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The Wigner-Ville Distribution in the Analysis of Deterministic Components of Spontaneous Oscillations

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The Wigner-Ville distribution (WVD) method has been applied for the analysis of spontaneous oscillations of the anodic copper dissolution process. The nonstationary character of the investigated process has been shown. The observed current oscillations contain deterministic components not revealed in the classic Fourier spectrogram. The WVD spectrogram allows the identification of frequency bands of spontaneous oscillations. The observed deterministic components take the form of frequency bands, dependent on time. The main disadvantage of this type of analysis is the formation of the so-called cross-terms, which are oscillatory in character. However, it was shown that it is possible to reduce them significantly by a low-pass filtration.

Key words: copper dissolution, spontaneous oscillations, Wigner-Ville distribution

Electrochemical signals can be divided into stationary and nonstationary ones. The above criterion is based on that whether the constancy of statistical moments of the signal as a function of time is maintained. The signal is defined as strictly stationary when all its statistical moments do not depend on time [1,2]. This is a very strict assumption, hence in practice the weak stationarity condition is used (stationarity in a wider sense) [1,2]. It requires maintaining of constancy of the moments only up to the second order, *i.e.*, the expected value and the variance. The signal, the expected value of which changes with time, is called nonstationary [1,2].

Basing on the behaviour of signals in the domain of frequency one may distinguish two categories. The frequency composition of signals in the first category does not change in time. They are stationary signals, correctly characterized by the Fourier transform in the domain of frequency. Nonstationary signals, the frequency composition of which evolves in time, belong to the second category. Methods of analysis of stationary signals are well known and widely applied. Correlation methods are most popular in the domain of time. They are based on determination and analysis of the autocorrelation function [1–3]. Stationary signals are analysed in the domain of frequency by determining the spectral power density. Analysis in the frequency domain was used by Li, Nobe and Pearlstein [5] and Li and Nobe [6] in the investigations of the kinetics of electrodissolution of iron. Fourier transformation was used by Basset and Hudson [7,8] in the studies of current oscillations during anodic dissolution of copper. However, the period of observed oscillations underwent changes in time.

Thus, in such a case the result of application of the Fourier transformation is average in character.

In the last decade new tools have been elaborated, which allowed the analysis of nonstationary signals. Flandrin [9] and Martin and Flandrin [10] discussed application of the Wigner-Ville Distribution (WVD) in the analysis of nonstationary signals. Priestley [11] and Janssen [12] elaborated a probabilistic interpretation of the WVD approach. Nonstationary processes are frequently encountered in electrochemical investigation practice. Spontaneous current oscillations of the anodic copper dissolution are an example. WVD has not been applied for analysis of this phenomenon. The proposed method of analysis is completely novel, and therefore, the aim of this work is to verify its applicability for the analysis of spontaneous oscillations accompanying the metal electrode dissolution.

DESCRIPTION OF THE METHOD

In accordance with the Wiener-Khinczyn theorem the power density spectrum is the Fourier transform of the autocorrelation function:

$$PS(t,f) = \int R(\tau, t)\exp(-j2\pi f\tau)d\tau \tag{1}$$

where: $PS(t,f)$ – power density spectrum, $R(\tau,t)$ – auto-correlation function of the nonstationary signal, f – frequency, t – time. Wigner and Ville [3] proposed a method of the determination of the autocorrelation function in the form:

$$R(\tau,t) = y\left(t+\frac{\tau}{2}\right)y^*\left(t-\frac{\tau}{2}\right) \tag{2}$$

where: $y(t)$ – analysed signal, $y^*(t)$ – conjugated signal. By combining (1) and (2) we obtain an expression describing WVD:

$$WVD(t,f) = \int y\left(t+\frac{\tau}{2}\right)y^*\left(t-\frac{\tau}{2}\right)\exp(-j2\pi f\tau)d\tau \tag{3}$$

where: $WVD(t,f)$ – Wigner-Ville distribution. The main inconvenience when applying WVD is the generation of the so-called cross-terms. The WVD of a signal being the sum of two components contains not only the corresponding terms describing each of them, but also a third term, being a cross term.

