Basic and Mixed Taste Analysis using Voltammetric Electronic Tongue

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ABSTRACT
A voltammetric electronic tongue consisting of a composite metal base electrode array for discrimination of basic taste has been presented. The electrode array consisting of Gold, Nickel, Palladium, Copper and Glassy Carbon as working electrode, has been used for transforming information of taste substances into electric signal. The electrodes output show different patterns for chemical substances that have different taste qualities such as saltiness, sourness, sweetness and bitterness. Experiments were carried out on 10 different chemical solutions eliciting 4 different basic tastes (namely salty, sour, sweet and bitter) at 1 M (or 1N) aqueous solution. Experiments have also performed on the mixed taste i.e., taste consisting of four basic taste parameters. Principal component analysis (PCA) was used for visual inspection of data set. Classification was performed by statistical method. A fairly high degree of discrimination was obtained.

General Terms
Signal Processing.

Keywords:
Electronic Tongue, Voltammetry, Basic Taste, Virtual Instrumentation.

1. INTRODUCTION
Taste is basically comprised of four basic qualities namely saltiness mainly produced by sodium chloride, potassium nitrate, potassium chloride etc; sourness produced by hydrogen ions of hydrochloric acid, sulphuric acid, glacial acetic acid etc; sweetness due to sucrose, glucose, fructose, glycine etc.; bitterness produced by magnesium chloride, quinine, caffeine, picric acid etc. But more recently, a fifth taste, savory (or umami), has been proposed by a large number of authorities associated with this field [1-4] which is produced by monosodium glutamate, disodium inosinate disodium guanylate etc. To humans, the sensation of flavour is due to three main chemoreceptor systems. These are gustation (sense of taste by tongue), olfaction (sense of smell by nose) and trigeminal (sense of irritation) [5]. In human, taste buds present in the tongue, contain the receptors for taste. They are located around tongue and the roof of the mouth. Each taste bud is made up of many (around 50-150) receptor cells. Each receptor in a taste bud responds best to one of the basic tastes. A receptor can respond to the other tastes, but it responds strongest to a particular taste. The parts of the food dissolved in saliva come into contact with taste receptors and these receptor cells send information detected by clusters of various receptors and ion channels to the gustatory areas of the brain via the seventh, ninth and tenth cranial nerves [6].

The electrode array used in the electronic tongue works in a similar process: like human receptors, each electrode has a spectrum of reactions different from the other. The information given by each electrode is complementary and the combination of all electrodes generates a unique fingerprint. The electronic tongue receives information from chemicals through electrode array and sends it to a pattern recognition system. The result is the detection of the tastes that compose the human palate.

Electronic tongue with ion selective and membrane base electrode has mainly discussed in different journal publication [7-9] for determining basic taste parameters, but these techniques have several disadvantages, as they require a long regeneration time [10]. And the most serious problem of ion-selective electrodes is interference from other, undesired, ions. No ion-selective electrodes are completely ion-specific; rather they are sensitive to other ions having similar physical properties, to an extent that depends on the degree of similarity. Most of these interferences are weak enough to be ignored, but in some cases the electrode may actually be much more sensitive to the interfering ion than to the desired ion. Moreover the effect of potential drift can easily be seen if a series of standard solutions are repeatedly measured over a period of time, thus limiting the use of ion selective electrode in industrial field.

Metal-based composite electrode array used in the present work have partially overlapping selectivity, which is utilized for obtaining many information variables with low specificity. Even though the specificity of each electrode is low, considerable information can be extracted through the combination of several electrodes. The developed electronic tongue system is very low cost as compared to the electronic tongue system available in the market, output result is repeatable and the metal based electrodes array can be used for long time which is necessary for any commercial purpose.

2. DESCRIPTION OF ELECTRONIC TONGUE

For determining the basic taste parameters, cyclic voltammetry is used in a three-electrode system to control a voltage cycle that forces electron transfer to and from analyte at particular voltage values. In voltammetry, information about an analyte is obtained my measuring the output current as the input potential is varied. In the present work voltage equivalent of output current is considered.

