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Design of Water Analyzer Using Pulse Voltametry

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ABSTRACT

This work proposes the development of a new approach for water sample authentication, in real life, using a pulse-voltametry-method-based electronic tongue instrumentation system. The system is developed as a parallel combination of several neural network classifiers; each dedicated to authenticate a specific category of water sample, and can be extended for more categories of water sample authentication. The system employs a slant let-transform (ST)-based feature extraction module and two popular variants of neural networks for classification. The proposed system hybridizes ST with two variants of back propagation-neural-network-based binary classifiers to develop an automated authentication tool. ST is regarded as an improved version of orthogonal discrete wavelet transform that can provide improved time localization with simultaneous achievement of shorter supports for the filters. This proposed system, implemented in a laboratory environment for various water samples available in India, showed encouraging average authentication percentage accuracy, on the order of over 80% for most water categories and even producing accuracy results exceeding 90%, for several categories.

Key words: Design water analyzer, pulse voltametry, electronic tongue

1 INTRODUCTION

Electronic tongues have been applied to many different fields in the last decades. However, it is in the food quality control and safety where the applicability of these biomimetic systems has been explored more. These electronic tongue systems are mainly optimized for the analysis of water samples. This technique is highly reliable, but it requires several experimental steps (sample preparation, DNA extraction, micro satellite amplification and gel electrophoresis) and skilled personnel to carry out. Recently, a review has covered the research done in the field of electronic and bioelectronics' tongues for the analysis of water samples. However, one special point that was not covered enough in this review is the data fusion of various measurement techniques (potentiometry, amperometry, conductance, spectrophotometry, gas sensing). These systems are called hybrid electronic tongues because they merge variables of different nature.

The E-tongue device is built with a potentiostat interfaced with an intelligent .A potentiostat is used for electrochemical characterization of redox active species and in evaluating thermodynamic and kinetic parameters of electron transfer events. A potentiostat is an electronic instrument that is capable of imposing electrical potential waveforms across a working electrode relative to a reference electrode. It also measures the resultant current through the cell at the third electrode.

In operation, the potentiostat is commonly interfaced to a three-electrode setup containing reference electrode, working electrode, and counter electrode. The reference electrode establishes a constant reference potential in the electrochemical cell, against which the working electrode potential may be determined with relatively high precision. Minimal current is drawn through the reference electrode because its current signal is made input to a very high impedance electrometer, thus ensuring the constant potential condition. The working electrode is the surface at which the electron transfer of interest occurs.

2 RELATED WORKS

Characterization of liquid substances and compounds has been often inexact due to inhomogeniety of the species in the liquid, fluctuations in the interaction with the sensor, and the difficulty in interpretation based on quantitative or qualitative analysis. The conventional sensor systems that are capable of overcoming these problems often become bulky and expensive. in recent years, multisensory systems have been developed, called electronic tongue (popularly known as e-tongue) systems, which are capable of sensing the characteristics of wet chemical by a special data Acquisition method called voltametric method. Time series signals and the corresponding raw data, representing the measurement from a multisensory system, can give rise to large Matrices, sometimes with several thousands of entries, and can be analyzed using multivariate statistical methods (e.g., principle component analysis (PCA). In most cases, these time series raw data contain noise due to drift, which may yield misinterpretation about qualitative discrimination. This is because the PCA method can only reduce the dimensionality of the time series raw data but cannot eliminate the effect of noise and drift. it is recently reported that wavelet transform (wt)-

based methods can also be advantageously used in these problems . They can compress, Denise, or smooth large complicated signals used in many fields, e.g., in electrochemistry. Several e-tongue systems have so far been developed for quality assessment of water and other beverages and also, several electronic nose systems have been developed for water and beverage quality assessment and odor or flavor classification. In, a fuzzy clustering technique has been developed to determine prototypes for good and bad quality from a set of training data, acquired from the pulse voltametry technique. This method has been applied for water and baby food quality assessment. In water quality assessment, although they recorded good results for tap water and river water, their results were not that encouraging for boiled river water and mixtures.