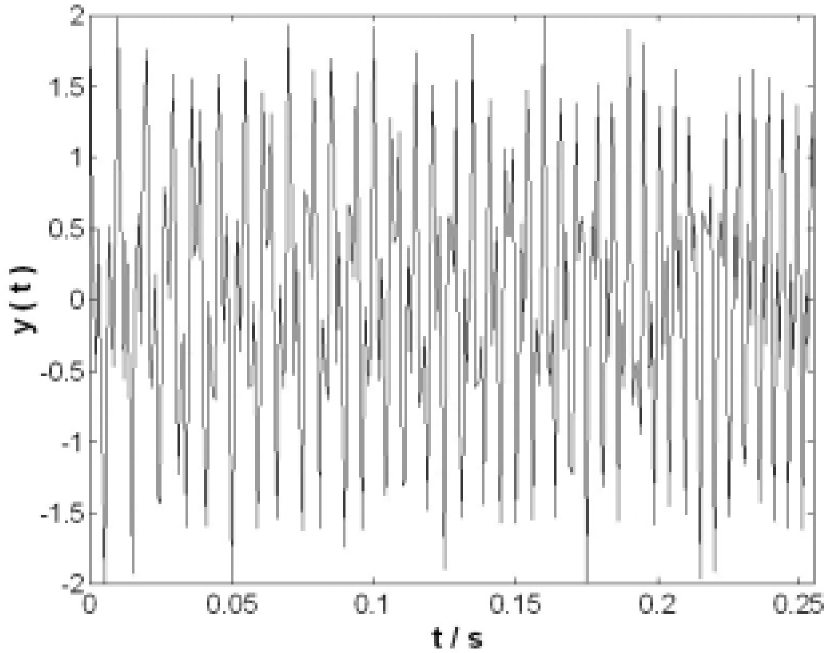

Figure 1. Simulated, non-stationary signal described by equation (4).

An exemplary nonstationary signal being a sum of two components was analysed. (Fig. 1):

$$y(t) = A_1\cos\left[2\pi\left(f_{01} + \frac{1}{2}\frac{df_1}{dt}t\right)t\right] + A_2\cos\left[2\pi\left(f_{02} + \frac{1}{2}\frac{df_2}{dt}t\right)t\right] \tag{4}$$

$$\frac{df_1}{dt} = \frac{f_{T1} - f_{01}}{T}; \quad \frac{df_2}{dt} = \frac{f_{T2} - f_{02}}{T}$$

where: A_1, $A_2 = 1$ – amplitudes of the components of the signal, $f_{01} = 100$ Hz – initial frequency of the first signal component, $f_{02} = 300$ Hz – initial frequency of the second signal component, $f_{\mathrm{T}1} = 200$ Hz – final frequency of the first signal component, $f_{\mathrm{T}2} = 400$ Hz – final frequency of the second signal component, $T = 0.256$ s – signal length. The corresponding WVD is presented in Fig. 2. Besides the expected two auto-terms at frequencies $f_1(t) = f_{01} + (df_1/dt)t$ and $f_2(t) = f_{02} + (df_2/dt)t$ also a strong cross-term is visible, located at the arithmetic mean of the frequencies of auto-terms: $[f_1(t) + f_2(t)]/2$. It describes oscillations of the instantaneous energy for the signal occurring at a frequency $f_1(t) - f_2(t)$. The linear change of the frequency of both

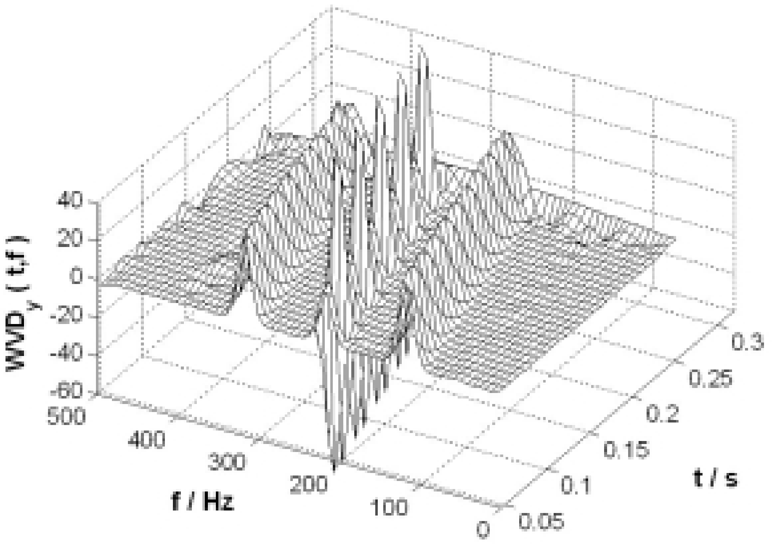

Figure 2. The Wigner-Ville distribution of the model non-stationary signal, described by equation (4).