The developed Electronic tongue setup is consisting of seven electrode, data acquisition card (DAQ), electronic circuit for connecting the valve and sequential connection of different working electrodes. USB 6009 DAQ card of National Instruments having 4 differential input and 8 digital input/ output channels are used for applying desired potential in the liquid samples through the electrodes and for collecting the signals.

Electrode array is consisting of seven electrodes. Gold, Nickel, Palladium, Copper and Glassy Carbon have been used sequentially as working electrode. Platinum and silver/silver chloride electrodes have been used as counter electrode and reference electrode respectively. Metal wires of purity more than 99% and diameter 1mm of Alfa Aesar make were crusted in Teflon rod. Only 2 mm of the metals are exposed in the solution and other end of the metals are soldered with copper wire for connecting it with the internal circuit of Electronic tongue.

The Electronic tongue setup is consisting of two chamber, one is testing chamber, for placing the electrode array, where testing process will hold and another chamber is used for pouring the liquid samples. Samples from this chamber will automatically flow to the testing chamber. Testing chamber is connected with a solenoid valve and over flow pipe. Any amount more than the specified volume will be removed from testing chamber though the overflow pipe. After each testing process, solenoid valve is activated and liquid from testing chamber removed through the drain out pipe. Block diagram and laboratory prototype of developed Electronic tongue setup is shown in figure 1 and figure 2 respectively. For electrochemical experiment in the developed Electronic tongue system, working Electrode, counter electrode and reference electrode are mounted in testing chamber, which is made up of Teflon and no commercial voltammetric cell has been used in the present work.

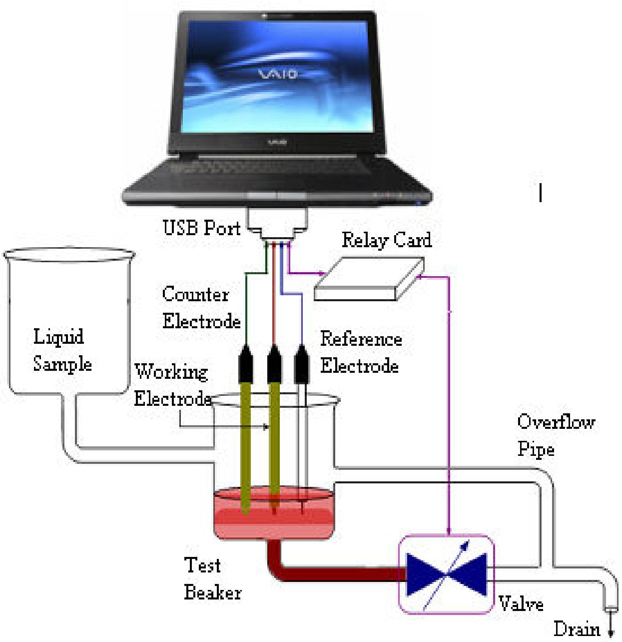

Figure 1. Customized Electronic Tongue Setup

Figure 2. Laboratory Prototype of Electronic Tongue

3. EXPERIMENTS

Pure chemicals for producing basic taste were purchased from Loba Chemie Pvt. Ltd. and QFC Fine Chem Industries. Most of the samples were delivered in the solid form and aqueous solutions of the samples were prepared for measurement with the Electronic tongue system. Distilled water from a single source was used throughout the experiments as for sample solvent and for rinsing of the electrode array and testing chamber. For each testing process in the Electronic tongue system, 100 gm of liquid samples were used. At the beginning of testing, liquid sample is to pour in the liquid sample chamber and automatically it goes to the testing chamber. Any amount more that the specified volume will overflow through the overflow pipe attached with the testing chamber. Controlled voltage with predefined amplitude and frequency is applied in the liquid samples. A computer with USB connection with the Electronic tongue controls the overall testing process. At the time of testing process the system continuously logs all the data in spreadsheet files and back up all of them with separate file names with date and time stampings for future references. Measurement time for each working electrode is 20 seconds and each testing process requires almost 2 minutes. Details of the chemical samples used in this work are shown in the table 1.

