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Electronic Tongue and Nose 3D Shape Receptors in the Eductor

Since 1985 the QQC has been sensing the 3D shape of items and using the SCIO Eductor to measure patient’s reactions to these patterns in the Xrroid.
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All Chemicals have Atoms with Electrons in their Outer Shell. Electrons Repel Each other and never touch. Chemicals + Atoms NEVER EVER TOUCH

All Chemical Reactions are a Result of Energetic, Electro-Magnetis-Static-Quantic Field Interactions

All Chemistry is Electro-Chemistry
All Living things emit and detect electro-magnetic-static fields. The shark has a powerful field detector over 5 million times stronger in detection than humans. The salt water greatly facilitates and amplifies the effect. The system in humans is quite subtle and is an unconscious system. To work the EPFX the signal of voltammetric stimuli has to be amplified ten to the sixth to produce the needed stimulation. This is the process of the Xrroid measure. A voltammetric field is applied to the body and the EPR reactivity index is measured and displayed.
Developmental origin of shark electroscopic organs

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SUMMARY. Vertebrates, having evolved electroscopic receptors that detect electric stimuli on the surface of the skin and transmit them stereotopically to the brain, in chondrichthyanous, the electroscopic system is composed of a cephalic network of ampullary organs, known as the ampullae of Lorenzini, that can detect extremely weak electric fields during hunting and navigation. Each ampullary organ consists of a gel-filled epithelium pit containing sensory hair cells and synaptic connections with primary afferent neurons at the base of the pit that facilitate detection of voltage gradients over large regions of the body. The developmental origin of electroreceptors and the mechanisms that determine their spatial arrangement in the vertebrate head are not well understood. We have analyzed electoreceptor development in the lesser spotted catshark (Scyliorhinus canicula) and show that Sox8 and HNK1, two markers of the neural crest lineage, selectively mark sensory cells in ampullary organs. This represents the first evidence that the neural crest gives rise to electroreceptors cells. We also show that pathfinding by cephalic mechanosensory and electroreceptors axons follows the expression pattern of EphA4, a well-known guidance cue for axon and neural crest cells in cephalochordates. Expression of EphA4, which encodes a ligand for EphA4, marks the positions at which ampullary placodes are initiated in the epithelium, and EphA4 is expressed in surrounding mesenchyme. These results suggest that Eph–Ephrin signaling may establish an early molecular map for neural crest migration, axon guidance, and placodal morphogenesis during development of the shark electroreceptive system.
QQC™ Electronic Trivector Tongue

The QQC Trivector Electronic Tongue Technology has been reviewed and published in PEER Reviewed Medical Journals and printed in Medical University Textbooks.

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FDA 510 (k) registration for the EPFX was obtained on October 13, 1989. The following is an excerpt from the original office 510(k) application:

"The EPFX measures the Electro-Physiologic Reactivity intensity of the patient to many QQC trivector voltammetry patterns. These are patterns of reactions to Sensations, Nasal, Allergies, Isodes, Nutritional, Herbs, Imponderable and Classic Homeopathics. The reaction patterns or profiles can relate disturbances of the patient. Therapies can then be arranged to develop harmonic reactions, desensitizations, biological resonance or rectification processes. All of these are applied and managed through biofeedback application. Biofeedback is the operation that allows for the cybernetic loop to of systemic feedback. The only indicated use of this device and all claims related to this device are under biofeedback. The loop of measured reaction and bio-varied resonance response allow for a true feedback for self corrective Electro-Physiological therapy. Hence it is called the Electro Physiological Feedback Xaroid."

**FDA Registration of EPFX**

**Electro-Physiological Reactivity = EPR**

The CE mark Class 2 registration includes **European Registration**

The following excerpt is from the medical claims part of the SCIO CE Mark:

"The SCIO is indicated for use as a Universal Electrophysiological Biofeedback System. The Universal Electrophysiological Biofeedback System is made up of the following Eight Universal Items which are functions of the SCIO:

1. Stress Reduction and Lifestyle Stressors Questionnaire;
2. Simple EEG [electroencephalography] biofeedback brain wave stress reduction;
3. Three-pole ECG [electrocardiography] simple heart awareness and biofeedback stress reduction;
4. EMG [electromyography] biofeedback for simple reeducation of muscles;
5. GSR [galvanic skin response] biofeedback and TVEP [Transcutaneous voltammetric evoked potential] biofeedback (electrophysiological reactivity);

Since GSR biofeedback requires a **microcurrent voltammetric** stimulation to measure GSR, then the microcurrent has the following secondary Therapeutic Functions which function as performed through the biofeedback loop:

6. Microcurrent Transcutaneous electro nerve stimulation (MENS) for pain reduction in the cybernetic biofeedback loop; Cranial Electro Stimulation (CES) for anxiety and addiction;
7. Trauma or wound healing in the biofeedback loop;
8. Global Voltammetric Charge Stability in the biofeedback loop;"
An Electronic Tongue Based on Voltammetry

- Fredrik Winquist
- Peter Wide
- Ingemar Lundström

Abstract

Presently, great interest is shown in the concept of an electronic nose. It consists of an array of gas sensors with different selectivity patterns, a signal collecting unit and pattern recognition software applied to a computer. Similar concepts, but for analysis in liquids have also been described, and since they are related to the tasting sense, the term ‘electronic tongue’ or ‘taste sensor’ was coined. This paper describes how various voltammetric techniques such as large and small amplitude pulse voltammetry can generate information when combined with a multivariate analysis method. A prototype of an electronic tongue was designed, based on the combination of voltammetry, using a double working electrode of gold and platinum, and principal component analysis. It is demonstrated how this electronic tongue is able to classify various samples such as fruit juices, still drinks and milk. It was also possible to follow aging processes of milk and orange juice when stored at room temperature.

Keywords--Voltammetry; Taste sensor; Electronic tongue
An electronic tongue based on voltammetry

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Abstract

Presently, great interest is shown in the concept of an electronic nose. It consists of an array of gas sensors with different selectivity patterns, a signal collecting unit and pattern recognition software applied to a computer. Similar concepts, but for analysis in liquids have also been described, and since they are related to the tasting sense, the term 'electronic tongue' or 'taste sensor' was coined. This paper describes how various voltammetric techniques such as large and small amplitude pulse voltammetry can generate information when combined with a multivariate analysis method. A prototype of an electronic tongue was designed, based on the combination of voltammetry, using a double working electrode of gold and platinum, and principal component analysis. It is demonstrated how this electronic tongue is able to classify various samples such as fruit juices, still drinks and milk. It was also possible to follow aging processes of milk and orange juice when stored at room temperature. © 1997 Elsevier Science B.V.

Keywords: Voltammetry; Taste sensor; Electronic tongue

1. Introduction

There is a growing interest for the concept of electronic noses [1,2]. An electronic nose consists of an array of gas sensors with different selectivity patterns, a signal collecting unit and pattern recognition software applied to a computer. The principle is that a large number of different compounds contribute to define a measured odour, the chemical sensor array of the electronic nose then provides an output pattern that represents a synthesis of all components. This pattern is given by the different selectivities of the various sensors.

The electronic nose is in a way similar to the human olfactory sense. In the former, the signal pattern from a sensor array is collected and handled by a computer, where a first pretreatment of data is carried out. This data is further processed by a pattern recognition routine. In the human olfactory sense, a signal pattern is generated from the receptor cells in the olfactory bulb. A first treatment of data is carried out by the mitral cells, and the pattern is further processed by the olfactory cortex for recognition and learning [3]. The basis of olfaction appears to be that although the selectivity of each receptor cell may be low, the combination of several selectivity classes has a very large information content.

Electronic noses have been established for qualitative analysis in various fields of analytical chemistry,
and there are already commercial instruments on the market [4–6]. Recently, similar concepts, but for analysis in liquids have been described. These systems are in similar ways related to the sense of taste, thus for these concepts the terms ‘electronic tongue’ or ‘taste sensor’ have been coined [7,8]. An electronic tongue was thus described based on a number of chalcogenide glass electrodes, combined with a pattern recognition routine for measurements of metal ions in river water [7]. A more complex sensor composition consisting of glass electrodes and poly(vinyl chloride) membranes for analysis of beverages was also described [9].

Other concepts of ‘taste sensors’ have also been described. Thus, a light addressable potentiometric sensor (LAPS) with artificial lipid membranes as ion selective materials has been described [10], as well as taste systems, based on a fibre optic sensor array using potential sensitive dyes [11] or on the surface photovoltage technique applied to Langmuir–Blodgett films [12].

A taste sensor based on lipid/polymer membranes on a multichannel electrode was also developed [8]. This concept has been commercialized [13] and has proven useful for various applications [14].

A common feature of these electronic tongues is the matching principle is based solely on potentiometry, the charging of a membrane being measured. This will limit the range of detectable compounds to charged species. Furthermore, potentiometric measurements are more sensitive to electronic noise, putting high demands on the electronics and measurement set-up.

There are, however, other measurement principles that can be used for an electronic tongue, such as conductometry, spectrophotometry, and voltammetry. Among these, voltammetry 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. Besides, voltammetry offers a wide range of different analytical possibilities, including cyclic, stripping and pulse voltammetry. Depending on the technique, various kinds or aspects of information can be obtained from the measured solutions. Normally, redox active species are being measured at a fixed potential, but by using e.g. pulse voltammetry, studies of transient responses when Helmholtz layers are formed, also give information concerning diffusion coefficients of charged species. Further information is also obtainable by using different type of metals for the working electrode or utilising stripping techniques. To summarize, a number of possibilities is available for obtaining information using voltammetry:

- Choice of potential applied (size, sweep rates, pulses etc.)
- Type of working electrode
- Stripping techniques

When using voltammetry in complex media consisting of several redox-active compounds and various ions, the selectivity of the system is often insufficient for specific analysis of single components, because the steps in the voltammogram are too close to be individually discriminated. Thus, rather complicated ‘spectra’ are obtained and the interpretation of data may be difficult due to their complexity. Still, the voltammograms contain a large amount of information and to extract this, multivariate analysis methods have found increasing interest and use in the field [15–18]. Examples include analysis of mixture of colorants [19], nitrofurans derivates [20] and metal ions [16,17].

To provide for additional information concerning the measured solution, arrays of different types of electrodes have also been used [18]. This concept was further developed into arrays consisting of microelectrodes of different kinds of metals or operated at different potentials [21,22]. The data obtained were treated with pattern recognition routines such as principal component analysis (PCA) and artificial neural nets.

The basic principle behind an electronic tongue is to combine non-specific and overlapping signals with pattern recognition routines. This paper describes how various voltammetric techniques can be applied to generate information when combined with a multivariate method. Based on these investigations, a prototype of an electronic tongue was designed, based on the combination of pulse voltammetry using two types of working electrodes and PCA. It is demonstrated how this electronic tongue was able to classify various samples, such as fruit juices, still drinks and milk. It was also possible to follow aging processes of milk and orange juice when stored at room temperature.
2. Theory

2.1. Principal component analysis (PCA)

The use of signal processing methods has been vastly expanded during the last decade. This is due to rapid developments within computer technology, making it possible to treat vast amounts of data, and the development of various methods for multivariate data analysis or pattern recognition. Two main issues are dealt with using these techniques; one is to search for a structure and correlation in the data, the other is to make a model from a calibration set of data, which is used to predict test data. PCA is a mathematical transform which is used to explain variance in a data matrix [23]. The data matrix, \( X \), consists of a number of experiments, each consisting of a number of variables (values). A PCA constitutes a factorization of the data matrix \( X \) into a product of two abstract orthogonal matrices, denoted scores \( Q \) and loading \( P \), such that:

\[
X = QP^T,
\]

where \( P^T \) is the transposed loading matrix.