Another e-tongue system where two fuzzy adaptive resonance theory map (art map)-based classifiers were developed to discriminate between different waters, and they could achieve classification accuracy rates of 91.1% and 93.3%, respectively. In, a voltametric-technique-based e-tongue system was developed for qualitative analysis of water, where discrete cosine- transform-based dimensionality reduction techniques were investigated. In, another pulse-voltametry-based E-Tongue system was developed for the assessment of water using the PCA technique. However, to the best of our knowledge and belief, the proposed work in this literature is the first work to utilize an e-tongue system for liquid authentication (in our case, the liquids considered are different categories of water). In the present research work, we have utilized ST to extract features from the no stationary signals, acquired as the output from the e-tongue instrumentation system for each water sample, treated as a finite-length data signal. For each such signal, we have extracted relevant ST filter coefficients, and then, we have implemented a supervised-neural-network-based classifier as a six-input–one-output system. The output of the neural network- based binary classifier belongs to either of the two labels: one corresponding to the correct water category, implying that the sample is authenticated, and the other corresponding to the incorrect water category, implying that the sample is not authenticated. Hence, for authenticating m category of water samples, m such artificial-neural-network (ANN)-based binary authentication modules are developed, which are implemented in parallel.

Both supervised and unsupervised neural networks have been successfully employed, over the years, for classification, pattern recognition, function approximation, and estimation purposes [13]. in our present work, we employed two types of back propagation neural networks (BPNNS), one utilizing levenberg–marquardt learning (called henceforth BPNNLM) and the other utilizing resilient back propagation learning (called henceforth BPNN-RP). The performances of these systems are evaluated in real life by implementing an e-tongue based instrumentation system with pulse voltametry method of experimentation, acquiring signals for samples tested from eight water categories and then building the water sample authentication system, utilizing ST-based feature extraction coupled with the neural-network-based authenticator. For each category of water, output signals were captured for two types of working electrodes (Ag and pt) in the e-tongue system, and the performance of the authentication system developed was tested for signals acquired from experimentations carried out with both sets of working electrodes. The proposed system showed encouraging authentication percent accuracy results for all categories of water samples, for both sets of working electrodes used.

3 METHODOLOGY

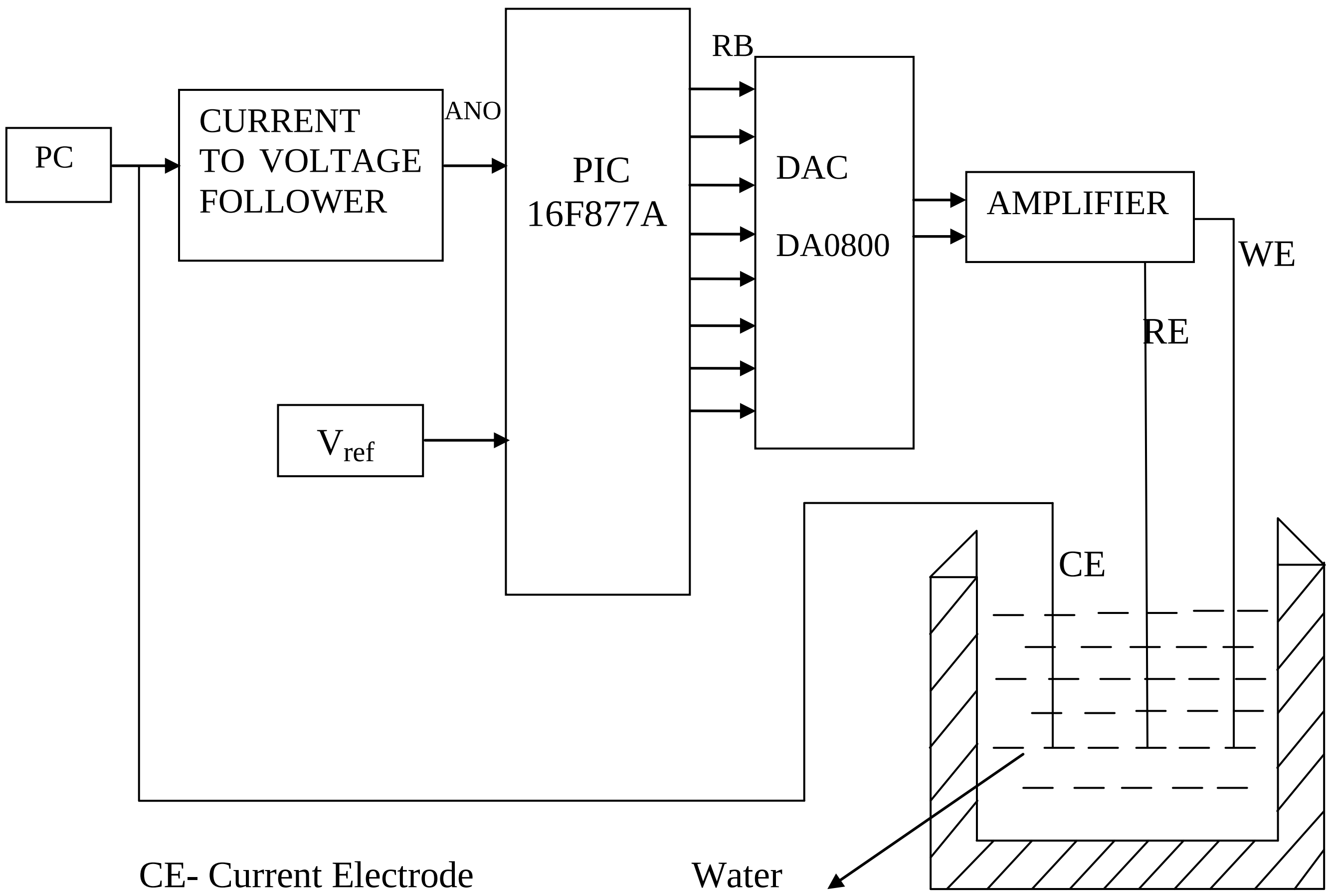
The E-tongue device is built with a potentiostat interfaced with an intelligent system (e.g., PC, microcontroller-based system, etc.). A potentiostat is used for electrochemical characterization of redox active species and in evaluating thermodynamic and kinetic parameters of electron transfer events. A potentiostat is an electronic instrument that is capable of imposing electrical potential waveforms across a working electrode relative to a reference electrode. It also measures the resultant current through the cell at the third electrode [2]. Potentiostat are widely used in electro analytical techniques to identify, quantify, and characterize redox active species, including inorganic, organic, and biochemical species.

