

Interpretation of Voltammetric Data by Neural Networks for Simultaneous Determination of Glucose, Fructose, and Ascorbic Acid

Paisit Susomrith¹, Werasak Surareungchai² and Ake Chaisawat¹

¹ Department of Control System Engineering, Faculty of Engineering,
King Mongkut's University of Technology Thonburi,
Pracha-Uthit Road, Toong-kru, Bangkok 10140, Thailand
Tel.: +66-2-4709091, Fax.: +66-2-4709096

² School of Bioresources and Technology, and Pilot Plant Development and Training Institute,
King Mongkut's University of Technology Thonburi,
Bangkhuntien-chaitalay Road, Bangkhuntien, Bangkok 10150, Thailand
Tel.: +66-2-4709732, Fax.: +66-2-4523455

e-mail: statespace@engineer.com, werasak.sur@kmutt.ac.th, ake.cha@kmutt.ac.th

Abstract: This work describes the use of neural networks (NNs) for interpreting voltammetric data, i.e., current-voltage spectra that obtained from the electrochemical reaction of analyte species at a gold electrode. Current-voltage spectra of glucose, fructose and ascorbic acid in mixtures obtained from dual-pulse staircase voltammetry (DPSV) was in the form of the mixed responses contain characteristics of the individual analytes approximately in proportion to their concentration. Extraction of individual analyte concentration from combined data was subsequently achieved using NNs. The combination of DPSV and NNs opens a possibility for simultaneous determination of mixtures of the species for fruit juices quality monitoring.

1. Introduction

Dual-pulse staircase voltammetry (DPSV) is an electrochemical detection technique based on a staircase potential waveform together with potentiostatic cleaning and reactivation of the electrode surface. DPSV plays two key attributes, permitting measurement of aliphatic organic compounds with reducing electrode passivation problems and yielding current-voltage peaks response corresponding to different compounds present in the solution. Fung and Mo [1] have used DPSV for simultaneous determination of glucose and fructose by employing simple linear calibration of two peak current measurements from each displaying different peak potentials. When a solution sample contains mixture of more than two compounds, the DPSV responses in which non-linear relationship and inter-analyte interference are observed. This would be difficulty to interpret voltammetric data for a calibration and quantitative measurement. In this context, neural networks (NNs) seem to be especially appropriate for the interpretation of the voltammetric responses generated by the electrode sensor. DPSV responses have recently been resolved by using NNs [2].

Glucose, fructose and ascorbic acid are commonly present in fruits and fruit drinks. There is a demand for the determination of these sugars and ascorbic acid for quality control, nutritional purposes and for monitoring the taste. Wet chemical analysis can be employed but is time consuming. The most common analytical instrumentation

for the determination of sugars and acids is liquid chromatography (LC) with either UV-visible spectrophotometric or refractive index detection. Even though the sophisticated analyzers are accurate, they need well-trained technicians and have a high cost. With aiming to use a single electrode sensor for rapid and simple simultaneous monitoring of the organic compounds, this paper describes the use of electrochemical detection approach such a DPSV in conjunction with NNs.

2. Materials and Methods

All chemicals were analytical grade and were used as received. The electrochemical cell consisted of a 1.0 mm diameter gold disk working electrode, a platinum wire counter electrode and a saturated calomel reference electrode. Cleaning electrode surface was described elsewhere [3]. Voltammetric measurements were performed using a computer-controlled potentiostat (Autolab[®] PGSTAT 10, EcoChemie). The analyte solution of glucose, fructose and ascorbic acid was prepared by dissolved in 0.1M sodium hydroxide (NaOH). The electrochemical cell contained 5.0 mL of 0.1 M NaOH to which a small volume of analyte solution was added. All experiments were carried out at room temperature.

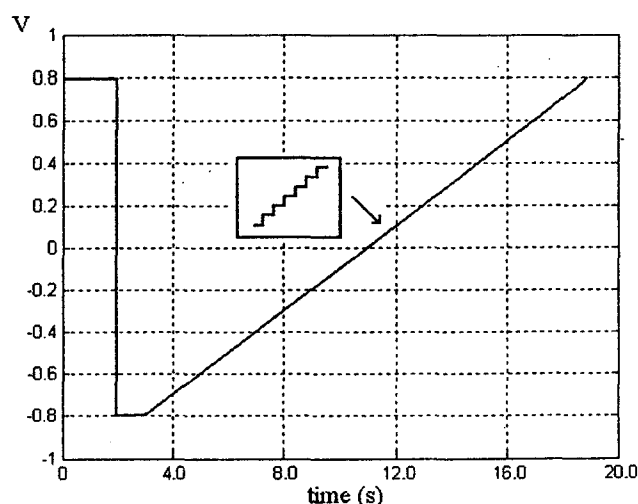


Figure 1. Typical DPSV waveform.