A vector is calculated which describes the direction of the largest variance, that is the direction that describes the largest differences between observations. This vector is called the first principal component. The second principal component is orthogonal to and thus independent of the first principal component. Further principal components can be calculated in a similar way, until most of the observations are explained. A new matrix, as defined by the principal components, is then formed, and the data set is considerably reduced, depending on the significance of the different principal components, but in many cases only to two dimensions. The principal components define a hyper plane which maximizes the variation in the original observations. Thus, PCA decomposes a data matrix into latent variables which successively account for as much variance as possible within the constraint of orthogonal score and loading vectors. The loading vectors describe the direction of the principal components in relation to the original variables, and the score vectors describe the direction of the principal components in relation to the observations. Thus, corresponding to the loading vectors a loading plot can be made, showing the relationships between the original variables and how much they influence the system. A corresponding score plot shows the relation between the observations or experiments, and groupings of observations in the score plot can be used for classifications. The major advantage of the technique is that no prior knowledge about samples or variables is required and that the data structure is represented by as few variables as possible. A drawback is the difficulty of giving meaning to the components extracted.

The interpretation of voltammetric data is often very cumbersome, especially for measurement in complex, multicomponent media. Often the responses obtained are complex and nonlinear due to the many different processes that may occur on the surface of the electrode. Still, the signal generated does contain information, which can be extracted by multivariate methods such as PCA. In the investigations described in this paper, the data generated have been treated by PCA.

2.2. Pulse voltammetry

Among the various techniques applicable in voltammetry, pulse voltammetry is of special interest due to advantage of greater sensitivity and resolution. In this investigation, two types of pulse voltammetry have been used, based on large amplitude pulse voltammetry and small amplitude pulse voltammetry, abbreviated as LAPV and SAPV, respectively.

In LAPV, the electrode is held at a base potential, at which negligible electrode reactions occur. After a fixed waiting period, the potential is stepped to a final potential. A current then flows to electrode, initially sharp when a Helmholtz double layer of charged species is formed and electroactive compounds next to the electrode surface are oxidized or reduced. The current decays exponentially as the double layer capacitance is charged and electroactive compounds are consumed, until the diffusion limited Faradaic current remains. The size and shape of the transient response reflects the concentration and diffusion coefficients of electroactive and charged compounds in the solution. When the electrode potential is stepped back to its start value, similar but opposite reactions occur. The excitation waveform consists of successive pulses of gradually changing amplitude between which the base potential is applied. The current response may be
measured during the forward step, or after return to the initial condition, or both.

The instantaneous Faradaic current at the electrode is related to surface concentrations and charge transfer rate constants, and exponentially to the difference of the electrode potential from the start value to the final potential.

In SAPV, a slow continuous DC scan is applied to the electrode on to which small amplitude voltage pulses are superimposed. This will cause a change in the concentration profile of the electroactive species at the surface. Since only small changes in the electrode potential are considered, this will result in small perturbations in the surface excitation. The current is sampled twice, once just before the application of the pulse, and one at the end of the pulse, and the difference between these is recorded as the output. The differential measurement gives a peaked output, rather than the usually obtained wavelike responses.

3. Experimental

3.1. Chemicals

The samples consisted of 6 different brands of orange juices, denoted OJA, OJB etc. to OJF, two types of orange still drinks, denoted OA and OB, apple juice AJ and pasteurized milk, M. The orange juice samples OJE and OJF had an extra high content of fruit fibres. The samples OJA, OJB and OJC were bought concentrated and diluted as recommended on the packages with distilled water. All samples were taken from newly opened packages. The buffers used were 0.1 M citrate at pH 5.0, 0.1 M phosphate at pH 7.0 and 0.1 M borate (as sodium salts), at pH 9.0. No extra pretreatment of the samples prior to analysis, such as de-aerating was performed.

3.2. Equipment

The experiments were carried out in a standard three electrode configuration, containing a double working electrode, an auxiliary electrode consisting of a 20×50 mm² plate of stainless steel, and Ag/AgCl 3 M KCl as reference electrode. The double working electrode consisted of one wire of platinum and the other of gold, both with a length of 5 mm and a diameter of 1 mm. The electrode configuration was placed in a 150 ml measurement cell, also containing a magnetic stirrer follower.

Current and current transient responses were measured by a potentiostat (Iskra, CHEMEL AB, Lund, Sweden) connected to a 286 processor-based PC via an A/D–D/A converter. The PC was used for onset of pulses and measurement of current transient responses and to store data. Via two relays, the PC was also used to change the type of working electrode (gold or platinum). A schematic diagram of the experimental set-up is shown in Fig. 1.

A software program was written for the measurement procedures. The PC used for data analysis was equipped with a Pentium 130 MHz processor.

3.3. Measurement procedure

The voltamograms recorded were based on LAPS and SAPV. Two measurement sequences were developed, the first of an exploration type, the second of an application type. In the exploration sequence, four separate voltamograms were recorded, a LAPS followed by a SAPV, applied consecutively to the two types of working electrodes. For the application sequence, all four voltammograms followed consecutively; also a smaller number of pulse were applied, resulting in faster measurements.

For both methods, a new measurement sequence was started by cleaning the working electrodes by rubbing them with a small test tube brush, followed by dipping in 1 M H₂SO₄ for 1 min, and rinsing in distilled water. They were placed in the measurement cell, and a 100 ml sample was placed in the cell. The magnetic stirrer was started. Before different measure-
mment series in a sequence, a special electrochemical clearing procedure of the working electrode was undertaken. Thus, a negative voltage of $-2.5\, \text{V}$ was applied to the electrode during 3 s, then a positive potential of $2.5\, \text{V}$ was applied for the same time, thereafter the voltage was set to $0\, \text{V}$ for 6 s before the start of measurements.

An electronic filter with a time constant of 0.1 s was applied to the potentiostat to smooth the time transient responses. All voltages referred to are vs. Ag/AgCl.

In general for LAFV, a measurement sequence started by applying a potential for 470 ms, then the voltage was set again to 0 V for the same time, whereafter the cycle started all over again. Between each cycle, the applied potential was decreased by a given value. Measurements values after the onset of a pulse at 100 ms and 430 ms, respectively, were collected as well as the measurement value obtained 100 ms after offset of the pulse making altogether 3 data points for each cycle. A typical recording is shown in Fig. 2 also showing the position of the measuring points. The pulse time and time between pulses are also indicated in the figure.

For SAPV, the potential was scanned from a start value to a final value and small voltage pulses were superimposed. Each cycle started by decreasing the potential with a step value for 180 ms, followed by increasing the potential with a superimposed value for 180 ms. Measuring points were collected 100 ms after onset of the step potential and 100 ms after offset of the superimposed potential. The difference between these two measurement points was also taken as a data point, making altogether 3 data points collected for each cycle. A typical recording is shown in Fig. 3 also showing the position of the measuring points. The pulse time and time between pulses are also shown in the figure.

For the exploration type of measurement, LAFV starts at $+900\, \text{mV}$ and stops at $-130\, \text{mV}$ divided into 71 steps. In each step, the voltage thus decreases by $14.5\, \text{mV}$. Altogether, 213 (71×3) values are collected. A measurement sequence takes 78 s.

SAPV starts at $+1300\, \text{mV}$ onto which 151 decreasing potential step values each of $12.6\, \text{mV}$ and a superimposed voltage step of 20 mV were applied. The voltammogram thus stops at $-600\, \text{mV}$. For these measurements, 453 (151×3) values were collected and a measurement sequence took 56 s. Before each sequence, an electrochemical cleaning step was performed.

The application type of measurement started using the gold working electrode with electrochemical cleaning followed by LAFV from $+900\, \text{mV}$ to $0\, \text{mV}$ divided in 20 steps, thus each step decreased by $45\, \text{mV}$. Thereafter, LAFV was applied between $+820\, \text{mV}$ and $-130\, \text{mV}$, with 32 voltage steps each of $30\, \text{mV}$, the superimposed voltage being 20 mV. For the first sequence, 60 (3×20) data points were collected. From the last sequence, only data for the first pulse and the pulse difference of each cycle were collected making altogether 64 (2×32) data points. After electrochemical cleaning, the working electrode was changed from gold to platinum, and the procedure repeated. For the complete measurement sequence, 248 measurement data were collected, which took 90 s to perform including the electrochemical cleaning steps.

### 3.4. Data analysis

Principal component analysis on the data obtained was performed with the program SIRIUS for Windows (Pattern Recognition Systems A/S, Norway).
4. Results and discussion

4.1. Exploration experiments

The initial experiments were performed to characterize the electrode system and to develop measurement procedures, useful for classifying various compounds or mixtures in solutions, the aim being to optimize the procedure in terms of speed and general classification capabilities. Experiments were carried out both in buffered solutions and in samples of a still orange drink. Three types of buffered solutions, applied to the two types of working electrodes, were investigated in duplicate, using the exploration type of LAPV and SAPV. Data from the platinum electrode were collected from buffered solutions of phosphate (denoted PdF), borate (PdB), citrate (PC) and from the orange drink (PO). Corresponding data for the gold working electrode are denoted Au2, AuB, AuC and AuO, respectively.

The data were collected in two matrices, one for the LAPV, measuring $16 \times 213$ data points and one for the SAPV, measuring $16 \times 453$ data points. These matrices were separately analyzed by PCA. The samples were standardized by dividing by the mean in each column prior to analysis. A score plot for the LAPV is shown in Fig. 4, where it can be seen that the various types of samples are clearly separated from each other. Data from the platinum electrode appeared to be more spread out than those from the gold electrode, thus indicating a larger classifying capability for the platinum electrode. It is also interesting to note that the orange drink samples is clearly separated from the other samples.

A loading plot for the data set is shown in Fig. 5. It indicates that all three types of measurement contribute information (data points 1–71 for the first series, 72–142 for the second and 143–243 for the last series).

A corresponding score plot for the SAPV is shown in Fig. 6, indicating similar features to those obtained with LAPV. The samples were normalized by dividing by the standard deviation in each column. Again in this plot, the data obtained from the platinum electrode are more spread out than those for the gold electrode, indicating better classification properties. The orange drink samples are not, however, as clearly separated as for the LAPV. In Fig. 7, the loading plot is shown, and for better clarity, only each fifth data point is shown. It can be seen from the Figure that the data series 1–151 and 152–303 are very close to each other, and thus contribute similar information. One of these series can thus be omitted in future analyses. As also can be seen,
4.2. Application experiments

From the above and other studies, the special application measurement sequence was designed. In this, LAPV is followed by SAPV consecutively for both types of working electrodes and altogether 248 measurement data are collected.

Recordings from 3 experiments performed on phosphate and borate buffer as well as on orange juice, are shown in Fig. 8. The differences in shapes and amplitude of the three voltammograms are clearly seen, also that the contribution of information apparently differs depending on the type of working electrode.

A ‘practical’ experimental series was performed; the samples investigated are shown in Table 1. The experiments were carried out consecutively, with a mechanical/chemical cleaning of the electrodes between each run, and one experiment took in the order of 5 min to perform. The whole experimental series took ca. 3.5 h and the samples were kept at room temperature during the experiment.