In operation, the potentiostat is commonly interfaced to a three-electrode setup containing reference electrode, working electrode, and counter electrode. The reference electrode establishes a constant reference potential in the electrochemical cell, against which the working electrode potential may be determined with relatively high precision. Minimal current is drawn through the reference electrode because its current signal is made input to a very high impedance electrometer, thus ensuring the constant potential condition. The working electrode is the surface at which the electron transfer of interest occurs. Popular choices for the working electrode material include platinum, gold, silver, iridium, etc. Current arising from the electron transfer events at the working electrode is measured at the counter electrode, and therefore, this electrode must be geometrically larger than the working electrode so that it does not limit the current density at the working electrode.

The underlying technique in E-Tongue is known as electro analytical method. Commonly used methods are the following:

1) Voltametry and 2) potentiometry.

There are also other methods which can be followed, e.g., conductometry and spectrophotometry. Among these, voltametry appears to have several advantages. The technique has been extensively used in analytical chemistry due to features such as its very high sensitivity, versatility, simplicity, and robustness. There are different types of voltametry methods employed, e.g., cyclic, stripping, and pulse voltametry methods. Depending on the technique employed, various kinds of information can be obtained from the analytic. Using voltametry, the response can be obtained in less than 30 s, while potentiometry requires several minutes to complete a measurement sequence. The time aspect is important in a quality monitoring system since quality change can occur fast, and a quick response is therefore required. In E-Tongue, having a three-electrode configuration, potential is applied at the working electrode while the resulting current between the working electrode and the counter electrode is measured.



WE-Working Electrode

RE-Reference Electrode

Fig 1 – Functional blocks of water analyzer

In the pulse voltametry method, the input waveform is formed by potential pulses of varying amplitudes with a base potential in between. Different amplitudes are used to increase the sensitivity and improve the discrimination between samples. The reason for improvement in the sensitivity is that all substances that are electrochemically active below the applied potential will add to the measured current. The response current from an input pulse is composed of two currents: the Faradic current *IF* and the charging current *IC*.