auto-term components as a function of time is also visible. For a superposition of the elementary signals $y(t) = y_1(t) + y_2(t)$ the respective WVD is described by the relation:

$$WVD_y(t,f) = WVD_{y1}(t,f) + WVD_{y2}(t,f) + 2\mathrm{Re}[WVD_{y1y2}(t,f)] \tag{5}$$

where: $WVD_y(t,f)$ – Wigner-Ville distribution of signal $y = y_1(t) + y_2(t)$, $WVD_{y1}(t,f)$ – Wigner-Ville distribution of signal $y_1(t)$, $WVD_{y2}(t,f)$ – Wigner-Ville distribution of signal $y_2(t)$, $\mathrm{Re}[WVDy_1y_2(t,f)]$ – a real part of the Wigner-Ville distribution of signal $y_1(t)y_2(t)$.

The Fourier spectrogram is shown in Fig. 3 for comparison. It consists two wide peaks. Each of them includes the band starting from the initial frequency f_{01}, f_{02} up to the final frequency f_{T1}, f_{T2} of the appropriate signal component (4). The observed internal structure of the peaks suggests that the numerical algorithm detected the spectral components inside the band. However, this representation is not correct as it indicates the presence of respective frequency components of duration equal to the length of the acquired data record. Therefore, the true instantaneous properties of the signal are not reflected in any way. Together with the increase of the number of frequency tones in the signal the WVD spectrogram gets more and more complicated, due to the appearance of undesirable cross-terms. For a long time this has been the main obstacle in the wide implementation of the Wigner-Ville distribution technique. Conversion of the signal into its corresponding analytical form is one of the methods of decreasing the interference introduced by cross-terms. In accordance with Boashash [4] such a procedure eliminates the cross-terms generated by negative fre-

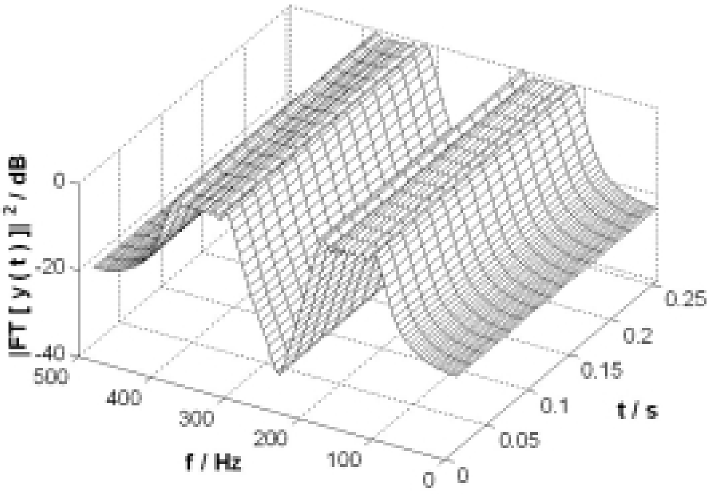

Figure 3. The Fourier spectrogram of the model signal, described by equation (4).

quency components of the real-valued signal. The procedure of conversion to the analytical signal is based on the transformation of the Fourier transform of the input signal, according to:

$$FT_a(f) = \begin{cases} 2FT(f) \mid f > 0 \\ FT(f) \mid f = 0 \\ 0 \mid f < 0 \end{cases} \qquad 6)$$

where: $FT_a(f)$ – Fourier transform of the analytical signal, $FT(f)$ – Fourier transform of a real-valued signal. Values of f denote positive and negative parts of the frequency domain. Taking inverse Fourier transform of the signal described in the frequency domain by FT_a (4), one obtains the analytical form of the input signal. It is characterized by lack of the negative part of frequency spectrum, however, it is not longer real-valued. Auto-terms are relatively smooth, while cross-terms are oscillatory in character. This suggests a possibility of the WVD decomposition into two-dimensional harmonic functions, localized in the total time-frequency domain (Gabor expansion), followed by using only lower harmonics in order to reduce the interference. The natural method of doing that is the application of a two-dimensional low-pass filter:

$$sWVD(t,f) = \int\int WVD(\zeta, \upsilon) H(t - \zeta, f - \upsilon) d\zeta\, d\upsilon \qquad (7)$$