A PCA plot for the whole series of samples is shown in Fig. 9. The samples were normalized by dividing by the mean in each column. A clear separation between

| Table 1 |
| Sample investigated in a ‘practical’ experimental series |
| Sample number | Sample type | Sample number | Sample type | Sample number | Sample type |
| 1 | Ph1 | 16 | M4 | 31 | OC4 |
| 2 | Ph | 17 | M5 | 32 | OA3 |
| 3 | Ph3 | 18 | M6 | 33 | OA4 |
| 4 | Ph4 | 19 | OE1 | 34 | OB3 |
| 5 | Ph5 | 20 | OE2 | 35 | OB4 |
| 6 | OA1 | 21 | OE3 | 36 | SA1 |
| 7 | OA2 | 22 | OF1 | 37 | SA2 |
| 8 | OB1 | 23 | OF2 | 38 | SA3 |
| 9 | OB2 | 24 | OF3 | 39 | SB1 |
| 10 | OC1 | 25 | OD1 | 40 | SB2 |
| 11 | OC2 | 26 | OD2 | 41 | SB3 |
| 12 | OC3 | 27 | OD3 | 42 | |
| 13 | M1 | 28 | A1 | 43 | |
| 14 | M2 | 29 | A2 | 44 | |
| 15 | M3 | 30 | A3 | 45 | |

The experimental series carried out consecutively. The samples are:
Phosphate buffer at pH 7.0: Ph
Orange juice: OA, OB, OC, OD, OE, OF
Milk: M
Apple juice: A
Orange still drink: SA, SB
Fig. 8. Recordings from experiments carried out on various samples using the application measurement sequence. In this, LAPV followed by SAPV is carried out at the gold working electrode, thereafter the sequence is repeated at the platinum working electrode. The samples investigated were: a) Phosphate buffer; b) Citrate buffer; c) Milk.

Fig. 9. Score plot for the large experimental series. The samples were investigated after each other as shown in Table 1.

the various samples can be seen. Samples of still orange drinks (SA and SB) differ markedly from the orange juice samples, and appear to be more similar to the apple juice samples. Sample MI is apparently an outlier. The orange juice samples are more spread out than the rest of the samples. Especially spread out are samples OF and OE, containing a high degree of fruit fibres; one reason may be that the fibres attach to the working electrodes, thereby altering their properties.

A linear loading plot from the experimental series is shown in Fig. 10. It can be seen that both working electrodes as well as SAPV and LAPV contribute information.

In another series of experiments, aging processes in milk and orange juice were investigated. A 100 ml sample was placed in the measurement cell, and the measurement procedure as previously described was performed each half hour. Measurements were performed at room temperature in an open measurement cell, so the sample thus was in contact with ambient air. Aging processes can be caused by oxidation processes, evaporation of volatile compounds and microbiological activity.

A PCA plot obtained from measurements of orange juice is shown in Fig. 11. As can be seen, the changes are largest in the beginning of the experiment, to become relatively small after ca. 8 h (after 16 measurement points). A corresponding PCA plot for the aging process in milk is shown in Fig. 12).
Fig. 10. Loading variables plot for the large experimental series.

Fig. 11. Aging process for orange juice as represented by a score plot. The time between each sample is 30 min.

Fig. 12. Aging process for milk as represented by a score plot. The time between each sample is 30 min.
It is difficult to estimate and explain these plots; one of the drawbacks of PCA is, as already stated, the difficulty of giving meaning to the principal components. Thus, when estimating these PCA plots, it is difficult fully to explain the relative distances between the points. It may be of some interest, though, to try to use PCA to give some meaning of how the processes proceed. For the orange juice, there are large changes in the beginning which may be due to initial evaporation processes of volatile compounds, followed by a slower oxidation process of e.g. ascorbic acid. These processes are mainly complete after 8 h. The aging of milk follows a different path, the difference being not so large in the beginning. After 9 h, the differences increase to reach a maximum between 17–19 h. This path might be explained by oxidation processes in the beginning followed by microbiological activity. It should also be emphasized that in the aging experiments, the electrodes are not mechanically cleaned between measurements sequences, thus phenomena such as protein adsorption on the electrodes also will influence the measurement results.

5. Conclusions

Several attempts are found in the literature regarding the concept of an electronic tongue [7–14]. In this paper, the concept of an electronic tongue based on voltammetry is presented which demonstrated its capabilities in being able to classify various fruit drinks and milk, and also to be able to follow some aging processes. This opens up future possible applications in e.g. the food industry.

The aim and purpose of the experiments described have not been to develop a complete analytical system, merely to investigate the possibilities of using pulse voltammetry combined with multivariate methods for classification purposes. The strategy has been to use PCA to extract information from the rather complicated voltammograms obtained.

A natural development of the concept is also to use other metals such as palladium, rhodium and iridium, as working electrodes. The system should also be miniaturized due to advantages such as favourable steady state diffusion profiles and ability to work in resistive media.

Acknowledgements

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References


"Oh My God You're Right, there are No Rods and Balls"

Electronic tongue: An analytical gustatory tool

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Abstract

Taste is an important organoleptic property governing acceptance of products for administration through mouth. But majority of drugs available are bitter in taste. For patient acceptability and compliance, bitter taste drugs are masked by adding several flavoring agents. Thus, taste assessment is one important quality control parameter for evaluating taste-masked formulations. The primary method for the taste measurement of drug substances and formulations is by human panelists. The use of sensory panelists is very difficult and problematic in industry and this is due to the potential toxicity of drugs and subjectivity of taste panelists, problems in recruiting taste panelists, motivation and panel maintenance are significantly difficult when working with unpleasant products. Furthermore, Food and Drug Administration (FDA)-unapproved molecules cannot be tested. Therefore, analytical taste-sensing multichannel sensory system called as electronic tongue (e-tongue or artificial tongue) which can assess taste have been replacing the sensory panelists. Thus, e-tongue includes benefits like reducing reliance on human panel. The present review focuses on the electrochemical concepts in instrumentation, performance qualification of E-tongue, and applications in various fields.

Keywords: Electrochemical concepts, electronic tongue, taste, taste masking

Introduction

Taste-sensing system is analytical sensory array units which can detect specific substances by means of different artificial membranes and electrochemical techniques.

There are various synonyms for these sensory array systems as taste sensors, taste chips, taste sensing system, electronic sensory array system, biomimetic sensor array system, or electronic tongue. From analytical sense, they are composed of various sensors with unique properties and characteristics of partial selectivity or cross-selectivity. Their unique property is measurement and characterization of complex liquid matrices. Due to these features, they have been first used in area of food industry. Later, their use have been widely spread in monitoring environment, medical diagnostics, herbal products, detection of endotoxins and pesticides, etc. The rationale to use electronic tongues for pharmaceuticals is rather new, but not surprising, as taste plays an important role in the development of a pharmaceutical formulation.

Recent changes in European regulatory requirements initiated the development of medicines intended for children use and demand the development of age-appropriate formulations. As lot of APIs show unpleasant taste, taste
masking has become utmost importance. In order to understand concepts of electronic tongue, human tongue structure and mechanism are dealt here under.

**Human Tongue Structure**

The tongue is a muscular hydrostat on the floors of the mouth of most vertebrate which manipulates food for mastication. It is the primary organ of gustation, as much of the upper surface of the tongue is covered in papillae and taste buds [Figure 1]. In human beings, in addition to tasting, the other function of the tongue is phonetic articulation. The tongue also serves as natural means of cleaning teeth. On the surface of tongue is present pink tissue called mucosa. The function of mucosa is to keep the tongue moist. Tiny bumps called papillae gives rough structure. Several thousands of taste buds are present on the surfaces of the papillae. Taste buds are collection of nerve cells that connect to nerves running into the brain. Different lipid molecules present in the taste buds of tongue plays a key role in sensing taste of food materials. The most common four tastes are sweet, sour, bitter, and salty. A fifth taste, called umami, results from tasting glutamate (present in MSG). The tongue has many nerves that help detect and transmit taste signals to the brain. Because of this, all parts of the tongue can detect these four common tastes.

![Figure 1: Anatomy of tongue](image)

**Taste Mechanism**

Taste has been the Cinderella of the senses. The tasted substance, or tastant, is detected by receptors which are present on the apical surface of taste cells, which are in contact with the oral compartment. It shows G-protein-coupled receptor activation, which in turn leads to the activation of intracellular enzymes that generate secondary messengers, which in turn modulate a membrane ion channel, depolarizing the cell membrane potential causing an influx of calcium ions and release of calcium ions from intracellular stores resulting in release of neurotransmitter molecules, which activate the post-synaptic sensory neurons. This is transduction mechanism. Another mechanism, which was recently revealed, was the involvement of transducin-like G protein. In addition to the above proteins, there exist another protein called as alpha-gustducin, which is specific for taste cells of the tongue and some chemoreceptor cells of intestine. Studies conducted on mouse taste cells revealed that cAMP being the secondary messenger transducing the sweet taste of sucrose. In frog preparations, cAMP was found to inactivate a K⁺ ion conductance, acting through the cAMP-regulated protein kinase A, and thereby to cause membrane depolarization. Astringent taste is generally exhibited by tannic acid and aluminium salts shows inhibition of Na⁺ influx transport across isolated epithelium.
How Taste Buds Works

The taste buds are chemoreceptors, they transduce, or translate, chemical signals in food into electrical signals in the body called as action potentials [Figure 2], travel to the brain through the nervous system, allowing sensation of taste. The cranial nerves are responsible for carrying the action potential initiated in taste buds to the brain, where taste is ultimately registered.

![Figure 2: Anatomy of taste buds](image)

The same concepts of human taste mechanism has been applied to electronic tongue and designed.

Instrumentation
Electronic tongue or taste sensors \cite{1} is an instrument, trained for screening the taste attributes of formulations in a rapid timeframe, when used in addition with human taste assessment data. Sufficient aqueous solubility of test compounds is necessary for application of the electronic tongue. Co-solvents like ethanol can be used to increase solubility of test compounds and the use of instrument can be widened. These devices have a same structure of three principal components, sensory array, the equipment of emitting and receiving signals, and pattern recognition. In recent years, three types of devices called electronic tongue, or taste sensors, had been developed, based on potential, impedance spectroscopy, and voltammetry. The gustatory sensors based on potential was first presented by Iiyama \textit{et al.} \cite{11} It is composed of several kinds of lipids/polyvinylchloride(PVC) membranes for transforming the taste quality information like saltiness, bitterness, etc., into electrical signals. Another type of potential taste sensors was presented by Vlasov \textit{et al.}, \cite{12} which was designed by several non-specific sensors based on chalcogenide glasses as transducer. The second electronic tongue which is based on impedance spectroscopy was first described by Riul and coworkers, in which the sensors were built by supramolecular thin films of conducting polymers with lipid-like material and were analyzed with impedance spectroscopy. The third kind being based on the principle of voltammetry was first designed by Winquist \textit{et al.} It consists of several metallic electrodes (platinum, gold, palladium, iridium, rhenium, and rhodium) which work as working electrode (Ag/AgCl reference electrode and stainless steel electrode as counter electrode for standard three-electrode systems).

**Basic Principle**

The main elements of an electronic taste-sensing system are number of different sensor types attached to arm, a sample table, an amplifier, and a computer for data recording. \textbf{Figure 3} gives a basic principle of electrochemical taste-sensing system. This system imitates what is happening when molecules with specific taste nature interact with taste buds on the human tongue. The taste buds are represented by sensors which interact with these molecules at the surface initiating changes in potential. These signals are compared with physiological action potentials which are recorded by computer, which correspond to the neural network at the physiological level. The data obtained can further be evaluated on the basis of already existing matrix of sensor responses which can be compared with human memory or association to already existing taste patterns. The most applied principle is potentiometry. Electrochemical concepts of Electronic tongue are dealt here under.

**Electrochemical Concepts**

The general concepts of electronic tongue used for analysis involves application of an array of nonspecific or low-selective sensors in order to produce signals during analysis of samples. The idea behind using low-selective sensors is based on analogy to biological organization of taste systems in mammals. In the region of tongue, there are several millions of nonspecific receptors that respond to different substances. The taste buds possess several dozens of receptors on the tongue of mammals. The taste signals from the receptors are transmitted to the brain and processed by network of neurons. So, the image of the sensed object is created.