2.1 Dual-Pulse Staircase Voltammetry

Potential waveform of the DPSV in this study is shown in Figure 1. Briefly, potential was applied in the following: the first pulse at +0.8 V for 3 s, to remove adsorbed fouling species and gold oxide formed on the gold electrode, and the second pulse at -0.8 V for 2 s, to regenerate the clean surface, and then followed by a scan from -0.8 to +0.8 V in steps of 10 mV at a rate of 0.1 V s⁻¹. The current-voltage was performed and recorded. In addition, the current-voltage responses can be exported.

2.2 Neural Networks

A multilayer feed forward network was chosen for the study. NNs were implemented in Q Net.Pro. (on Windows 2000). The work reported here, the model of each reagent i.e., glucose, fructose and ascorbic acid and their current-voltage peak responses from DPSV were defined as the correlation matrix according to equation 1:

$$C_i = f_i(S_1^m)_i \quad (1)$$

where $i = 1, 2, 3, \dots, n$ is the number of the response current obtained for training the neural network, C_i is the matrix of concentration of glucose, fructose and ascorbic acid, and S_1^m is the matrix of voltammetric data varied from 1 to m .

NNs algorithm in this study comprised of mode of training and recall. Training mode for NNs was obtained by using patterns of the voltammetric responses. The weight-correction procedure was conducted by back-propagation algorithm. Recall mode is the use of the trained NNs in order to display the desired concentration. The step of the algorithm can be consulted from a flow chart seen in Figure 2.

