Using various metal phthalocyanine mixed with graphite for selective electrodes of electronic tongue to classify several types of hot drink

A Jityen1*, R Jaisuthi2 and T Osotchan1

1 Materials Science and Engineering Program, School of Materials Science and Innovation, Faculty of Science, Mahidol University, Rama VI Road, Bangkok, Thailand
2 Department of Physics, Faculty of Science and Technology, Thammasat University, Pathum Thani, Thailand

[*] j.arthit89@gmail.com

Abstract. Metal phthalocyanine (MPc) is a metal organic compound which can be formed with several metal atoms at the center. Although MPc has semiconductor property, in order to fabricate the selective electrode for cyclic voltammetry (CV) measurement, the other material with high electrical conductive materials is required to mix in order to achieve sufficient electrochemical current. In this work, graphite powder with particle size less than 20 µm from Sigma-Aldrich Pte. Ltd. was mixed with several MPc powders including cobalt, iron, zinc and manganese phthalocyanine powders in the ratio of 20:1 by weight, respectively. The mixture powder was grinded together to achieve the uniform mixing with some powder size. In order to fabricate the selective working electrodes, the mixture was fill into a hollow Teflon rod with inner copper rod at the other end. During CV measurement, the electrodes indicated the anodic and cathodic peaks at various voltage depending on the type of metal atom of MPc therefore these modified graphite electrodes are suitable to be utilized as a selective probe for electronic tongue system. To demonstrate the classification ability of this electrode array, a variety of hot drink was used including three types of coffee, cocoa and chocolate malt. The hot drink was prepared with boil water and cooled it down to 30°C before performing the CV measurement by five electrodes. With principle analysis, the extracted feature can separate each data group of five hot drinks and even can distinguish three types of the coffee. Thus, these graphite modified electrodes can be utilized in an electronic tongue application with low cost and high stability.

1. Introduction

Metal phthalocyanine (MPc) is an organic semiconductor whose central metal atom can be varied for fabricating nonspecific sensor array in electronic tongue application. The distinctive performance of sensor array modified with a number MPc compounds is a variety of metal chemical reaction for desired analyzed solutions. These chemicals has cross-response properties for electrochemical analysis used in electronic tongue applications. The basic principle of electronic tongue is to measure a fingerprint of compound by using sensor arrays. Each sensor can response to certain chemical composition and generate cyclic voltammetry (CV) response by converting the chemical reaction to electrical signal. Therefore, multi-sensor array is widely used in electronic tongue application.

To enhance the electrical signal, graphite has been used as working electrode because of its electrical conductivity thus the carbon paste electrode fabricated mixture between MPc and graphite is an opportunity for developing sensor array for electronic tongue. An electrochemical property of MPc...
modified sensor were studied by a number of groups [1-3]. The capability of CV leads to observing the redox reaction in which involve electron transfer over potential window therefore a variety of substance species can be classified by CV pattern.

2. Experiment
In order to fabricate carbon paste electrode (CPE), the prepared powder containing graphite powder with particle size less than 20 µm from Sigma-Aldrich Pte. Ltd. and MPC powder including cobalt, iron, zinc and manganese phthalocyanine (CoPc, FePc, ZnPc and MnPc) powders were blended with 1.5 mL of a mineral oil in agate mortar for 60 minutes. Then this paste was embedded in hollow Teflon rod which inserted aluminium rod at the other end. Four nonspecific sensor modified with MPC were prepared from blending between 100 mg of MPC and 2000 mg of graphite.

In this work, nonspecific sensor, Ag/AgCl, and platinum were used as working electrode, reference electrode, and counter electrode, respectively. The electrodes were operated with potentiostat (DY2100 Series Multi-Channel) in order to measure CV signals. To prepare the analysed solution, 4g of measuring sample was taken from a new package then put into boiled deionized water (18MΩ Milipore) then cooled down at 30°C. Potential window was operated in the range from -1.5 to +1.5 V vs. Ag/AgCl with scan rate of 0.05 V/s and step potential of 0.005 V.

To reduce the variation of signal, five CV loops of each sensor were measured and for the measurement was repeated for six times. In this analysis work, the third scan loop was used in feature extraction and data processing. For feature extraction, CV signals were redrawn to make loop signal to be series analyzed signal. The analyzed signal was extracted feature by using wavelet analysis then performed in principle component analysis (PCA) [4-5].

3. Results and discussion
The modified sensors fabricated by mixing graphite with MPC were used as a working electrode in order to measure the CV response of several hot drink including Robusta coffee, blend coffee I, blend coffee II, cocoa, and chocolate malt. The CV of several types of hot drink was indicated in Figure1. The characteristic of CV response depends on charge transfer process at MPC surface. Electron transfer process through modified electrodes was carried out by CV measurement on CPE blended with ZnPc, MnPc, CoPc, and FePc.

![Figure 1. CV patterns for three types of coffee, cocoa and chocolate malt obtained CPE mixed between graphite and (a) ZnPc; (b) MnPc; (c) CoPc; and (d) FePc powders](image_url)
The CV response of ZnPc sensor shows peak response for hot drink scanning in the range from -1.5 to +1.5V vs Ag/AgCl with 0.05 V/s of scan rate as shown in Figure 1(a). For chocolate malt, there are significant peaks at +0.5 V and +0.7 V. Moreover, CV also appears a strong peak occurring at about -0.75V. The CV responses of robusta and blend I and II coffee indicate similar characteristics and show slightly difference around +0.25 to +1.0V. The similarity of CV response indicates the existence of the similar chemical component. The CV loop for cocoa is narrower than that of other samples and appears oxidation peak at about +0.37 and +0.65V. The similarity of chemical component in chocolate malt and cocoa was indicated by close oxidation peaks of chocolate malt and that of cocoa.