The idea of reproducing artificially the human response to external stimuli was first published in 1943. \cite{13} Thus, this concept has been extended to build an "electronic brain" and artificial intelligence based on neural computing. The first analytical tool of these concepts was an "electronic nose" (1982) \cite{14} used for analysis of gases. "Electronic

In literature, electronic tongue is defined as “The electronic tongue is an analytical instrument comprising of an array of nonspecific, low-selective, chemical sensors with high stability and cross-sensitivity to different species in solution, and an appropriate method of pattern recognition (PARC) and/or multivariate calibration for data processing.” [16]

**Sensing Materials for Sensor Arrays**

Based on the principle involved used, the sensing material for sensor arrays varies. [17] If the principle involved is potentiometry, then the materials used are Chalcogenide and oxide glasses, [16],[18] noble metals for amperometric signal detection. [19] Sensing materials based on plasticized organic polymers have been applied for potentiometry [17],[18] and optical sensors. [20] The selectivity and detection limits of a sensor array depend on composition and properties of the sensing materials. [21] The number of sensors in the array may range from 4 to 40. [20] Potentiometric sensors are the most widespread type of sensors used in electronic tongues system.

Selectivity of potentiometric sensors, such as ion-selective electrodes (ISE), defined by selectivity coefficient, \( K_{ij} \), and primary ion, \( i \), against the interfering ion, \( j \), in the Nikolsky-Eisenman equation,

\[
E = E^0 + \frac{RT}{Z_i F} \ln \left[ a_i + \sum_j K_{ij} a_j^{Z_j/Z_i} \right]
\]

Where, \( a_i \) and \( a_j \) are activity of the primary ion and interfering ion, respectively; \( K_{ij} \) is the selectivity coefficient; \( E^0 \) is the sum of the standard potential of the electrode and the junction potential; \( E \) is the potential difference for the electrochemical cell composed of the ion selective and reference electrode; \( Z_i \) and \( Z_j \) are charge numbers of the primary and interfering ion, respectively. A number of conventional ISEs, e.g., pH glass electrode, sodium and chloride-selective electrodes can also be included in the system. Potentiometric measurements must be carried out by using a multichannel voltmeter with high-input impedance. Values of the sensor potential should be measured against a conventional Ag/AgCl reference electrode and stored as computer data files.

Mathematical signal processing procedures like pattern recognition (PARC) and multivariate calibration (artificial neural network), principle component analysis, and self-organizing map techniques are used to analyze the response of the sensor array because output of the sensor array in a multispecies solution is complex and cannot be described by using theoretical equations (The Nernst or Nikolsky-Eisenman equation).

The most novel electrochemical techniques for electronic tongue developed was multifrequency large amplitude pulse voltammetry. It is designed by several large amplitude pulse voltammetry with deferent step lengths. [22]

**Potentiometric Concepts with Lipids as Transducers**

In general, lipids are the most important material for transforming chemical information into electrical signals. [23],[24],[25],[26] Taste substances are effective on membrane potentials because of their electric charges. Hence, multichannel taste sensors using 8 lipid membranes have been developed. Here, lipid membranes act as transducers of taste information and a computer as a data analyzer. It has sensitivity, durability, and superior to human tongue. [27],[28],[29],[30] Here, lipid membrane is prepared by mixing lipid with PVC, Dioctylphenyl phosphate (plasticizer). This mixture is dissolved in tetrahydrofuran and mixture is transferred to Petri dish and stored at 300°C for 24 hours. This membrane possesses electric charge due to lipids. This acts as working electrodes. The reference
The electrode is made with Ag wire whose surface is plated with Ag/AgCl with an internal cavity filled with 3MKCl solution and opening tube filled with 100 mM KCl and agar.

Eight kinds of lipid membranes were studded on the multichannel electrode as shown in Figure 4. The system contains Ag/AgCl electrode in 100 mM KCl solution/lipid membrane/reference electrode in taste solution. Taste substance change the membrane potential, and then the electric signal from each membrane is converted to digital code by a digital voltmeter through a high-input-impedance-amplifier and an eight-channel scanner, and finally recorded in a computer. The sensor output comprises of eight electric potentials from eight kinds of lipid membranes.

![Figure 4: Experimental setup of potentiometric multichannel taste sensor system](image)

Various lipids which are used as multichannel transducers are as follows:

Toko et al. prepared taste-sensing membranes by adding lipids with silicone rubbers. Lipids which are used are dioctyl phosphate, trioctyl phosphate, and methyl ammonium chloride and molar mixture of dioctyl phosphate and trioctyl methyl ammonium chloride. Riul Jr. et al. designed an electronic tongue composed of polyaniline oligomers (16-mer) and polypyrrole (Ppy), which were able to distinguish salt, sweet, bitter, acidic solutions, different brands of mineral water, tea, and coffee, proving that conducting polymers are useful sensing materials.

Hayashi et al. examined lipid and ion exchange cellulose as transducer materials of a taste sensor.

**Performance Qualification of SA402B Taste-Sensing System**

Performance qualification of taste-sensing system SA402B (Insent Inc., Atsugi-chi, Japan) equipped with seven lipid membrane sensors for bitter taste assessment. These sensors represent the gustatory stimuli bitterness, umami, saltiness, saltiness, sourness, and the nociceptive sensation astringency. Specificity, linearity, range, accuracy, precision, and detection were established for each sensor type referring to ICH guidelines Q2 (R1). Standard substance used is quinine hydrochloride, as it is the bitterest one with bitter value 200 000. Equipment qualification contains four basic elements: DQ, OQ, IQ, and PQ.

The underlying measurement principle is potentiometric and sensor response are recorded as mV values. According to Nernst equation, the electrode potential depends on activity of the substance.

\[
U = U^0 + \frac{RT}{zF} \ln a_i
\]

Where, \(U\) is electrode potential; \(U^0\) is standard electrode potential; \(R\) is universal gas constant; \(T\) is temperature (K); \(Z\) is ionic valence of the substance; \(F\) is Faraday constant; and \(a_i\) is activity of the substance.
\[ a_i = f_i c_i \]

Where, \( c_i \) is the concentration of the substance; \( f_i \) is the activity coefficient of the substances.

Sensor check is done routinely before every measurement to ensure that sensors are working in the correct mV range. Each sample was measured four times; one measurement cycle consisted of measuring the reference solution (\( V_r \)) for 30 seconds, then sample solution (\( V_s \)) for 30 seconds. The after taste was measured by determining change of membrane potential caused by adsorption of the substances to the lipid membrane after short cleaning procedure for 6 seconds, then washed with reference solution (\( V_{r'} \)) for 30 seconds and measured, followed by complete washing for 330 seconds.

Sensor output for taste, also called Relative value (R)

\[ R = V_s - V_r \]

Sensor output aftertaste, also called CPA value (change of membrane potential caused by adsorption)

\[ CPA = V_{r'} - V_r \]

The whole procedure is done for all samples for four times [Figure 5].

**Applications of Electronic Tongue**

E-tongue is specially designed for taste analysis in R and D, formulation, food product Development, and food process improvement applications. It has got several applications in various industrial areas: The pharmaceutical
industry, food and beverage sector, etc. It can be used to:

- Analyze human urine for the detection of urinary system dysfunction and creatinine levels. [37]
- Evaluate Italian wine for taste and flavor. [38]
- Detect alcohols in beverages by using porphyrin-based potentiometric electronic tongue. [39]
- Analyze flavor ageing in beverages (for instant fruit juice, alcoholic or non-alcoholic drinks, flavoured milk).
- Quantify bitterness or spicy levels of drinks or dissolved compounds.
- Quantify taste-masking efficiency of pharmaceuticals (tablets, syrups, powders, capsules, etc.).
- Analyze stability of medicines regarding taste.
- Benchmark the target products.
- Differentiate the different kinds of mineral water based on hardness of water. [40]
- Differentiate varieties of tomato by measuring crushed tomatoes. [41]
- Discriminate fresh from spoiled milk. [42]
- Differentiate different brands of coffee of different origin. [43]
- Monitor agriculture and industrial pollution of air and water.
- Identify toxic substances.
- Search for drugs, explosive.
- Searching for chemical/biological weapon.
- Identify unpleasant taste of pharmaceuticals.
- Quantify taste and foodstuff recognition.
- Monitor Herbal medicine.
- Monitor environment with respect to water, metal ions, endotoxins, pesticides.
- Characterize APIs like Caffeine, Paracetamol, phenylthiourea, Quinine hydrochloride, etc.
- Characterize amino acids like L-isoleucine, L-leucine, and L-phenylalanine. [44]
- Evaluate coated microparticles of Ibuprofen and roxithromycin. [45]
- Study sweet taste evaluation with lipid/polymer membrane. [46]
- Measure solid food. [47]
- Detect trace amounts of organic substances. [48]
- Evaluate taste of crude drugs and Kampo Formula. [49]

**Conclusion**

Electronic tongues are emerging and promising fields in recent chemical sensor science. It has a concept of global selectivity. It is a valuable tool for assessment and prediction of the taste of pharmaceuticals and related products. It replaces human panels in routine analysis in pharmaceutical development and production. The exposure and risk of using human panel to test products is greatly reduced, permitting better analytical results to quickly define the best formulation and get the product to market.

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Electroanalysis

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**Keywords:**
- Electronic tongue;
- Nonspecific chemical sensors;
- Food analysis;
- Pattern recognition

**Abstract**

An electronic tongue comprising 29 potentiometric chemical sensors and pattern recognition tools for the data processing has been applied for the analysis of Italian produced mineral waters and dry red wines. The electronic tongue appeared to be capable to distinguish between different sorts of mineral waters, between contaminated by organic matter waters and pure ones and between Barbera wine samples of the same denomination but from different vineyards. Simultaneously with qualitative recognition, quantitative determination of some components in the water and the wine has been performed. The electronic tongue can be highly valuable in food quality control.

**A hybrid electronic tongue**
Abstract

A hybrid electronic tongue is described based on a combination of potentiometry, voltammetry and conductivity. It was used for classification of six different types of fermented milk. Using ion-selective electrodes, pH, carbon dioxide and chloride ion concentrations were measured. The voltammetric electronic tongue consisted of six working electrodes of different metals (gold, iridium, palladium, platinum, rhenium and rhodium) and an Ag/AgCl reference electrode. The measurement principle is based on pulse voltammetry in which current transients are measured due to the onset of voltage pulses at decreasing potentials. The data obtained from the measurements were treated by multivariate data processing based on principal components analysis and an artificial neural net. The hybrid tongue could separate all six samples. Also, the nature of the micro-organisms in the different fermentations was reflected in the principal component analysis.

Keywords

- Electronic tongue;
- Taste sensor;
- Pulsed voltammetry;
- Fermented milk;
- Pattern recognition;
- Principal components analysis
«Electronic tongue» — new analytical tool for liquid analysis on the basis of non-specific sensors and methods of pattern recognition

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- A.V Legin
- A.M Rudnitskaya
- A D'Amico
- C Di Natale

Abstract

Development of promising sensor instrument — “electronic tongue” based on sensor arrays with data processing by pattern recognition methods have been described. The attention is paid to “electronic tongue” based on an array of original non-specific (non-selective) potentiometric chemical sensors with chalcogenide glass membranes. Principles of research, criteria for the development of non-selective sensing materials, pattern recognition methods have been described. Possible applications and some results of integral qualitative analysis of beverages and of quantitative analysis of complex liquids, containing heavy metals are reported. Discriminating power obtained and possibility of multicomponent analysis permit to consider “electronic tongue” as a perspective analytical concept.