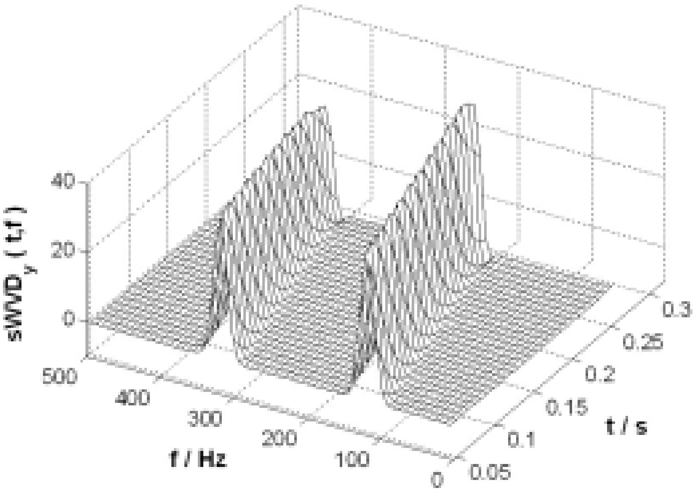

Figure 4. Smoothed Wigner-Ville distribution of model non-stationary signal, described by equation (4).

where $sWVD(t,f)$ – smoothed Wigner-Ville distribution, $H(t,f)$ – two dimensional low-pass filter. (7) presents the two dimensional convolution of the WVD with smoothing function of both time and frequency $H(t,f)$ which acts as a low-pass filter. As the low-pass filter causes smoothing of the signal, the procedure described above is known as a calculation of the smoothed WVD. Low-pass filtration usually significantly decreases cross-terms, however, it also leads to a decreased resolution of the time-frequency representation. The smoothed WVD spectrogram is presented in Fig. 4. It reflects changes of the instantaneous properties of the signal and simultaneously avoids the interference caused by the cross-terms. Problems described above concern with the realization of WVD in domains of continuous time and frequency. Application of digital machines introduces the necessity of adaptation of the described technique to discrete data. The discrete-time form of the WVD calculation algorithm can be presented by a relationship [3]:

$$DWVD[y(nT_s)](nT_s,f) = 2T_s \sum_{k=-(2L-1)}^{2L-1} y[(n+k)T_s]\,y^*[(n-k)T_s]\exp(-j4\pi fkT_s) \tag{8}$$

where: $DWVD$ – discrete-time Wigner-Ville distribution of signal y, T_s – time sampling step, $4L+1$ – length of the rectangular data window, symmetric with respect to zero. The problem, which appears when move to discrete analysis, is the WVD frequency band. In accordance with (8) the frequency domain period of DWVD is equal to the value of the Nyquist frequency $f_s/2$. Thus, the highest allowed frequency component of the input signal is $f_s/4$, contrary to $f_s/2$, required by the Shannon theorem.

Hence, an increase of the sampling frequency is required. This type of resampling is usually performed by an interpolation filter [3]. Another method is the resignation of the half of the frequency band, what in turn causes the necessity of low-pass filtration. Obviously, all these techniques are connected with an increase of the complexity of the calculation algorithm and a longer data processing time.

EXPERIMENTAL

The process of copper dissolution was investigated at potentiostatic conditions for a 0.15 mol/dm^3 $CuSO_4$ + 5.0 mol/dm^3 H_2SO_4 solution [13–15]. Studies were performed in a three electrode system. A copper class 5N electrode was used. The area of the working electrode was 0.2 cm^2. A platinum mesh was the auxiliary electrode, while a copper rod was a reference electrode. Solutions were prepared from weighted amounts of sulphuric acid (p.a.), copper sulphate (p.a.) and triply distilled water. Before measurement the working electrode was mechanically polished with sandpaper up to grade 1000 and then degreased with ethanol. The measurement setup was made up of Elpan EP-20 potentiostat and MIO-16XE-50 National Instruments acquisition board controlled by a PC computer. G-Math Toolkit, being the sub-packet of Lab-View 4.0 software, was used for data elaboration.