For MnPc sensor, chocolate malt indicates oxidation peaks at about +0.5 and +0.75 V while reduction peaks appear at about -0.65 and -1.25V. For robusta, blend coffee I and II, the MnPc modified sensor shows similar broad peak as shown in Figure 1(b). However, there are differences appearing between -1.5 to -0.5 V and +0.25 to +1.0V. For cocoa, the CV loop shows symmetric response with oxidation peaks at about +0.25, +0.75 V and reduction peak near -0.65V. The same location of oxidation-reduction peak is one of evidence showing the similarity of chemical component for chocolate and cocoa.

For CoPc sensor, the chocolate malt shows oxidation peak at +0.75V and reduction peak at -0.25 V while cocoa shows reduction peak at -0.25 V and two broad oxidation peaks at about +0.75V and +0.25V, as shown in Figure 1(c). In case of robusta, blend coffee I and II, the CV response indicates asymmetric loop with broader on positive voltage and narrow loop on negative voltage.

For FePc sensor, the chocolate malt shows strong and broad cathodic peaks at +0.5V and +0.75V, respectively, whereas the anodic peak occurs at -0.5V. The CV response for cocoa indicates anodic peak at nearby position of -0.5V while the broad cathodic peaks exhibit at about +0.5 as well as +0.75V. For robusta coffee, blend coffee I and II, the characteristic of CV responses are quite similar and show the asymmetric response. These CV peaks can be described by the oxidation of the MnPc molecule and donating an electron to platinum electrode as shown in Figure 1(d).

The saccharine and phenolic compounds are major chemical components that can interact with the central atom of MPc. It affects the different oxidation-reduction reaction which can be observed from these CV responses.

The analyzed signals were evaluated from absolute and different values of loop data. Third scan CV loop data consisting of 1202 points was used for analysis. In order to redraw the loop data to single line data, the data was arranged into three zones. The 300 data points in zone I was prepared from absolute value of cathodic current between -1.5 to 0 V while the absolute zone III includes 600 points of cathodic current ranging from 0 to +1.5V. To create continuous boundary, the zone II data was prepared by the combination of cathodic current at 0V (I0) and the 601 data of difference between current values at the same voltage for forward and backward scans. Therefore the 1202 data points of analyzed data from three zones can represent the CV loop data and used for extract feature into the line form as shown in Figure 2(b).

**Figure 2.** (a) Typical CV loop patterns for blend coffee II measured by CPE mixed between CNT and ZnPc and (b) analyzed line signal obtained from absolute and different current values at the same voltage.

To extract feature from analyzed line data, the wavelet analysis was used as a feature extractor which can extract significant coefficients obtained from 1201 points of analyzed signals. Haar wavelet was used as a mother wavelet and operated at the seventh levels of decomposition then the ten
approximated coefficients were extracted from each analyzed line signal and arranged into 30×40 correlation matrix. The classification of characteristics for five types of hot drink with various modified electrodes can be easily demonstrated by evaluating PCA and the PCA results showed in Figure 3. after extracting by Haar mother wavelets.

![Figure 3. PCA plot of five types of hot drink with extracted feature based on Haar mother wavelet](image)

The PCA result of the analysed data extracted by Haar mother wavelet shows the separated classification groups with variance values of 82% and 9% from PC1 and PC2, respectively. This means the PCA with only PC1 and PC2 can represent overall variance of 91.69 %. The percentage accounted in variance of correlation matrix can indicate that the variable PC1 and PC2 can be used to describe the main feature of CV loop.

The PCA score indicated separate distribution of five data groups. The cocoa and chocolate malt data group appeared on the left side and quit separate from others. Robusta,blend coffee I and II data appeared on right side and clearly separated from other groups while the blend coffee I data appeared below. Thus it was possible to clearly separate between five groups of hot drink by using Haar wavelet. The pattern classification based on PCA is successful with ability of selecting feature coefficient from the analyzed line signal. Therefore, the correlation matrix can indicate the feature coefficient and possible to extract distinguishable feature from wavelet analysis.

### 4. Conclusion

The modified CPE sensors based on mixture between graphite and several MPc powders were successfully fabricated and used as working electrode in order to separate group of several hot drinks. The wavelet analysis was used to extract significant feature coefficients from line signal obtained from the CV loop signal. The ability of wavelet analysis for extracting feature coefficient depends on wavelet filter at particular window range and can provide suitable protocol for classifying discriminate CV data in electronic tongue application.

### Acknowledgments

This work was partially supported by National Nanotechnology Center (NANOTEC) through Capability Building Unit for Nanoscience and Nanotechnology, Faculty of Science, Mahidol University.

### References

[1] Almario A and Caceres T 2014 *Am. J. Anal. Chem.* 5 266
[2] Varvolgyi E, Gere A, Szollosi D, Sipos L, Kovacs Z, Kokai Z, Csoka M, Mednyanszky Z, Feket A and Korany K 2015 *Arab. J. Sci. Eng.* 40 125
[3] Lopetcharat K, Kulapichitr F, Suppavorasatit I, Thanawee C, Phatthara-aneksin A, Pratontep S and Borompichaichartkul C 2016 *J. Food Eng.* 180 60
[4] Chan Y T 1995 *Wavelet Basics* (Massachusetts: Kluwer Academic Publishers) p 1
[5] Misiti M, Oppenheim G, and Poggi J M 1996 *Wavelet Toolbox User's Guide* (The MathWorks, Inc.) Chapter 1 pp 7-16