Keywords
- Electronic tongue;
- Liquid analysis;
- Pattern recognition

The combination of an electronic tongue and an electronic nose
Abstract

The combination of an electronic tongue and an electronic nose for classification is described. The 'electronic nose' consists of an array of gas sensors with different selectivity patterns, signal handling and a sensor signal pattern recognition and decision strategy. The 'electronic tongue', which was developed for the taste analysis of liquids is based on pulsed voltammetry. Measurement data from the artificial smell and taste sensors are used to produce sensor-specific opinions about these two human-like sensing modalities. Using principal component analysis, it is shown that both the electronic nose and the electronic tongue alone are able to discriminate reasonably between experimental samples. When combining information from both the electronic nose and the electronic tongue, however, the classification properties are clearly improved.

Keywords

- Electronic tongue;
- Electronic nose;
- Sensors

Multicomponent analysis of Korean green tea by means of disposable all-solid-state potentiometric electronic tongue microsystem

- Larisa Lvova;
- Andrey Legin;
- Yuri Vlasov;
- Geun Sig Cha;
- Hakhyun Nam

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Abstract

All-solid-state ‘electronic tongue’ microsystem comprised of polymeric sensors of different types such as highly cross-sensitive sensors based both on PVC and aromatic polyurethane (ArPU) matrices doped with various membrane active components, electrochemically deposited conductive films of polypyrrole (PPy) and polyaniline (PAn) and potentiometric glucose biosensors has been developed and applied for the analysis of beverages: natural coffee, black tea and different sorts of green teas. The system can discriminate different kinds of teas (black and green) and natural coffees. Components that are responsible for giving unique taste such as caffeine, catechines, sugar, amino acid L-arginine have been determined for green tea samples with unknown manufacturer specifications.

Keywords

- All-solid-state potentiometric ‘electronic tongue’;
- Cross-sensitive potentiometric sensors;
- Potentiometric glucose biosensor;
- Taste of green tea

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Larisa Lvova received her MSc degree (1996) and her PhD (1999) in physical chemistry from St. Petersburg State University. Her PhD work was concerned with the development and investigation of film sensing materials and application of them for multicomponent qualitative and quantitative analysis of complex liquid media, elaboration of the sensors arrays and multisensor systems, an electronic tongue in particular. She continued her research in area of chemical sensors development as postdoc fellow in the Chemical Sensors Research Group in the Chemistry Department of Kwangwoon University, Seoul, South Korea. At present, Larisa Lvova is a junior scientist in the laboratory of Soil Biochemistry in Biology Research Institute of St. Petersburg University. Her current research interest involves the development of
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Andrey Legin graduated from Leningrad University (Chemistry Department) in 1981. After a 4-year work as a post-graduate student he received his PhD in Chemistry from Leningrad University in 1985 for the thesis devoted to chemical sensors on the basis of chalcogenide glasses. Since 1985, he has been working as a research scientist at the Research Institute of Chemistry of St. Petersburg University and at present time he is senior research scientist/associate professor. His current research interest involves the investigation of new sensing material synthesis, their transport properties, surface and interfaces investigation, electrochemical and sensing mechanism studies. Special attention is paid for analytical application of chemical sensors such as development of principals of sensor application, the development of analytical procedures, implementation of the sensors into industrial process control systems, application of the sensors for environmental monitoring, development and application of multisensor systems (‘electronic tongue’). Dr. Legin has authored about 180 scientific papers and took part as a speaker in a number of international conferences devoted to sensor science and analytical problems.

Yuri Vlasov received his MSc degree in chemistry from Leningrad (now St. Petersburg) University in 1957. He received his PhD degree in 1964 and the Doctor of Science degree in chemistry in 1986. From 1959 to 1974, he worked in Leningrad University as a teacher, research scientist and dean assistant. From 1974 to 1990, he was the Director of the Research Institute of Chemistry at Leningrad University and concurrently the Head of the Laboratory of Ion-selective Electrodes and Solid Electrolytes. Since 1988, Professor Vlasov has been the Head of the Laboratory of Chemical Sensors and the Head of the Radiochemistry Department. Professor Vlasov is the Professor of Chemistry, a full member of the Russian Academy of Natural Sciences, an active member of the New York Academy of Sciences, the Head of the Radiochemistry Department, and the Head of the Laboratory of Chemical Sensors. Professor Vlasov is a well-known scientist in the field of the development, fundamental study and analytical applications of chemical sensors including ion-selective field-effect transistors (ISFETs) and non-selective sensors (‘electronic tongue’). His research involves the study of the properties of membrane materials, the electrochemical behavior and analytical characteristics of chemical sensors, and the determination of the sensing mechanism of ion-selective electrodes of different types. Professor Vlasov is the author of more than 400 scientific papers.

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_Hakhyun Nam_ received his BS degree from Seoul National University in 1982 and PhD in Physical Chemistry from Michigan State University in 1989. He continued his postdoctoral work in laser spectroscopy at the University of California at Berkeley until 1992. He is now a Full Professor of Physical Chemistry at Kwangwoon University. His current research interests involve the development of various types of chemical sensors based on molecular recognition principles, electrochemical detection methods for microfluidic systems, and industrialization of chemical sensor systems.

**Multicomponent analysis on polluted waters by means of an electronic tongue**

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Abstract

In this paper the simultaneous measurements of the concentrations of a number of chemical species in solutions performed by a sensor array of ion sensitive electrodes are presented and discussed. By analogy with the well known electronic nose this sensor array operating in solutions, will be here called electronic tongue. In order to extract optimized information from the electronic tongue output data, many different techniques have been applied; they were based on chemometrics, non-linear least squares and neural networks. The best results have been achieved by the introduction of modular models which make use, at the same time, of both qualitative and quantitative information.

Keywords

- Electronic tongue;
- Multicomponent analysis;
- Chemometrics
Cross-sensitivity evaluation of chemical sensors for electronic tongue: determination of heavy metal ions

- Yuri Vlasov,
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- Alisa Rudnitskaya

Abstract

The development of the promising new field of sensor applications, multisensor arrays for liquid analysis based on the principles of the electronic tongue, implies some new demands on sensor material research and development. Stable and reproducible sensors with partial specificity and considerable cross-sensitivities to different components in solutions are of primary interest. Solid-state potentiometric sensors, both crystalline and vitreous, are likely to be the most promising ones for multisensor devices designed for long-term analytical application in natural and artificial complex media. The present paper deals with development of a method of evaluation of integral heavy metal cation sensitivity of solid-state sensors with special consideration of cross-sensitivity features. The method involves a comparative study of different sensor materials in individual component solutions, using several criteria based on integral response parameters. The procedure scheme can be applied to evaluate cross-sensitivity of any kind of potentiometric sensors for liquid media.

Keywords

- Cross-sensitivity;
- Liquid media chemical sensors;
- Multisensor arrays

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Measurement Science and Technology Volume 9 Number 12


Monitoring of freshness of milk by an electronic tongue on the basis of voltammetry

F Winquist†, C Krantz-Rücker†, P Wide‡ and I Lundström†

Abstract

We describe an electronic tongue which consists of a reference electrode, an auxiliary electrode and five wires of different metals (gold, iridium, palladium, platinum and rhodium) as working electrodes. The measurement principle is based on pulsed voltammetry, in which successive voltage pulses of gradually changing amplitudes are applied to the working electrodes connected in a standard three-electrode configuration. The five working electrodes were successively connected and corresponding current-response transients are recorded. The electronic tongue was used to follow the deterioration of the quality of milk due to microbial growth when milk is stored at room temperature. The data obtained were treated with principal component analysis and the deterioration process could clearly be followed in the diagrams. To make models for predictions, projections to latent structure and artificial neural networks
were used. When they had been trained, both models could satisfactorily predict the course of bacterial growth in the milk samples.

Multifrequency large amplitude pulse voltammetry: A novel electrochemical method for electronic tongue

- Shi-Yi Tian,
- Shao-Ping Deng, 
- Zhong-Xiu Chen

Abstract

A novel electrochemical method, multifrequency large amplitude pulse voltammetry (MLAPV) for electronic tongue was introduced in this paper. It was constructed by several large amplitude pulse voltammetry (LAPV) with deferent step length. The applied waveform of MLAPV comprises three individual frequency segments, 1 Hz, 10 Hz and 100 Hz. The electronic tongue based on MLAPV was constructed by several metallic working electrodes, such as platinum, gold, titanium, nickel, palladium, a Ag/AgCl reference electrode and a pillar platinum electrode as counter electrode for standard three-electrode systems. Principal component analysis (PCA), a kind of multivariate data analysis (MVDA) was used for processing the data from the electronic tongue. In the present study, six Chinese distilled spirits and seven Longjing teas were analyzed by the electronic tongue based on MLAPV and were successfully discriminated by the working electrodes at different frequency segments. The results showed that frequency segments on the working electrode played a key role in discriminating various samples. MLAPV made the same metallic working electrodes have different separation ability at each segments. Better discrimination ability can be achieved by the combination of working electrodes with specific frequency segments. The present work showed that MLAPV is a useful method to reveal the specific frequency segment for each working electrode in various analysis systems.

Keywords

- Multifrequency large amplitude pulse voltammetry;
- Electronic tongue;
- Chinese distilled spirits;
- Longjing tea
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Comparison of a voltammetric electronic tongue and a lipid membrane taste sensor

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- Yukiko Kikkawa
- Fredrik Winquist
- Christina Krantz-Rülcker
- Nils-Erik Höjer
- Keshi Hayashi
- Kioshi Toko
- Ingemar Lundström

Abstract

An electronic tongue based on voltammetry and a multichannel lipid membrane taste sensor based on potentiometry are compared using two aqueous examples: detergents and teas. The electronic tongue consists of four electrodes of different metals, a reference electrode and a counter electrode. The measurement principle is based on pulse voltammetry in which current is measured during the change of the amplitude of the applied potential. The taste sensor is based on eight different lipid/polymer membranes. The voltage difference between the electrodes and an Ag/AgCl reference electrode is measured when the current is close to zero. The responses from the two sensors systems are treated separately with multivariate data analysis based on principal component analysis and then merged to examine if further information could be extracted. It is shown that although the two sensor systems are
about equal in separation ability in the two cases, extra information can be gained by combination of the two sensor systems.

Keywords

- Electronic tongue;
- Taste sensor;
- Tea;
- Detergent

**Recognition of six microbial species with an electronic tongue**

- C. Söderström
- F. Winquist
- C. Krantz-Rülcker

**Abstract**

An electronic tongue based on pulsed voltammetry over an array of electrodes with different selectivity and sensitivity patterns was used to recognize six different microorganisms: one yeast, two bacteria, and three molds. Measurements were performed during the whole growth period, from the lag phase to the stationary phase. The electrode array was dipped into the malt extract growth medium and voltage was applied over the electrodes in pulses of different amplitude and the resulting current data was sampled and collected in a matrix. Evaluation of the electronic tongue data was made with principal component analysis (PCA) and soft independent modeling of class analogy (SIMCA). PCA was performed on data from the lag, the logarithmic, and also the stationary growth phase. In the lag growth phase no recognition of species was visible in the PCA score plots. After further growth however all the included microbial species could be recognized from each other. The ability to predict membership of new replicates of the species to the right classes was verified with SIMCA.

**Keywords**

- Electronic tongue;
- Recognition;
- Microorganisms;
- Voltammetry;
Compression of electronic tongue data based on voltammetry — a comparative study

- Susanne Holmin
- Per Spångeus
- Christina Krantz-Rülcker
- Fredrik Winquist

Abstract

In this paper, three data compression methods are investigated to determine their ability to reduce large data sets obtained by a voltammetric electronic tongue without loss of information, since compressed data sets will save data storage and computational time. The electronic tongue is based on a combination of non-specific sensors and pattern recognition tools, such as principal component analysis (PCA). A series of potential pulses of decreasing amplitude are applied to one working electrode at a time and resulting current transients are collected at each potential step. Voltammograms containing up to 8000 variables are subsequently obtained. The methods investigated are wavelet transformation (WT) and hierarchical principal component analysis (HPCA). Also, a new chemical/physical model based on voltammetric theory is developed in order to extract interesting features of the current transients, revealing different information about species in solutions. Two model experiments are performed, one containing solutions of different electroactive compounds and the other containing complex samples, such as juices from fruits and tomatoes. It is shown that WT and HPCA compress the data sets without loss of information, and the chemical/physical model improves the separations slightly. HPCA is able to compress the two data sets to the largest extent, from 8000 to 16 variables. When data sets are scaled to unit variance, the separation ability improves even further for HPCA and the chemical/physical model.