Table 1. List of samples measured by the Electronic Tongue

Samples	Taste Attributes	Amount Used in 1 liter distilled water
Sodium chloride (NaCl)	Salty	58.5 gm
Potassium nitrate (KNO3)	Salty	101 gm
Potassium chloride (KCl)	Salty	74.5 gm
Sulphuric acid (H2SO4)	Sour	27.77 cc of 36 (N)
Glacial acetic acid	Sour	66.71 cc of 14.99 (N)
Hydrochloric acid (HCl)	Sour	83.33 cc of 12 (N)
Sucrose (C12H22O11)	Sweet	342.30 gm
Glycine (CH2 (NH2)-COOH)	Sweet	75 gm
Picric acid (Tri nitro phenol)	Bitter	229.1 gm
Magnesium chloride (MgCl2)	Bitter	83 gm

4. DATA ANALYSIS

Virtual instrumentation based Labview software has been used for interfacing the Electronic tongue with the computing. In the process of testing, [182 x 1] data points are generated for each working electrode. For whole set of working electrodes, the data matrix of size [182 x 5] is generated and stored in the computer with sample information provided at the time of testing. Data processing consisted of noise reduction, recognition and classification. Noise reduction was performed using wavelets [11-12]. Recognition was performed mainly by principal component analysis (PCA) and classification by calculating the standard deviations and Mahalanobis distance of the data set.

4.1 Data De-noising

In many applications, the signal of interest is corrupted by a large amount of additive noise, which makes it necessary some sort of signal pre-processing [13]. Noise reduction or de-noising is the process of removing noise from a signal. Noise reduction techniques are conceptually very similar regardless of the signal being processed, however a priori knowledge of the characteristics of an expected signal can mean the implementations of these techniques vary greatly depending on the type of signal. All recording devices, either analog or digital, have traits, which make them susceptible to noise. The underlying model for the noisy signal is basically of the following form:

$$s(n) = f(n) + \sigma e(n)$$

Where time n is equally spaced. In the simplest model, suppose that $e(n)$ is a Gaussian white noise N (0,1) and the noise level σ is supposed to be equal to 1. The de-noising objective is to suppress the noise part of the signal s and to recover f .

For noise reduction, in build Matlab function 'wden' [14] has been used which performs an automatic de-noising process of a 1-D signal using wavelets. De-noised version of input signal is obtained by suitably choosing the thresholding in the wavelet coefficients.

4.2 Principal Component Analysis

Principal Component Analysis involves a mathematical procedure that transforms a number of possibly correlated variables into a smaller number of uncorrelated variables called principal components [15]. PCA is mathematically defined as an orthogonal linear transformation that transforms the data to a new coordinate system such that the greatest variance by any projection of the data comes to lie on the first coordinate (called the first principal component), the second greatest variance on the second coordinate, and so on. PCA is theoretically the optimum transform for given data in least square terms. For a data matrix, X^T , with zero empirical mean, where each row represents a different repetition of the experiment, and each column gives the results from a particular probe, the PCA transformation is given by $Y^T = X^T W = V \sum^T$ where the matrix Σ is an m-by-n diagonal matrix with nonnegative real numbers on the diagonal and $W \sum V^T$ is the singular value decomposition of X.

The data collected through multi-electrode array has been subjected to PCA. The PCA algorithm has been implemented using Matlab function and has shown in figure 3. PCA clustering shows that samples belonging to a particular taste are clustering in a well-defined manner, indicating the possibility of identification of different basic taste parameters and mixed taste by electronic tongue consisting of metal based electrode array.