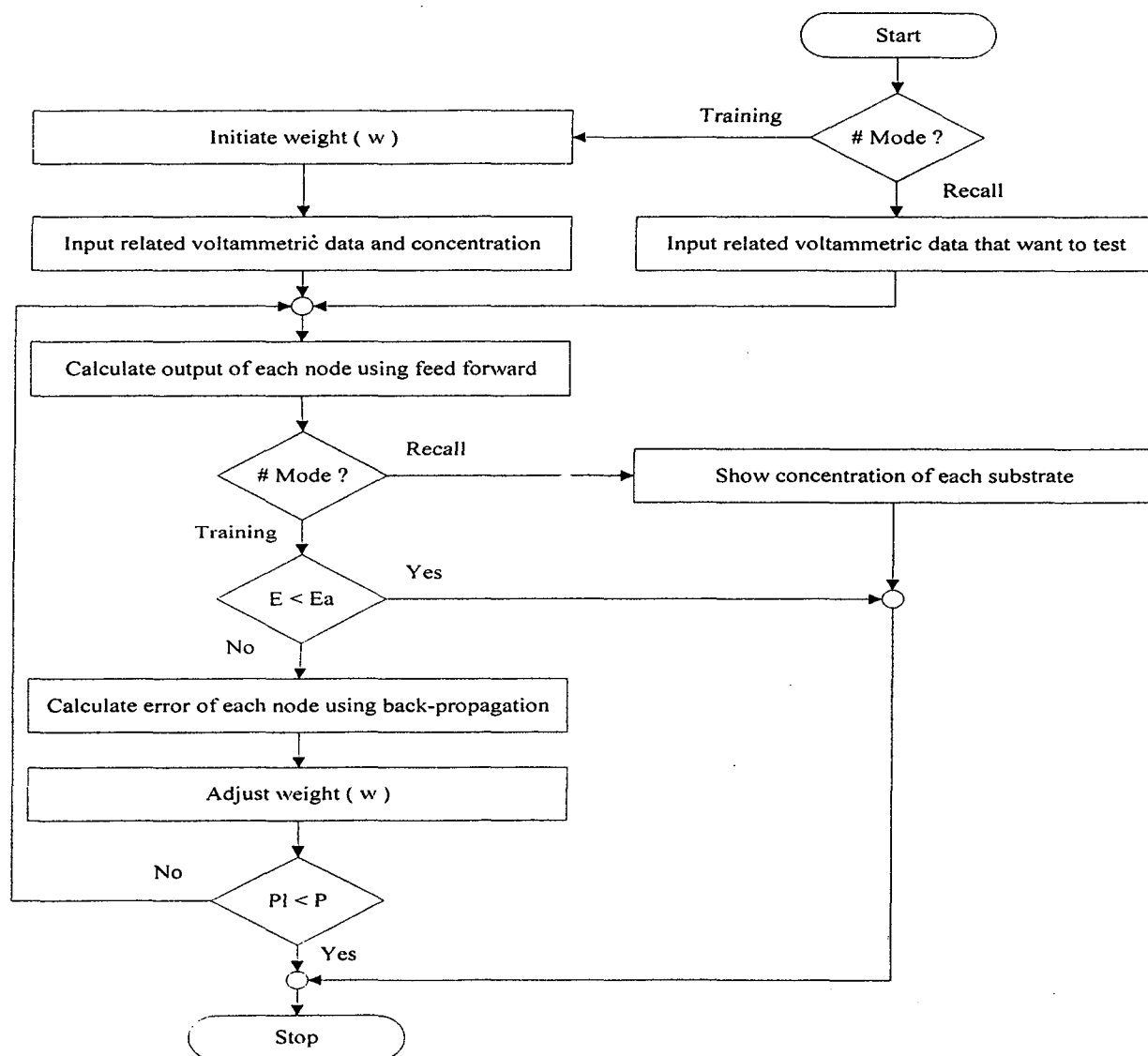


Figure 2. Schematic flow chart of the NNs algorithm.

3. Results

The typical DPSV responses obtained from the three analytes, i.e., glucose, fructose, and ascorbic acid are shown in Figure 3. It is clear that the key feature of the fructose response is a peak around +0.2 V (curve a in Figure 3) while the glucose yields two peaks, one around -0.5 V and another around +0.2 V (curve b in Figure 3). Ascorbic acid peak response appears at about -0.2 V (curve c in Figure 3). Since each analyte possess a distinctive response, it is plausible that the voltammogram of a mixture of the three would produce a combined response, as evidenced in Figure 3, curve d. The virtual separation of mixed response by DPSV incorporating with an appropriate resolving method would allow the resolution and simultaneous quantification of glucose, fructose and ascorbic acid in mixture solutions.

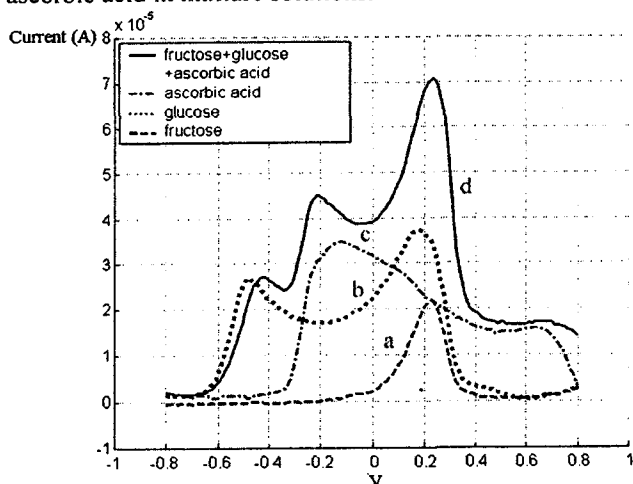


Figure 3. DPSV responses for glucose, fructose and ascorbic acid.

Training data were acquired by carrying out DPSV in known mixtures of the three analytes in the concentration range of 0–10 mM in each analyte. Using these concentrations gave a total of 81 data set which represents to 16 different ratios of three analytes concentration with five discrete concentrations and at zero concentration, as shown in Figure 4.

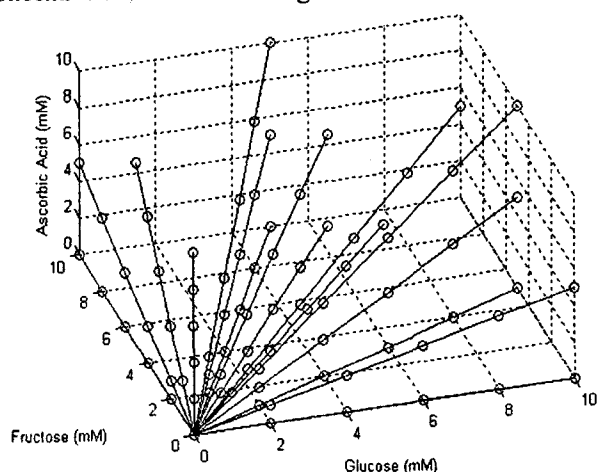


Figure 4. Typical training pattern for the model.