Keywords

- Chemical/physical model;
- Data compression;
- Electroactive compounds;
- Electronic tongue;
The electronic tongue and ATR–FTIR for rapid detection of sugars and acids in tomatoes

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Abstract

The electronic tongue and attenuated total reflectance–Fourier transform infrared spectroscopy (ATR–FTIR) have been evaluated as novel rapid techniques in taste research. The electronic tongue, consisting of 27 potentiometric sensors, and ATR–FTIR, a well-established spectroscopic technique, have been used to determine the sugar and acid profile of four tomato cultivars: Aranca, Climaks, Clotilde and DRW 73-29. The most abundant sugars (glucose, fructose and sucrose) and organic acids (citric acid, malic acid, tartaric acid, fumaric acid and succinic acid) in tomatoes were measured with HPLC as a traditional reference technique. The ability of the novel techniques to detect differences in sugar and acid profiles between these four tomato cultivars has been studied by means of unsupervised and supervised multivariate data analysis techniques such as principal components analysis (PCA) and canonical discriminant analysis (CDA). Canonical correlation analysis (CCA) was applied to compare the information content of the reference technique with that of the electronic tongue and ATR–FTIR. The potential of both the electronic tongue and ATR–FTIR to predict the chemical composition of a sample has been evaluated using partial least squares (PLS) models. Both the electronic tongue and ATR–FTIR have the potential to measure taste determining compounds. Tomato cultivars can be classified based on their sugar and acid profile. However, the prediction of individual components in tomato juice is still inaccurate and needs further optimization.
Keywords

- Tomato;
- Acids;
- Sugars;
- HPLC;
- Electronic tongue;
- ATR–FTIR;
- Multivariate data analysis

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Joseph Irudayaraj has a PhD in Agricultural and Biological Engineering in the area of numerical modeling of food systems. His present research focuses on sensor methodology development addresses the monitoring of food quality and safety attributes. Techniques examined are spectroscopy and z-nose for chemical fingerprinting and optical biosensors for microorganism detection. His teaching responsibility includes instruction in the areas of instrumentation and measurements, biosensors, and food engineering.

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## Prediction of the Port wine age using an electronic tongue

- **Alisa Rudnitskaya**
- **Ivonne Delgadillo**
- **Andrey Legin**
- **Sílvia M. Rocha**
- **Ana-Maria Costa**
- **Tomás Simões**

### Abstract

The electronic tongue multisensor system was applied to the measurements in about 160 samples of the Port wines of different ages (from 2 to 70 years old) and of different types including Tawnies, Vintages, Late Bottled Vintage (LBV) and harvest wines. Multivariate calibration for the prediction of the Port wine age was made applying PLS regression to the electronic tongue and chemical analysis data. Orthogonal signal correction (OSC) was evaluated as data pre-processing method. OSC filtering was applied to the both data sets and the results were compared. The age of the Port wine was predicted with similar accuracy using both electronic tongue and chemical analysis data. The accuracy of age prediction was improved to about 1.5 years when using only the samples aged from 10 to 35 years for the calibration. This appears to be acceptable for the practical applications.

### Keywords
Use of an electronic tongue to analyze mold growth in liquid media

C. Söderström, H. Borén, F. Winquist, C. Krantz-Rülcker

Abstract

The feasibility of employing an electronic tongue to measure the growth of mold in a liquid medium was studied. We used the electronic tongue developed at Linköping University, which is based on pulsed voltammetry and consists of an array of different metal electrodes. Instead of focusing on a single parameter, this device provides information about the condition or quality of a sample or process. Accordingly, the data obtained are complex, and multivariate methods such as principal component analysis (PCA) or projection to latent structures (PLS) are required to extract relevant information. A gas chromatographic technique was developed to measure ergosterol content in mold biomass and was subsequently used as a reference method to investigate the ability of the electronic tongue to measure the growth of mold in liquid media. The result shows that the electronic tongue can monitor mold growth in liquids. In PLS analysis, the electronic tongue signals correlate well with the amount of ergosterol in the mold biomass as well as the microbially induced changes in the pH of the medium.

Electronic tongue for sensing taste changes with apricots during storage

David B. Kantor, Geza Hitka, Andras Fekete, Csaba Balla
Abstract

The present paper is aimed at application of electronic tongue (ET) to the recognition of different apricot varieties and detecting taste changes during storage. Effect of 1-methylocyclopropene (1-MCP) treatment and controlled atmosphere (CA) storage on ripeness and taste of fruits was also investigated. Three apricot varieties and four different CA conditions were studied. The pH and Brix measurement were used as reference methods and sensory analysis was performed with three parameters. Classification of apricot samples was done by canonical discriminant analysis (CDA). Calibration models for determination of correlation between ET data and reference methods were made by partial least squares (PLS) regression. Results of sensory analysis were carried out by variance analysis (ANOVA). The electronic tongue system proved to be suitable for apricot juice measurements. Classification of apricot varieties and determination of correlations between ET, chemical properties and sensory analysis were performed.

Keywords

- Electronic tongue;
- Apricot;
- Controlled atmosphere storage;
- 1-MCP;
- Taste

David B. Kantor received his MSc degree in food engineering at Corvinus University of Budapest in 2005. Currently he is working as a post-graduate student in the last year of his PhD. His main research interest involves sensor systems and their application for food purposes.

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Andras Fekete received his MSc in agricultural engineering (Agricultural University, Budapest/Godollo) in 1961, PhD in 1972, DSc in 1989. He performed R&D at the Hungarian Institute of Agricultural Engineering. He is professor at Faculty of Food Science, Corvinus University of Budapest. His research interest is in the field of physical properties of agricultural materials and foods, nondestructive methods and instrumentation, non-contact measurement methods and instruments for quality assessment, application of electronic tongue for quality assessment of liquid foods, instrumentation and control systems.
Csaba Balla has been MSc in food engineering (Corvinus University of Budapest) since 1974. He received his PhD in 1996 at Corvinus University of Budapest and is now associate professor and head of Department of Refrigeration and Livestock Products Technology. His research interests are post-harvest handling, cold store of fruits and vegetables, refrigeration technology of milk, poultry, meat and meat products and freezing technology of fruits and vegetables, meat and dairy products.

A composite sensor array impedentiometric electronic tongue: Part II.

Discrimination of basic tastes

G. Pioggia, F. Di Francesco, A. Marchetti, M. Ferro, R. Leardi, A. Ahluwalia

Abstract

An impedentiometric electronic tongue based on the combination of a composite sensor array and chemometric techniques aimed at the discrimination of soluble compounds able to elicit different gustative perceptions is presented. A composite array consisting of chemo-sensitive layers based on carbon nanotubes or carbon black dispersed in polymeric matrices and doped polypthiophenes was used. The electrical impedance of the sensor array was measured at a frequency of 150 Hz by means of an impedance meter. The experimental set-up was designed in order to allow the automatic selection of a test solution and dipping of the sensor array following a dedicated measurement protocol. Measurements were carried out on 15 different solutions eliciting 5 different tastes (sodium chloride, citric acid, glucose, glutamic acid and sodium dehydrocholate for salty, sour, sweet, umami and bitter, respectively) at 3 concentration levels comprising the human perceptive range. In order to avoid over-fitting, more than 100 repetitions for each sample were carried in a 4-month period. Principal component analysis (PCA) was used to detect and remove outliers. Classification was performed by linear discriminant analysis (LDA). A fairly good degree of discrimination was obtained.

Keywords

- Composite sensor array;
- Impedentiometric electronic tongue;
Clinical analysis of human urine by means of potentiometric Electronic tongue

Larisa Lvova, Eugenio Martinelli, Francesca Dini, Alberto Bergamini, Roberto Paolesse, Corrado Di Natale, Arnaldo D’Amico

Abstract

The Electronic tongue (ET) composed of different kind of potentiometric chemical sensors has been applied for the detection of urinary system dysfunctions and creatinine levels. The creatinine contents evaluated by ET were compared with those obtained by automated Jaffe’s method and GC-MS, obtaining a satisfying agreement for both methods. Partial least square regression discriminate analysis (PLS-DA) and feed forward back-propagation neural network (FFBP NN) classified 51 urine specimens from healthy volunteers in four classes, according to the creatinine content, showing that both techniques can satisfactorily differentiate urines according to this parameter. The best accuracy result of 92.2% correct classification of unknown samples was achieved with FFBP NN. Moreover, the possibility of ET system to distinguish between urine samples of healthy patients, and those with malignant and non-malignant tumor diagnosis of bladder has been shown.

Keywords

- Potentiometric electronic tongue;
- Urinary system dysfunctions detection;
- Creatinine analysis
Original Paper

An electronic tongue for honey classification

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Abstract. An electronic tongue system was developed based on 20 all-solid-state potentiometric sensors and chemometric data processing, with polymeric membranes applied on solid conducting silver-epoxy supports and a Ag/AgCl reference electrode. The sensor array was applied to 52 commercial honey samples obtained randomly from different regions of Portugal. These samples were analysed independently for their pollen profiles by biological techniques and the data collected with the tongue were evaluated for discrimination of the samples with multivariate statistical methods (principal component analysis and linear discriminant analysis), to investigate whether the device may provide an analytical alternative for classification of honey samples with respect to pollen type, a task which is time consuming and requires skilled labour when performed by biological techniques. It was found that the tongue has a reasonable efficiency for classification of honey samples of the most common three types (with *Eríca, Echium* and *Lavandula* as predominant pollens). With linear discriminant analysis, the honey samples yielded about 84% classification accuracy and 72% for crossed validation. In this study, the honey samples correctly classified for the different types of the dominant pollen were: 53% for *Lavandula*, 83% for *Eríca* and 78% for *Echium* pollen.

Keywords: Honey; pollen; electronic tongue; multivariate analysis

Multi-sensor arrays that provide global information on complex samples have deserved much interest recently. Instead of measuring specific parameters, these devices acquire global information which, after treatment by appropriate chemometric methods, can be used for multicomponent classification analysis, taste evaluation, etc. Electrochemical sensor arrays or electronic tongues built with non-specific, low-selectivity, chemical sensors with high stability and cross sensitivity to different species in solution, are suitable for analysing complex liquid samples [1]. Electronic tongues or taste sensors based on different electrochemical principles, such as potentiometry [2-6] or voltammetry [7, 8], have been described. Several array types have been tested for potentiometric devices, namely chalcogenide glass sensors [3-5], lipid/polymeric membranes [2, 6] and ion selective membranes [9]. The signal profiles generated by such devices vary with the characteristics of different samples and upon data treatment with multivariate statistical methods for pattern recognition (identification, classification...
Simultaneous determination of phenolic compounds by means of an automated voltammetric “electronic tongue”

Abstract This contribution describes the simultaneous determination of three phenolic compounds, o-cresol, p-chlorophenol and 4-chloro-3-methylphenol, using direct oxidation and amperometric detection coupled by signal deconvolution, accomplished via chemometric methods. Direct oxidation of phenolic compounds is performed at the surface of an epoxy-graphite transducer, by linear scan voltammetry. Due to strong signal overlapping, artificial neural networks (ANNs) were used during data treatment, in a combination of chemometrics and electrochemical sensors known as an “electronic tongue”. To calibrate this system properly, a total of 80 mixed samples were prepared automatically by employing a sequential injection analysis (SIA) system designed to automatically generate the information needed to train the network. The phenolic compound concentration varied from 1 to 70 μM for o-cresol, from 0.5 μM to 140 μM for p-chlorophenol and from 1 μM to 100 μM for 4-chloro-3-methylphenol. A good prediction capability was obtained, with correlation coefficients > 0.964 when the obtained values were compared with those expected for a set of 24 external test samples not used for training. The results presented here indicate that this technique is a simple and robust analytical method of environmental interest.