RESULTS AND DISCUSSION

Fig. 5 presents spontaneous current oscillations recorded during an anodic copper dissolution in a sulphate solution. Experimental conditions were identical as those described by Dolata and Kawczyński [13–15]. The data obtained were analysed by FT, WVD and sWVD. Fig. 6 presents the respective three-dimensional FT spectrogram. In accordance with previous observations, FT shows a wide frequency band. The spectral power density for this band does not depend on time and therefore the

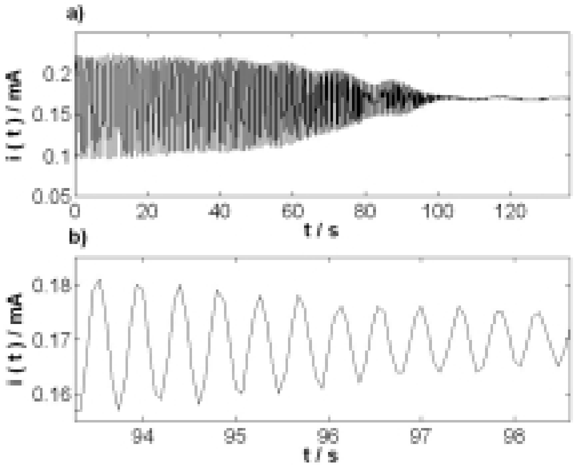

Figure 5. Time course of spontaneous current oscillations of copper dissolution reaction in a 0.15 mol/dm^3 $CuSO_4$ + 5.0 mol/dm^3 H_2SO_4 solution (a). Fragment of record showing the structure of individual current peaks (b). Electrode potential $E = 200$ mV, surface of the working electrode $A = 0.2$ cm^2, sampling frequency $f_s = 15$ Hz.

Fourier transformation does not allow to observe the instantaneous properties of the anodic copper dissolution process. It is possible to obtain only an averaged energy distribution of the process in the domain of frequency. The WVD spectrogram presented in Fig. 7 is of a different character. It is composed of several bands dependent on time. Hence, it shows the changes of the instantaneous energy of the signal as a function of time. For each band, the changes of the instantaneous frequency, different from its mean value, obtained by FT, are shown. The presence of interference result-

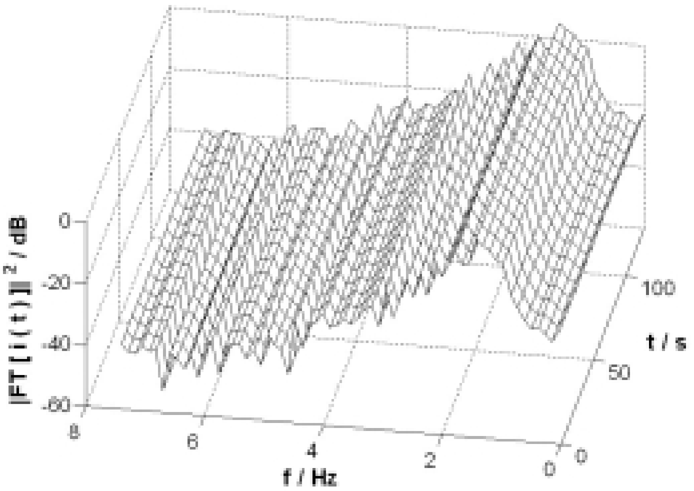

Figure 6. The Fourier spectrogram of signal depicted in Fig. 5a. Electrode potential $E = 200$ mV, surface of the working electrode $A = 0.2$ cm^2, sampling frequency $f_s = 15$ Hz.

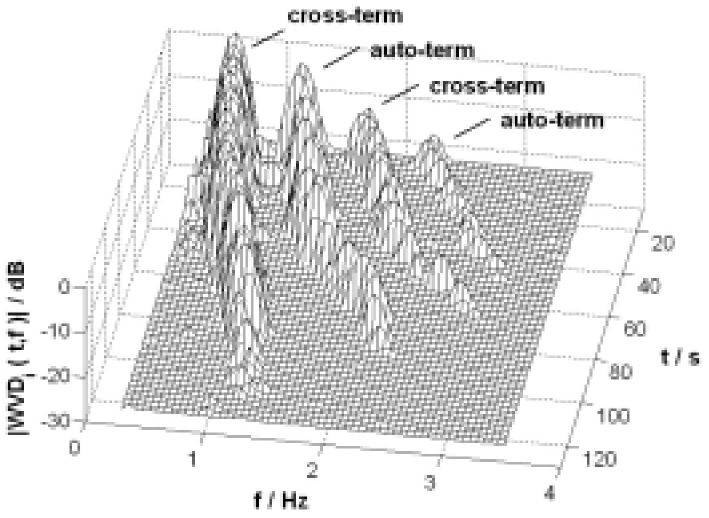

Figure 7. The Wigner-Ville distribution of spontaneous current oscillations of a copper dissolution in a 0.15 mol/dm^3 $CuSO_4$ + 5.0 mol/dm^3 H_2SO_4 solution. Electrode potential $E = 200$ mV, surface of the working electrode $A = 0.2$ cm^2, sampling frequency $f_s = 15$ Hz.