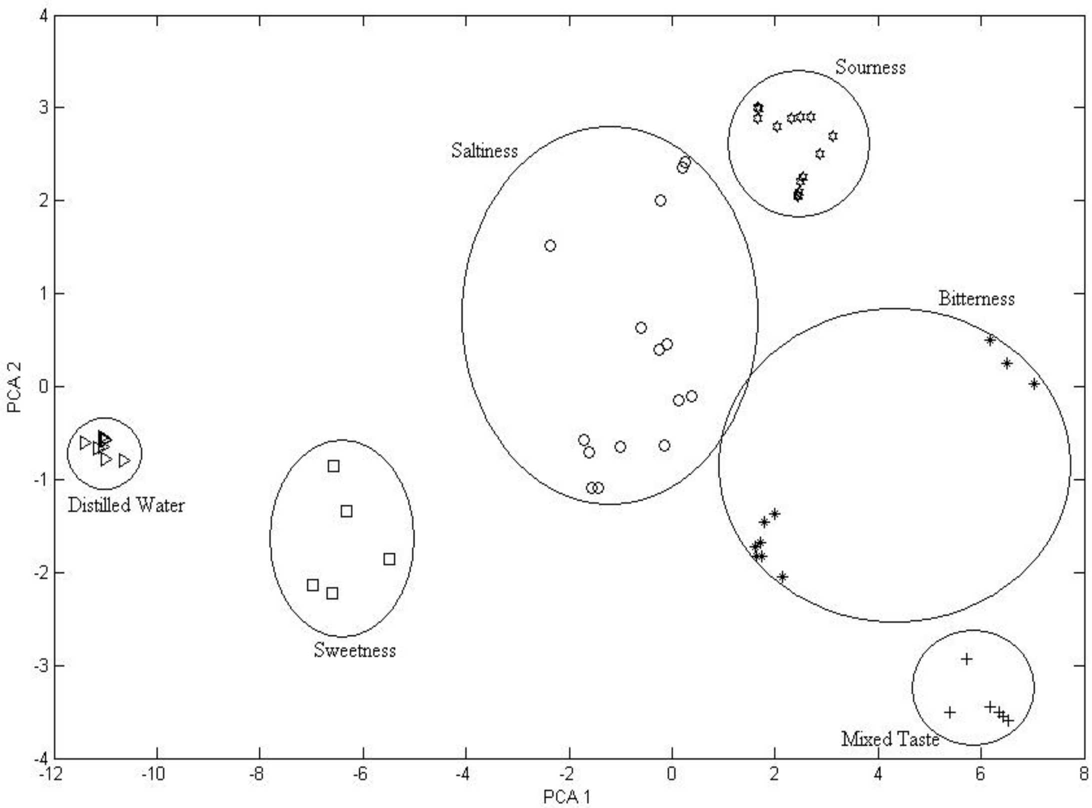

Figure 3. PCA plot of basic tastes, mixed taste and distilled water

4.3 Data Analysis using Statistical Method

4.3.1 Data Analysis using Standard Deviations

Exploratory data analysis has been performed using statistical method (Standard deviation, Mahalanobis distance calculations) on the data set. Standard deviation (denoted as σ) is a measure of the dispersion of a collection of values [16]. It is defined as the root-mean-square (RMS) deviation of the values from their mean. If the data points are x1, x2… xn, then its standard deviation σ can be calculated as

$$\sigma = \sqrt{\frac{1}{N}\sum_{i=1}^{n}\left(x_i - \bar{x}\right)^2}$$

Where $\bar{x}$ is mean of the points.

The variations of standard deviation values of collected signal for different basic tastes, mixed taste and solvent for sample preparation i.e., in this case distilled water are shown in table 2.

Table 2. Standard Deviation (SD) Values of different measured samples

Samples	Taste Attributes	SD Values
NaCl	Saltiness	1.3573
KCl	Saltiness	1.3970
H2SO4	Sourness	1.1291
Glacial acetic acid	Sourness	0.9658
Glucose	Sweetness	1.6976
Scurose	Sweetness	1.5532
MgCl2	Bitterness	1.2595
Picric acid	Bitterness	1.7904
NaCl, H2SO4, Glucose, MgCl2,	Mixed	2.0322
Distilled water	Neutral	0.7456

4.3.2 Data Analysis using Mahalanobis Distance

Many data processing and pattern recognition tasks involve calculating abstract "distances" between data. Euclidean distance calculation is one of these algorithms. But Euclidean distance has two basic drawbacks: first, the Euclidean distance is extremely sensitive to the scales of the variables involved and secondly, the Euclidean distance is blind to correlated variables. The Mahalanobis distance [17] takes into account the covariance among the variables in calculating distances. With this measure, the problems of scale and correlation inherent in the Euclidean distance are no longer an issue. The Mahalanobis distance of a multivariate vector $x = (x_1, x_2, x_3, \ldots, x_N)^T$ from a group of values with mean $\mu = (\mu_1, \mu_2, \mu_3, \ldots, \mu_N)^T$ and covariance matrix S is defined as:

$D_M(x) = \sqrt{(x-\mu)^T S^{-1} (x-\mu)}$ Mahalanobis distance of different taste attributes from neutral taste i.e., distilled water has been shown in the in table 3.