Keywords Phenols · Voltammetry · Artificial neural networks · “Electronic tongue”

Introduction

Water pollutants such as inorganic heavy metals, phosphates, sulphates, and various families of organic compounds are the main species that need to be determined in water purification plants. Given that the water supply is put to a vast range of uses, extensive water quality control is mandatory for human consumption and environmental reasons. One particular group of organic substances, classified as high priority organic pollutants in water, are phenolic compounds. Phenolic compounds derive from various industrial activities, human wastes and also from biological degradation. Therefore, the presence of phenols can be used as a marker for the freshness of food and beverages, for example. On the other hand, several manufacturing activities in the mining, plastic and pharmaceutical industries generate waste phenols. The extreme toxicities of some of these phenolic compounds makes their determination and quantification of great relevance in environmental analysis.

There are various ways to quantify phenolic compounds when there are several different species in a sample. Heavy laboratory instruments, such as HPLC or HPLC-MS, must be used because the compounds have similar chemical behaviours and so are difficult to separate and quantify [1, 2]. These procedures usually require additional preparative steps, like the use of preconcentration in order to enrich analysis. If separation is not well performed or incomplete, signal overlapping will occur, making it difficult to quantify the compounds separately.

Alternatively, several methods for total phenolic compound quantification have been used for many years. Global spectrophotometric determination of the coloured complex formed between the phenolic compounds and an organic reagent (such as 4-aminoantipyrine) and its subsequent extraction into a suitable solvent is a widely used method [3].
Review

Amperometric electronic tongue for food analysis

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Abstract. This review covers electronic tongues based on amperometric sensors and applied in food analysis. A brief overview of the development of sensors is included and this is illustrated by descriptions of different types of amperometric sensors used in electronic tongues. Analysis of multivariate data is also an essential part of any electronic tongue. Pattern recognition techniques are described, with a particular emphasis to the most advanced methods, such as artificial neural network and genetic algorithms. Finally, uses of the electronic tongue in model analyses and in food, beverage and water monitoring applications are also discussed.

Keywords: Electronic tongue; amperometric detection; food analysis; sensor array; pattern recognition

How much of our life quality depends on the taste of our food? Eating has become one of the pleasures in life, and taste and flavour are now known to be the primary factors influencing food choice. Not surprisingly, the connection between taste, flavour and consumer profile is likely the key for retaining and increasing customer satisfaction in the near future.

Unfortunately, we are inherently limited by our inability to objectively, consistently and accurately test food quality by our faculties of smell, sight, sound, touch and taste. There are various type of analytical methods applied to food that can provide information concerning physical and chemical characteristics of food. However, these methods are often complicated and time consuming while the food industry has general need for methods suitable for processing and quality control that are simple, rapid and able to provide time data and information on processed food.

The most used analytical procedures to estimate food quality is the sensorial analysis based on a trained panel of experts. In practice, a number of judges makes its preferences on taste qualities before being trained with model foods. Limitations on this approach are of course related to the unreliability of the human senses, which change during time, are affected by environmental interferences (lights, sounds, colours), depend on the health conditions, etc.

Taste sensation arises by means of physico-chemical interactions of some molecules present in food and the complex system of hundred of cell buds located on the human tongue. However, how specific tastes are detected is often misinterpreted. In fact, the sensation of taste is commonly connected with the chemotopic representation of the tongue. But, the belief of the existence of a correspondence between specific zones on the tongue and specific tastes, such as the highest taste sensitivity for sucrose-sweet at the tip, sour for HCl at the sides and bitter at the back for quinine, was

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Original Paper

Automatic sequential injection analysis electronic tongue with integrated reference electrode for the determination of ascorbic acid, uric acid and paracetamol

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Abstract. A new approach towards a voltammetric electronic tongue has been developed. Automation of the system was achieved by the use of a sequential injection analysis (SIA) system. Design and construction of a small detection device containing 3 working electrodes was carried out. Platinum, gold and epoxy-graphite discs were used for this purpose. An Ag/AgCl reference electrode was integrated into the measuring cell in order to minimise electrical noise. Three oxidizable compounds of clinical interest i.e., ascorbic acid, uric acid and paracetamol, could be quantified by the system. Employing the voltammograms as departure information, artificial neural networks (ANN) have been used as chemometric tool for the modelling of the system.

Key words: Electronic tongue; SIA; neural networks; ascorbic acid; uric acid; paracetamol.

Analytical determinations in samples containing different compounds is sometimes difficult due to interfering overlapping effects. The use of separation stages such as in chromatography, can sometimes avoid this drawback but it is normally an expensive option. Alternatives presented some years ago are the multivariate analytical systems, already established i.e., with spectrophotometrical determinations. Nowadays, there are multivariate systems based on the use of chemical sensors, as for example electronic tongues [1, 2]. These systems pretend to mimic human taste sense [3]. For this purpose an array of non-specific sensors is used as detection system, trying to obtain cross-sensitivity in their measurements.

Several electronic tongues have been developed in the last years, especially in qualitative analysis in industrial process control [4], environmental monitoring [5-8] or food industry [9-12]. Quantitative applications are much less developed and literature in this trend is not as significant as that for the qualitative determinations, but it is of enough importance to be considered [1]. Both potentiometric and voltammetric tongues have been developed as found in the bibliography [5, 13]. In the case of voltammetric electronic tongues there are some important works that can be found in the literature, specially those concerning the Swedish group from Linköping [4, 5, 10-12, 14, 15].

One of the features that sometimes are considered as a drawback when using electronic tongues is the huge amount of previous knowledge or data needed for the modelling or training of these systems. Because of this fact, automation in sample or standard solutions handling and preparation is an alternative in order to reduce time and reagent consumptions. Combination of automatic flow systems and electronic tongues has been already reported [14-17].
A Voltammetric Electronic Tongue

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Key words: artificial sense, electronic tongue, multivariate data analysis, process supervision

Introduction
When an array of sensors with partially overlapping selectivities is utilized, many information variables with low specificity on each variable are obtained. Even though the specificity of each variable is low, considerable information can be extracted through the combination of several selectivity classes. The information in the vast number of data material processed with the help of multivariate data analysis (MVDA). One sensor system using this technique is the voltammetric electronic tongue which was developed at Linköping University (Winquist et al., 1997). This sensor system can be used to measure foodstuffs in order to try to mimic the human tongue, as the name ‘electronic tongue’ suggests, but it is far from the only application. Often it is desirable to be able to differentiate between one good situation and all other possible (bad) situations. Examples of such applications include monitoring a factory process or a biological growth process to ensure that the process is going the way it is suppose to, or controlling liquid flows or sample reiteration to ensure the same quality through and between batches. Voltammetric methods provide high sensitivity, a wide linear range and simple, robust instrumentation.

Measurement principle and data analysis
In voltammetric measurements a current is measured between the metal working electrode and the counter-electrode when a voltage pulse is applied over the working electrode and the reference electrode. A set of pulses can be put together to form a pulse train in order to extract as much information as possible from the solution. When the potential is applied, electro-active compounds that react to that potential will be reduced or oxidized and a current, that can be measured, will arise.

In measurements with the voltammetric electronic tongue, data are collected over the whole pulse and not only at the end of the pulse, as in traditional electrochemistry. This is done since it has been found that extra information is also found at the beginning of the pulse (mainly conductivity and mobility).

The electronic tongue creates a data matrix that is treated with MVDA, e.g. principal component analysis (PCA). PCA explains the variance in the experimental data and reduces the large data set to plots that can be easily surveyed. PCA produces a ‘score plot’ that visualizes differences between the experiments. This can be used for classification or grouping of the experiments.

Equipment
The electronic tongue consists typically of four working electrodes made of the metals gold, iridium, platinum and rhodium, an Ag/AgCl reference electrode and a stainless steel counter electrode. A relay box is used, enabling the working electrodes to be connected consecutively to form four standard three-electrode configurations. The potential pulses/steps are applied by a potentiostat which is controlled by a PC. The PC is used to set and control the pulses, measure and store current responses and to operate the relay box. The set-up is illustrated in Figure 1.

Results
Extensive research has been conducted on the voltammetric electronic tongue. Examples of investigations of foodstuffs include juices (Winquist et al., 1997), milk (Winquist et al., 1998), spirit (Comina et al., unpublished data) and tea (Ivarsson et al., 2001). However, most of the work has focused on supervising processes, including water cleaning processes (Krantz-Rülcker et al., 2001), dishwasher processes (Ivarsson et al., 2003), the wet-end process of a paper machine (Carlsson et al., 2001) and the process of mold growth (Söderström et al., 2003). As an example of such a process, a score-plot of a dishwasher process is shown in Figure 2. The process from the main wash through the two rinses can be observed.

It is also possible to combine the electronic tongue with other sensor systems. An electronic tongue based on the combination of
Electronic tongues and their analytical application

Abstract Electronic tongues for liquid analysis, based on the organizational principles of biological sensory systems, developed rapidly during the last decade. A brief historical overview of the research and development in the field of electronic tongue systems is presented. Current achievements of scientific groups working in this field are outlined and critically reviewed. The performance of electronic tongues in quantitative analysis and in classification of multicomponent media is considered. The exciting possibility of establishing a correlation between the output from an electronic tongue and human sensory assessment of food flavour, thereby enabling quantification of taste and flavour, is described. Application areas of electronic tongue systems including foodstuffs, clinical, industrial, and environmental analysis are discussed in depth. Prospective research and development in the field of electronic tongues is discussed.

Keywords Electronic tongue · Multi-sensor systems · Classification · Multicomponent analysis · Taste quantification

Introduction
This paper is an attempt to review the main analytical applications, during the last decade, of multi-sensor systems and devices for liquid analysis that can be collected under the term “electronic tongue”. Articles in reviewed journals and books are considered in this publication, because the format of conference papers is such that they do not usually give a detailed description of both the systems and their applications. Analytical results are mainly mentioned, with a brief overview of sensors (only for liquid phase analysis) and related sensing principles. Multidimensional data processing, a significant issue in electronic tongues and multi-sensor systems, is not considered in this paper, because this topic deserves detailed and serious consideration in a separate publication. Commercial devices are also not described, because their principles are often undisclosed by the manufacturers, and analytical applications are advertised rather than practically implemented.

Chemical sensors are widely known analytical instruments. Some, e.g. ion-selective electrodes, are almost one hundred years old. The first potentiometric sensor – an ion-selective electrode (ISE) – was a glass pH-selective sensor suggested in 1909 by Haber and Klemensiewicz [1]. It is still, with minor modifications, the most selective and widely used sensor for liquids. Traditionally, research and development in the field of chemical sensors (and other analytical methods) was directed toward obtaining the highest possible selectivity for an analyte. As a result, several highly selective sensing materials for ISE were developed and applied to practical tasks. The number of selective sensors available for analytical purposes still remains significantly restricted, however, despite the hectic efforts of many researchers. One possible way of enhancing the analytical application of chemical sensors is utilization of not only highly selective but also of less selective, cross-sensitive sensors, combined in sensor arrays, and with sophisticated data processing techniques to interpret their outputs. This idea was firstly implemented in systems for gas analysis now widely known as “electronic noses” [2]. Later researchers paid attention to realization of similar ideas for liquid analysers, which were called “electronic tongues”.

