Investigation of using wavelet analysis for classifying pattern of cyclic voltammetry signals

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Abstract. Wavelet analysis is an excellent technique for data processing analysis based on linear vector algebra since it has an ability to perform local analysis and is able to analyze an unspecified localized area of a large signal. In this work, the wavelet analysis of cyclic waveform was investigated in order to find the distinguishable feature from the cyclic data. The analyzed wavelet coefficients were proposed to be used as selected cyclic feature parameters. The cyclic voltamogram (CV) of different electrodes consisting of carbon nanotube (CNT) and several types of metal phthalocyanine (MPc) including CoPc, FePc, ZnPc and MnPc powders was used as several sets of cyclic data for various types of coffee. The mixture powder was embedded in a hollow Teflon rod and used as working electrodes. Electrochemical response of the fabricated electrodes in Robusta, blend coffee I, blend coffee II, chocolate malt and cocoa at the same concentrations was measured with scanning rate of 0.05V/s from -1.5 to 1.5V respectively to Ag/AgCl electrode for five scanning loops. The CV of blended CNT electrode with some MPc electrodes indicated the ionic interaction which can be the effect of catalytic oxidation of saccharides and/or polyphenol on the sensor surface. The major information of CV response can be extracted by using several mother wavelet families viz. daubechies (dB1 to dB3), coiflets (coiflet1), biorthogonal (Bior1.1) and symlets (sym2) and then the discrimination of these wavelet coefficients of each data group can be separated by principal component analysis (PCA). The PCA results indicated the clearly separate groups with total contribution more than 62.37% representing from PC1 and PC2.

1. Introduction
Wavelet analysis is mathematical operation used in data processing. It is a waveform of limited duration and also maps the time information into a two dimensional function. The application of wavelet analysis range from quantum physics to digital signal processing. Wavelet analysis was firstly developed by Alfred Haar in the 1910 that successfully developed set of rectangular basis function. For transient signals, the low-frequency content is the most important part since it is what gives the identical signal. Therefore, wavelet analysis is used as low pass filter which forbids high frequency to pass. In this work, the wavelet analysis of CV was studied by extracting the major feature coefficients of the width of cyclic data being a transient signal. The analyzed wavelet coefficients were proposed to be used as selected cyclic feature parameters. Concerning coefficients selecting, some points of the width of cyclic data were selected in order to extract major feature of CV.
The carbon nanotube (CNT) has high conductivity depending on Peierl’s distortion and electron configuration within molecular orbit. Moreover, CNT properties contribute to utilize for electron transfer in electrochemical application. Therefore, CNT paste electrode (CPE) has introduced as multi-sensor from which composed of CNT and several types of metal phthalocyanine (MPcs) including cobalt phthalocyanine (CoPc), iron (II) phthalocyanine (FePc), zinc phthalocyanine (ZnPc) and manganese phthalocyanine (MnPc) powders. The electrochemical behavior of MPc multi-sensor relies on central atom of MPc. The differences of central atom contribute to cross-response. Consequently, CV obtained from the four multi-sensors, was used as sets of cyclic data for classifying each type of coffee including Robusta, blend coffee, cocoa and chocolate malt. The certain characteristic of each type of coffee can be achieved by principal component analysis (PCA).

2. Experiment

To fabricate CPE, 700 μL of a mineral oil and prepared powder consisting of CNT and MPc were mixed into agate mortar for 60 minutes then embedded in hollow Teflon rod which inserts aluminium rod at the other end. Four types of modified sensors were fabricated by mixing 100 mg of MPc with 100g of CNT. The CV data was obtained from four types of modified sensor, Ag/AgCl and platinum electrodes used as working, standard-reference, and counter electrodes, respectively. To measure the sample, 4g of measuring sample was extracted from a new packet then mixed with boiled deionized water (18MΩ Milipore) at 90°C then cooled down at 30°C. CV measurement was operated from -1.5 to +1.5 vs. Ag/AgCl with scanning rate of 0.05 V/s, as well as step potential of 0.005 V.

To evaluate the variation of signal, five CV measurement loops of each modified sensor were performed for six times; and only last scan loop was used in data processing. The analyzed signal used in PCA was represented by the width of CV loop. The difference between forward and backward electric current at the same voltage, or width of CV loop was realized as an analyzed signal.

For wavelet analysis, there are six kinds of wavelet including daubechies (dB1 to dB3), coiflets (coiflet1), reverse biorthogonal (rBior1.1) and symlets (sym2). They can extract the coefficients being a major feature of analyzed signal. All wavelet families were operated at sixth levels. The ten points of analyzed signal were selected from each CV and arranged in a 30×40 correlation matrix in case of dB1 and RevBior1.1. However, the twelve points of analyzed signal were chosen from each CV and arranged in a 30×48 correlation matrix in case of dB2 and sym2. In addition, the fourteen points of analyzed signal were extracted from each CV and arranged in a 30×56 correlation matrix for dB3 and Coif1. To conduct classification and to build recognition model, the PCA collaborated with six types of wavelet were performed.