Table 3. Mahalanobis distance between different taste attributes and distilled water

Taste Attributes	Mahalanobis Distance
Saltiness	358.1
Sourness	2473.5
Sweetness	1246.9
Bitterness	552.2
Mixed	1757.0

In the present work, experiments have also done with the taste samples at different concentration. For each of the different taste attributes, samples of 0.25 M, 0.5 M, 0.75 M and 1 M concentration were prepared for the data analysis. Mahalanobis distance of each of the different taste attributes from the neutral taste i.e., distilled water have been presented in the table 4.

Table 4. Mahalanobis distance of basic taste attributes at different concentration

Taste Attributes	Concentration (M)	Distance
Saltiness	0.25	418.49
Saltiness	0.50	362.73
Saltiness	0.75	339.06
Saltiness	1.00	333.98
Sourness	0.25	2069.8
Sourness	0.50	2203.4
Sourness	0.75	2271.8
Sourness	1.00	2567.4
Sweetness	0.25	1290.6
Sweetness	0.50	1294.5
Sweetness	0.75	1130.3
Sweetness	1.00	1259.9
Bitterness	0.25	562.02
Bitterness	0.50	533.37
Bitterness	0.75	536.02
Bitterness	1.00	560.25

5. RESULTS AND DISCUSSIONS

In the present work, cyclic voltammetry (CV) has been used for applying voltages to the liquid samples. Cyclic voltammetry is most commonly used electrochemical techniques, and it is based on a linear potential waveform i.e., the potential is changed as a linear function of time. In this case, the voltage is swept between two values at a fixed rate, however now when the voltage reaches V2 (in figure 4) the scan is reversed and the voltage is swept back to V1

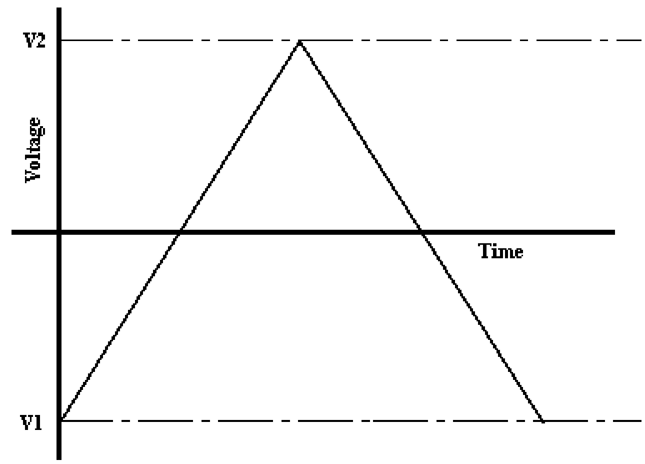

Figure 4. Type of signal applied in the samples

Cyclic voltammetry is important in investigating the kinetics and mechanisms of redox reactions. In this process, the potential applied to an electrode, designated as the working electrode, is scanned in a linear fashion between two potential values. The working electrode serves as the surface where the electron transfer of the redox reaction occurs. The redox reaction occurs within the potential range defined by the two chosen potential values, and the potential at which the reduction or oxidation takes place provides qualitative information about the analyte of interest. The voltammograms of two different electrodes is shown in figure 5 and figure 6.