The data set was formed comprising of 109×81 element input matrix and 3×81 target matrix. The training method for the NNs structure was back-propagation of errors, composing of 109-node input layer, 4 hidden layers with 20 nodes per layer and 3-node output layer which represent to glucose, fructose and ascorbic acid. The transfer functions of hidden layers and output layer are defined as bipolar sigmoid where the learning rate is 0.6 and the momentum is 0.5. Data input was voltammetric signals obtained from glucose, fructose, and ascorbic acid in mixed solution. It took about 50,000 epoch of computing iterations during the training. Finally, the root mean square error (*rms* error) was 0.017, obtained from equation 2 [4], after carefully generated the training pattern.

$$rms \text{ error} = \sqrt{\frac{\sum_{x=1}^{n_x} \sum_{i=1}^n (Ca_{si} - Co_{si})^2}{n_x n}} \quad (2)$$

where Ca is actual concentration (mM), and Co is model output concentration (mM).

In order to verify our NNs model, we select randomly concentrations of the analytes and then run the model; the test concentration that were not the training data were verified. The output was compared with the test concentrations to analyze the ability of interpretation of voltammetric data by NNs. Figure 5 shows the comparison between the test concentrations and concentrations predicted by the NNs.

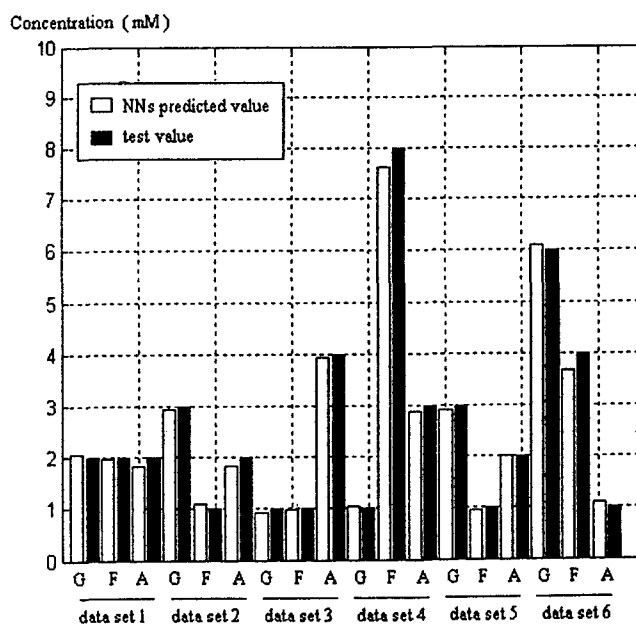


Figure 5. Comparison of test and predicted values obtained by the NNs. G, F and A stand for glucose, fructose and ascorbic acid, respectively.

Errors from the prediction, referring to the absolute percentage error and the mean absolute percentage error of each data set can be calculated from equation 3 and 4 [4].

$$\text{absolute percentage error} = \left| \frac{Ca_i - Co_i}{Ca_i} \right| \times 100 \quad (3)$$

$$\text{mean absolute percentage error} = \frac{1}{n} \sum_{i=1}^n \left| \frac{Ca_i - Co_i}{Ca_i} \right| \times 100 \quad (4)$$

The minimum absolute percentage error was 0.0545%, and the maximum absolute percentage error was 9.1745. The minimum mean absolute percentage error of data set was 2.2708. The maximum mean absolute percentage error of data set was 6.5954.

In conclusion, this work describes the ability of interpretation of voltammetric data by neural networks for simultaneous determination of glucose, fructose, and ascorbic acid. Results showed that *rms* error after feeding input; the training data can be minimized. The tested values by using of random concentration data of analytes also produce the low absolute percentage error. A focus of future work will consider real samples e.g., fruit juices, which contain many compounds and finally will be able to verify how successful the DPSV in conjunction with NNs for real situations.

References

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