ing from the inherent non-linearity of the calculation method is a disadvantage of the presented representation. The legibility of the obtained spectrogram can be improved again by applying the low-pass filtration. Fig. 8 presents a spectrogram obtained by applying WVD. The substantial minimization of interference bands is visible. Due to a greater legibility, the smoothed spectrogram describes better the instantaneous properties of the analysed signal.

The results present the analysis of a signal of an assumed characteristic, as well as of a signal recorded during measurement of the electric current associated with an anodic copper dissolution. Both signals are characterized by nonstationarity, manifesting itself as the variation of their frequency composition. Both courses were analysed by classical Fourier approach. Determination of the above changes was found to be not possible, due to the lack of information on the time evolution of the process. This was caused by the averaging character of FT. One of the methods of the total time-frequency analysis, the Wigner-Ville distribution has been presented as a solution of this significant inconvenience. Additional modifications have been presented, particularly essential for the implementation of the method in the discrete version. The suitability of the above approach has been shown as a tool allowing the investigation of the instantaneous, time dependent properties of a nonstationary signal. It has been shown that the basic inconvenience of WVD, *i.e.* the generation of cross-terms not corresponding to a real localization of the energy of a signal in the total time-frequency domain, can be effectively minimized. This was achieved by a two-dimensional low-pass WVD filtration. Smoothed WVD spectrograms, obtained

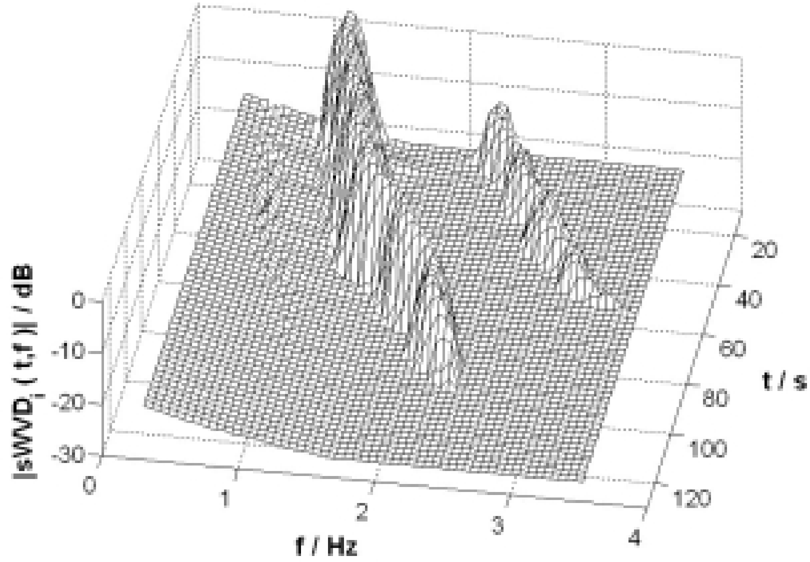

Figure 8. Smoothed Wigner-Ville distribution of spontaneous current oscillations of copper dissolution in a 0.15 mol/dm^3 $CuSO_4$ + 5.0 mol/dm^3 H_2SO_4 solution. Electrode potential $E = 200$ mV, surface of the working electrode $A = 0.2$ cm^2, sampling frequency $f_s = 15$ Hz.

in this way, correctly describe the character of signal energy changes in the time-frequency domain. On the other hand, a possible deterioration of the resulting spectrogram resolution and a significant increase of the calculation time are the disadvantages of the method. However, these inconveniences are not of fundamental importance, since even the smoothed WVD has the same resolution as other time-frequency analysis methods [3]. The problem of serious complexity of calculations also becomes less important, due to a continuous increase of the calculation power of computers. Due to the above, the WVD distribution method can be considered as an effective tool for the detailed quantitative analysis of nonstationary signals, as *e.g.* for current oscillations in metal dissolution.

Acknowledgments

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