appropriate reactions at proper time. The frequency of the processes of formation and decay of cerium ion and bromide ion alternately is an important parameter related with the kinetics of BZ reaction. Wavelet transform, presented in previous section, allows both to decompose analyzed chemical signal on details corresponding to the particular chemical transitions and to track them during the investigated process. It may provide valuable information about kinetics of BZ reaction. Thus the systematic wavelet analysis of chemical oscillations is justified.

Figure 3 presents the discrete-time scalogram of single oscillatory structure presented in figure 2a. Reconstructions of the first four wavelet coefficients (details) are considered. Maxima of the representation obtained are well correlated with two types of potential course shape changes. According to the theory of wavelets [21], in the case of application of the shortest Daubechies wavelet of order 2 minima of the scalogram represent extremal points of potential value.

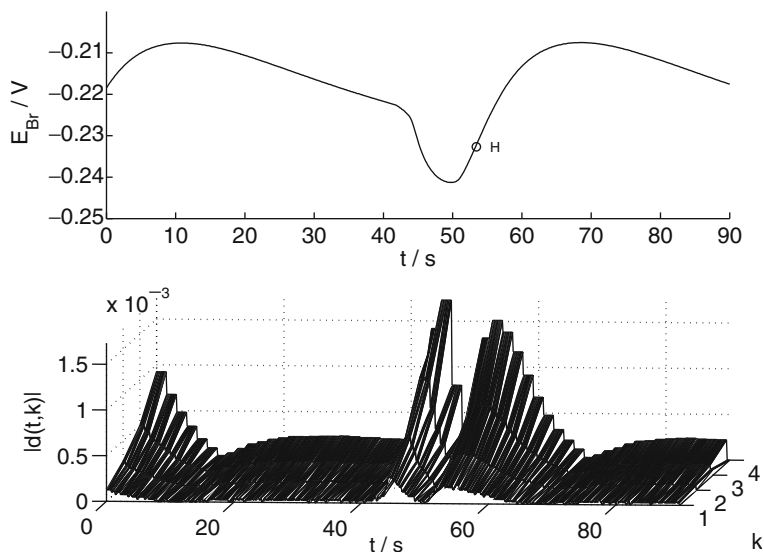


Figure 3. Scalogram of single oscillation of signal presented in figure 2a, k denotes the number of the analysis level. $|d(t, k)|$ is the modulus of consecutive reconstruction from detail k .

Taking into account the mathematical model of reaction they can be related to the moments of triggering of different stages of the reaction under considerations. However, detection of extremal points of singular chemical oscillations is rather simple task and does not need to be supported by wavelet decomposition. Much more interesting feature of DWT scalogram is connected with its maxima. It can be observed that they are correlated with moments of abrupt changes of $E(t)$. Direct estimation of time instants on the basis of time-domain record is complicated, especially taking into account point **H** corresponding to one of the reactions from the process **B**. In the presented example time location of discussed point is determined on the basis of analysis of maxima of scalogram. It is worth noting that, distinctly visible, discontinuity in the investigated oscillation, represented by point **H** on the scalogram, is hardly recognizable in time domain.

In the figure 4 results of similar analysis are presented. The oscillations persistence was extended to five full cycles of potential changes. It can be observed that similar structure of scalogram is obtained for all oscillations. Vertical lines connect the moments of change in reaction represented by local maxima of the scalogram and described earlier point **F** from which the onset of reactions of process **B** begins.

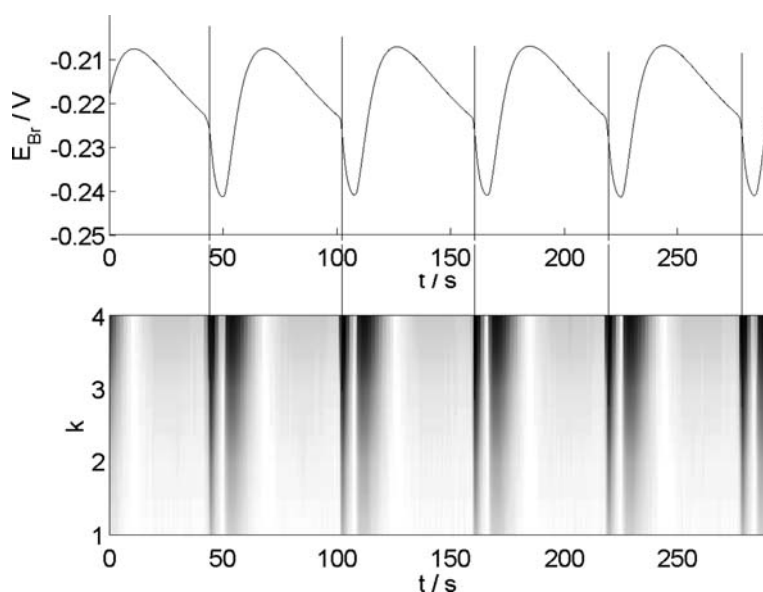


Figure 4. Scalogram of a fragment of signal presented in figure 2a. Daubechies wavelet of order 2 applied.

4. Conclusions

Most chemical oscillations, from statistical point of view, are nonstationary signals. Such signals need appropriate method of analysis. The suitable method for nonstationary signals analysis is wavelet transform. In this paper a simplified theory of wavelets with example of application of discrete wavelet transform in the analysis of oscillatory BZ reaction has been presented. Processing of the chosen experimental potential oscillations, generated during BZ reaction in the closed system, allowed recognizing particular stages of reaction. The characteristic moments, corresponding to the chemical transitions, are clearly visible as the details of decomposition on the calculated scalograms. It has been shown that the method can deliver information on the dynamics of chemical oscillations, for example on the basis of local maxima analysis in the wavelet scalogram the character of oscillations frequency attenuation may be determined. In case of investigated electrode potential oscillations the most suitable wavelet basis has been identified. The Daubechies order 2 are experimentally found to be very appropriate for wavelet analysis of chemical oscillations. Basing on the presented results we may state that better understanding of complicated dynamics of chemical oscillations can be obtained through further wavelet analysis of more complex transients of BZ reaction.

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