3.1 BACK PROPAGATION-LEARNING-BASED NEURAL NETWORK AUTHENTICATOR

BPNNs are popularly employed for supervised learning to determine complex nonlinear multidimensional mathematical mapping. Over the years, different popular improved variations of BPNN have been proposed to specifically address several important issues, namely, reduction of convergence time, avoiding local minima and arriving at the global minimum, ease of computational burden, reduced memory requirement, etc.

In this paper, we consider two popular variants of BPNN, namely, BPNN-LM and BPNN-RP. For our problem under consideration, i.e., the development of an *M*-category authentication system, we have developed *M* such binary classifiers where each classifier can authenticate a specific category of water samples. The system so developed is generic in nature, and such parallel implementation of neural networks is hoped to be successfully extended for a large variety of *M* values.

This method adopts the famous technique of constructing a multiclass classification system using many single-class binary classifiers, with each classifier developed using all-against-one methodology. Hence, each BPNN authenticator is developed as a binary classifier where the class level is chosen as either +1 (for the signals pertaining to the correct water category under authentication) or −1 (corresponds to signals pertaining to all other water categories). Then, the binary classification problem for each authenticator module can be formulated on the basis of a given data set (Ω), with **x***i* input features and *di* classification output, of the form

$$\Omega = \{(\mathbf{x}1, d1), (\mathbf{x}2, d2) \ldots (\mathbf{XN}, Dn)\}$$

Where $\mathbf{x}i \in \_m$, $di \in \{+1,-1\}$, m is the dimension of the feature vector, and N is the number of training samples/exemplars.

A. BPNN-LM Algorithm

The BPNN-LM algorithm is popular for providing fast convergence in the training phase, provided that the system can support the memory requirements . They essentially employ multilayer perceptions with optimization techniques to train the free adaptable weights. In this algorithm, the cost function is formulated as the sum of squared errors over all exemplars (N) in the training data set, in a given epoch (k).

The LM algorithm for computing weight updates is given as

$$\mathbf{Wk}{+}1 = \mathbf{w}k - [\mathbf{H} + \mu\mathbf{I}]-1\mathbf{g}$$

Where $\mathbf{w}k$ = weight vector in kth epoch, $\mathbf{H}$ = the Hessian matrix, μ = the learning rate, and $\mathbf{g}$ = the gradient vector. Here, the Hessian matrix $\mathbf{H}$ can be approximated as and the gradient vector $\mathbf{g}$ can be computed as

$$\mathbf{H} = \mathbf{J}\mathrm{T}\mathbf{J}$$

$$\mathbf{g} = \mathbf{J}\mathrm{T}\mathbf{e}$$

Where $\mathbf{J}$ = the Jacobean matrix containing the first-order derivatives of the neural network errors with respect to weights and biases and $\mathbf{e}$ = the vector of neural network errors. This ensures that no explicit calculation of the Hessian matrix is required.

B. BPNN-RP Algorithm

The BPNN-RP algorithm is also popular for providing fast convergence. Let E be the sum of squared errors over all exemplars (N) in the training data set, in a given epoch (t), and let wij be the weight between the ith input node and jth output node between two successive layers. This variation of BPNN algorithm achieves convergence by adapting weights and biases, considering the polarities of $\partial E/\partial wij$ only and not considering the magnitude of $\partial E/\partial wij$. Here, each incremental weight Δwij (t) after tth epoch is determined by a fixed step Δij (t) whose sign, positive or negative, will be determined by the sign of $\partial E/\partial wij$. Hence, after each epoch t, all the weights and biases in all layers get similarly affected. This is believed to be the driving force for this algorithm behind potential faster acceleration toward convergence.

4 CONCLUSION

This paper has proposed the development of a pulse- voltametry-method-based E-Tongue instrumentation system that can be successfully employed in real life for water sample authentication. The proposed system uses a hybrid combination of ST-based feature extractor, with BPNN-based binary classifiers, to develop an automated authentication tool. The system is developed as a parallel combination of several neural network classifiers, each dedicated to authenticate a specific category of water sample. The system can be logically extended for large categories of water samples. The system has been implemented in a laboratory environment for various water samples, commonly and commercially available in India, and the experimentations were performed for two types of working electrodes, silver and platinum. The authentication performances were largely found satisfactory, mostly in the upper 80% and often quite exceeding 90%. It was also found that merely increasing the number of features for development of the authentication system does not always really help, and in fact, in our system, it degraded the overall performance when the number of features was increased from 10 to 20.

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