3. Results and discussion

The modified sensors fabricated by mixing CNT with MPc were used as a working electrode in order to measure the CV response of several types of drink at 30°C including three types of coffee and two types of cocoa. The analyzed signals were evaluated from absolute and different values of loop data. The single scan loop with 1202 data points was used in data processing. There are three zones of analyzed loop signal of which consist zone I, II, and III as shown in Fig. 1. The 300 data points in zone I was prepared by absolute value, cathodic current, of CV between -1.5 to 0V while the absolute zone III including 300 data points ranges from 0 to +1.5V. In order to make continuous signal, the zone II was prepared by the combination of cathodic current at 0V and the 601 data points of difference between current values at the same voltage for forward and backward scans, so that the 1201 data points of analyzed data from three zones can represent the CV loop data with extract loop feature into the line feature which can be analyzed by normal protocol.
The CV measurement for four types of electrode and five types of hot drink were conducted for six repeats and the CV loop data was converted into line data as shown in Fig. 2. The analyzed signal of fabricated sensor modified with CoPc showed similar signal for Robusta, blend coffee, cocoa and chocolate in zone I and III; however, there were different pattern among Robusta, blend coffee, cocoa and chocolate malt in zone II. In case of FePc blended CPE, the analyzed signal for all of the sample exhibited different signal feature in zone I and III. Moreover, the analyzed signal is narrow; there are distinctive peak for blend coffee II and for chocolate malt in zone II as shown in Fig. 2b. The analyzed signal of MnPc modified sensor indicated similar signals for Robusta, blend coffee, cocoa and chocolate malt in zone I whereas there were different signal for the entire sample in zone II and III as shown in Fig. 2c. In case of analyzed signal for ZnPc fabricated sensor, the similar signals for overall samples were observed in zone I while there are discriminated signal for all samples in zone II and III as shown in Fig. 2d.
The wavelet analysis was used as a feature extractor which can extract significant coefficients obtained from 1201 points of analyzed signals. The used mother wavelet including dB1, dB2, dB3, dB4, coif1, Bior1.1, and sym2 were operated at seventh levels of decomposition. For dB1 and Bior1.1, the 10 coefficients were extracted from 1201 points of analyzed signals and arranged into a 30×40 correlation matrix. In addition, the 12, and 14 coefficients were extracted from each CV and arranged 30×48 and 30×56 correlation matrix were formed in case of dB2, sym2, and dB3, Coif1, respectively. The classification of characteristics for various modified electrodes can be easily demonstrated by evaluating PCA as results shown in Fig. 3 for dB1 and Bior1.1 mother wavelets.

![Figure 3](image1)

**Figure 3.** PCA plot of three different types of coffee, cocoa and chocolate malt powders with extracted feature base on (a) db1, and (b) Bior1.1 mother wavelets.

The PCA obtained from db1 and Bior1.1 indicated the classification of groups with overall variance of 67.46% representing from PC1 and PC2. The entire percentage accounted for the variance of correlation matrix that the variable PC1 and PC2 can used to describe the main feature of CV loop. Furthermore, the 30×48 correlation matrix of dB2 and sym2 wavelets was extracted and classified in PCA as shown in Fig. 4.

![Figure 4](image2)

**Figure 4.** PCA plot of three different types of coffee, cocoa and chocolate malt powders with extracted feature base on (a) dB2, and (b) sym2 mother wavelets.

PCA results for dB2 and sym2 showed the factor classification of five discriminate groups with entire variance of 64.74% representing from the PC1 and PC2. Similarly, entire variance for dB2 and sym2 wavelets causes resulted about the same overall variance of both.
Figure 5. PCA plot of three different types of coffee, cocoa and chocolate malt powders with extracted feature base on (a) dB3, and (b) coif1 mother wavelets.

The PCA score of both dB3 and coif1 mother wavelets indicated separate distribution of five data groups. The cocoa and chocolate malt data group appeared on the left side and settings separate from each other. Oppositely, Robusta, as well as blend coffee II data appeared on right side and clearly separated from other groups while the blend coffee I data appeared below and clearly separated far from others. Thus it was possible to clearly separate between groups by using either dB3 or coif1. These PCA results showed the pattern classification with overall variance of 66.08% and 62.37% for dB3 and coif1 wavelets, respectively. The pattern classification based on PCA was likely to be more successful if the ability of extracting major feature coefficient from the analyzed signal increase. Therefore, the size of correlation matrix indicated the existent of more feature coefficient. It is possible to extract distinguishable feature from all of the mother wavelet as shown in Fig.3, 4 and 5. However, the coiflets1, as well as dB3 can be the best feature extractor since correlation matrix created by either coiflets1 or dB3 was the largest size of correlation matrix.

4. Conclusion
The modified sensors based on CPE mixed between CNT and several MPc powders were successfully fabricated and used as working electrode in order to separate group of various coffee, cocoa, chocolate. The wavelet analysis was used to extract significant feature coefficients from transient line signal obtained from the analyzed loop signal. The ability of wavelet analysis for extracting feature coefficient depends on wavelet filter which is based on linear algebra of each wavelet type. This procedure provided suitable protocol for classifying discriminate CV data.

5. References
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