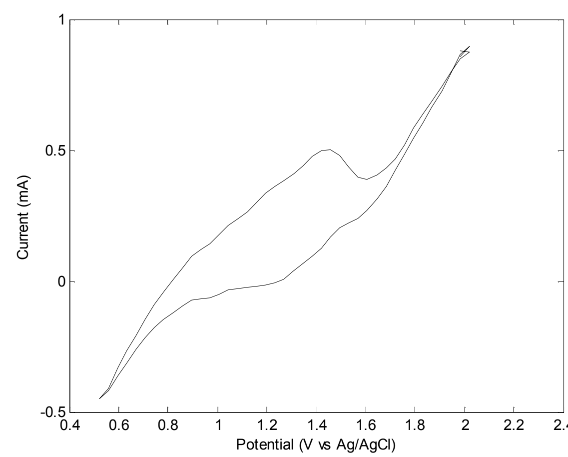

Figure 5. Voltammogram of Palladium electrode

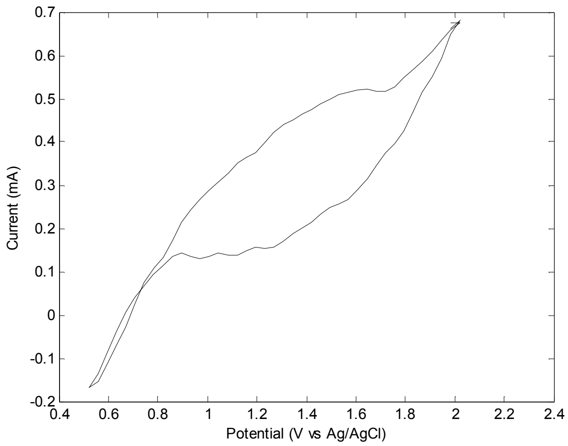

Figure 6. Voltammogram of Gold electrode

Experimentation with the Electronic tongue has been performed with samples of four different basic tastes parameter and sensors output signatures have been logged instantaneously in computer. We have analyzed the collected dataset and found that different signal pattern is obtained for different basic tastes. The PCA was performed on this set of data and the analysis shows that four different basic tastes and mixed taste are clustering at different points and the results are shown in figure 3.

We have analyzed the collected dataset using statistical method and the results are shown in table 2, table 3 and table 4. The sum of the standard deviation values of five different electrodes is shown for four basic taste parameters, mixed taste and distilled water. From the result it is clear that different chemical compound have different standard deviation values whereas different chemical compounds comprising of same basic taste have standard deviations very close to each other. Though the values of standard deviations in case of bitterness (for MgCl2 and Picric acid) have large difference, these values are not overlapping with other basic taste parameters and different chemical compounds can be distinguish using the standard deviations values of collected data through Electronic tongue. Table 3 shows the Mahalanobis distance between distilled water (here solvent) and different basic taste attributes. From the table 3 it is clear that Mahalanobis distance between different taste attributes have clear difference that can enable to identified different taste attributes very easily. Table 4 shows the Mahalanobis distance between neutral tastes and basic taste attributes at different concentration. The experimental results shows in case of saltiness, Mahalanobis distance decrease with increase of the saltiness concentration and in case of sourness, Mahalanobis distances increases with the increase of sourness concentration. For sweetness, Mahalanobis is minimum at concentration 0.7 M and 0.8 M and for bitterness, Mahalanobis distances is minimum at concentration 0.5 M to 0.75 M but the ranges of Mahalanobis distances are different for each of the basic taste parameters.

In this work virtual instrument based programmable, portable, and low cost Electronic tongue for classification of different basic taste parameters has been described. This study establishes the feasibility of the application of the electronic tongue, consisting of metal electrode array, as a useful instrument for identification of taste of different samples.

6. CONCLUSION

In the present study, a voltammetric technique based Electronic tongue has been used for classification of basic taste parameters. The results obtained are quite encouraging and established that the electronic tongue consisting of metal based electrode array can be used for classification of different taste attributes. The electronic tongue system described here is fast, user friendly and independent of human variations. The sense of taste largely depends on subjective factors of human feelings; in this context developed electronic tongue system can be used for taste determination of different beverages in an objective manner.

7. ACKNOWLEDGEMENT

The authors are grateful to Mr. Jayanta Kumar Roy and Rabindranath Kanjilal of CDAC, Kolkata, India during the course of experiment. National Tea Research Foundation under Tea Board, Government of India, has sponsored this project.

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