Development of the electronic nose [2] and, to a lesser extent, of the electronic tongue was obviously inspired by biological sensory systems, primarily mammalian olfaction. The olfactory system consists of a large number of non-specific receptors (sensors) that react to volatile compounds and transfer stimuli via the nervous system to the brain, where a neural network processes the signal pattern. Mammals are able to recognize thousands of odours,
Electronic Tongue: A Review

Submitted by Anonymous (not verified) on Sun, 05/07/2006 - 19:25

P. D. Chaudhari

The formulation’s organoleptic properties such as taste, mouth feel and appearance are of considerable importance in differentiating products in the market and can ultimately determine the success of the product.

Pharmaceutical taste assessment requires human test panel that increases time and money to the development process. During the last decade, a multisensor system and a device for the liquid analysis that can be collected under the term “Electronic tongue” was developed. The electronic tongue is capable of discriminating between substances with different taste modalities and can also distinguish different substances eliciting same taste. The electronic tongue proved capable of distinguishing between formulations with different levels of sweetener and flavour in a manner that was consistent with their masking efficiency. In this review article development and prospective research and development in the field of electronic tongue is discussed.

Taste is a survival mechanism, alerting us to potential harmful or potential nutritious substances. Approximately 10,000 chemoreceptors or taste buds reside on the tongue. These chemoreceptors or taste buds fall into five basic categories: sour, bitter, salt, sweet, and umani, with grouped receptors dissipated over the surface of the tongue for each stimulus. Taste depends on physiological and psychological factors'. Physiological factors such as temperature and texture clearly affect the perception of taste. Psychological factors can
influence taste perception. Assessment of the taste of oral drug preparation is of major interest in pharmaceutical industry, particularly for research-based companies. Appropriate activity, selectivity and ADME (absorption, distribution, metabolism, and elimination) are the influencing characteristic of any pharmaceutical compound. But it is more interest to formulate the active moiety into patient consumable form. As the active moiety in pharmaceutical product cannot be therapeutically beneficial unless it has preference and acceptance by the patient. Thus, pleasant taste is important for the therapeutic success of the drug formulation.

Major Cause Non –Compliance

Many pharmaceutical drugs have unpleasant or bitter taste, which significantly affect patient acceptance, preference, compliance and after efficiency and safety, are of upmost importance in determining market success. Unpleasant taste has major consequence of low compliance level from infants, children and the elderly person. So, pleasant taste is not only necessary for the patients having difficulty in swallowing solid dosage form but also to improve acceptance level from the different age groups.

Pleasant Taste: Complicates the Process

Many scientific techniques are employed for the avoidance of unpleasant or bitter sensory sensation:

a) The addition of aromas, sweeteners or cooling agents.

b) Microencapsulation, oral disintegrating tablets, ion exchange resin and other coating techniques.

These additional processes in formulation increase the development time and cost and delay the marketing of the new drug entity. To date, the only method employed for determination of taste intensity was human sensory test. Drawbacks associated with these tests were: individual variability, impossibility
of on-line monitoring, subjectivity, adaptation, infections, harmful exposure to hazardous compounds and mental state of panelists. To facilitate the work and address the difficulties associated with human panel test, a safe, reliable, fast analyzing objective instrument was required. Thus, an analytical instrument capable of assessing taste properties with great benefit in making the process of drug formulation safer, faster and eventually cheaper was developed called “Electronic Tongue” an intelligent chemical sensor array system for taste classification.

Electronic tongue is also called as artificial tongue, taste sensor. Electronic taste instrument have been developed and optimized to answer some of these issues: reduces human sensory test panels, precise measurement of taste, formulation development time and cost and increases number of formulation candidates in prescreening steps. These sensor-based analyzer systems make a global analysis of total complex chemistry of the sample. Using organoleptic and chemical properties they perform qualitative as well as quantitative analyses of the product. The first multi-sensor system for liquid analysis was based on a poor selectivity approach introduced by Toko et al in 1990 and termed it as taste sensor system. Later the instrument was named as “Electronic tongue”. The multi-sensor array system or electronic tongue shows the clear correlation of the instrument output with human perception for various substances. We can state Electronic tongue as “the system for automatic analysis of liquid including an array of non-specific chemical sensors with partial specificity for different component in liquid samples and an appropriate pattern recognition capable of recognizing the qualitative and quantitative composition of sample and complex solutions”. These system shows the following advantages: (a) requires small sample volume, (b) decreased measurement time, (c) objectivity compared to sensory panel, (d) small size of sensors, (e) easily operated by unskilled personnel and (f) amenability to fully automatic long-term routine application.

*Important benefits of electronic tongue*

- Evaluate and quantify bitterness scores of new chemical entities (NCE).
· Optimizes and increases the formulation development process.

· Within the formulation, it measures the efficiency of complexation/coating.

· Various combinations of sweeteners, enhancers, exhausters, aromas and masking agents can be tested in less time.

· Benchmark analysis: compares the palatability of new formulations with competitor’s products.

· Serving a quality control function for flavored products and excipients.

· Developing suitable matching bitter placebo for double blind clinical testing.

· During the scale-up process from small production batches to full-scale manufacturing, it defines consistency of organoleptic quality.

Objectives

1. Identification between bitter, sweet and sour substances by using electronic tongue; study the possible memory effect of these substances on its sensors.

2. Separating the different substances eliciting the same taste (sour, bitter, sweet).

3. Evaluation of the ability of the electronic tongue to identify drug preparations containing active substance and placebo substance.

4. Check ability of electronic tongue to quantify the content of selected bitter and sweet substances.
5. Assessment of different taste masking approaches i.e. addition of different quantities of sweeteners and flavors to active substance to reduce its bitter intensity.

6. Quantification of the effect of taste masking of bitter substances by sweet ones.

**Correlation between human tongue and electronic tongue (Fig1)**

![Figure 1: The Electronic Tongue Concept](image)

Mechanism involved for taste recognition in human and electronic tongue shows the same three levels: the receptor level [taste buds in humans, lipid membrane of sensors in the electronic tongues], the circuit level [neural transmission in humans, transducers in the electronic tongues], the perceptual level [cognition in the thalamus in humans, statistical analysis by software in the electronic tongues]. At the receptor level, to detect dissolved organic and inorganic compounds the sensor-probe assembly is used by the electronic tongue. Each probe shows cross-sensitivity and selectivity so that each sensor could concurrently contribute to the detection of most substances found in the liquid matrix. These sensors are composed of an organic coating sensitive to the species to analyze in the samples and a transducer that allows converting the response of the
membrane into signals that will be analyzed. At the circuit level, the sample is quantified, digitized and results are recorded [potentiometric readings]. At the perceptual level, process of taste perception or sensation that occurs in the computer where the electronic tongue systems statistical software interprets the sensor data into taste patterns. Depending upon the application for which it is applied, the data analysis can produce a variety of information.

**Principle**

As previously been established that the intensity of human response to taste stimuli depends logarithmically on the concentration of the stimuli.\(^{10}\) Response of potentiometric chemical sensor is also logarithmic in relation to the analyte concentration as follows the Nernst or Nikolsky-Eisenmann equation.\(^{11,12}\) This suggested that potentiometric sensors, exhibiting appropriate sensitivities, might be particularly suitable for the instrumental evaluation of taste. Thus, the principle of the electronic tongue\(^{13,14}\) is based on utilization of non-specific or low-selective potentiometric chemical sensors with enhanced cross-sensitivity to as many different components in solution as possible. Cross-sensitivity means that the sensor responds not to a single analyte but to several substances simultaneously present in the analyzed media. Different sensors should exhibit different sensitivity and selectivity pattern that might be partly overlapping or even completely distinct. The responses of the sensors are defined by the interaction with ionic and redox species, both inorganic and organic at the membrane-solution interface. By comprising non-specific sensors in a multisensor system, information about multiple substances or groups of substances in complex media can be obtained. Pattern recognition and/or multivariate calibration methods should be used to interpret complex signals from such sensor arrays and for predicting both qualitative features and quantitative parameters of analyzed multicomponent media.

**Instrumentation** (Fig 2)
Liquid Autosampler

Recently, liquid autosampler by ALPHA M.O.S. (Fig 3) consist of 16 beakers (80-ml capacity) and 48 beakers (20 ml capacity). A programmed sample agitator, a robotic sensor head and individual connections for each sensor are present. The autosampler allows running automatically upto 15 different liquid samples plus one extra for sensor cleaning purpose.

Chemical Sensor or Sensor array

Chemical sensors have been widely used in such applications as critical care, safety, industrial hygiene, process controls, product quality controls, human comfort controls, emission monitoring, automotive, clinical diagnostics and home safety alarms. In these applications, chemical sensors have resulted in both economic and social benefits. Chemical sensors can be defined as small devices that result in transformation of chemical or biochemical information of a qualitative or quantitative type into an analytical useful signal by the process of chemical interaction between sample and sensors devices. Currently these technologies are based on electrochemical sensors. The oxidation and reduction of chemical species on a conducting electrode can be observed by measuring the movement of charge. There are two primary methods of sensing electrochemical reactions. Potentiometric and amperometric potentiometric sensors can be used to measure the equilibrium potential established between the electrode material and the solution, a potential that is dependent on the chemistry involved. Amperometric sensors measure the current generated by a
reaction and thus give a measure of reaction rates. Other sensing methods applied are voltammetry, optical sensors and biosensors. By controlling the potential of the electrode relative to the solution and measuring the charge flow induced the presence of specific ions can be determined by observing the potential at which they undergo oxidation or reduction. This process is called a voltammetry. Biosensors are the sensors that use biomolecules and structures to measures something with biological importance or bioactivity. They are also called the subsets of chemical sensors, as the transduction mechanism is similar to those of chemical sensors. The sensors are made up of silicon transistors with organic coating that are necessary for the sensitivity and selectivity of each individual sensor to ensure good repeatability, sensitivity and selectivity. The detecting sensor part consist of lipid/polymer membranes. These lipids membrane are made up of different types of lipids, which are pasted on the opening of the sensors. Different types of lipids (in table 1) used are decyl alcohol (DA), Oleic acid (OA), Dioctyl phosphate (DOP), DOP: TOMA (5:5), DOP: TOMA (3:7), Triocylmethyl ammonium chloride (TOMA), Oleylamine (OAm).

Table 1. Lipid used for the lipid/polymer membranes by Toko et al.

<table>
<thead>
<tr>
<th>Working electrode (channels)</th>
<th>Lipid (Abbreviation)</th>
<th>Content (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Decyl alcohol (DA)</td>
<td>0.4</td>
</tr>
<tr>
<td>2</td>
<td>Oleic acid (OA)</td>
<td>0.4</td>
</tr>
<tr>
<td>3</td>
<td>Dioctyl phosphate (DOP)</td>
<td>0.4</td>
</tr>
<tr>
<td>4</td>
<td>DOP: TOMA (5:5)</td>
<td>0.107: 0.135</td>
</tr>
<tr>
<td>5</td>
<td>DOP: TOMA (3:7)</td>
<td>0.064: 0.189</td>
</tr>
<tr>
<td>6</td>
<td>Triocylmethyl ammonium chloride (TOMA)</td>
<td>0.269</td>
</tr>
<tr>
<td>7</td>
<td>Oleylamine (OAm)</td>
<td>0.05</td>
</tr>
</tbody>
</table>
These lipid/polymer membranes were prepared by mixing each lipid with Polyvinyl Chloride (PVC), plasticizer (Dioctylphenylphosphonate). The mixture is then dissolved in tetrahydrofuran and immediately the mixture is transferred to petridish that is stored at controlled temperature of 30 for 24 h.

The membrane obtained is transparent, colourless, and soft film of approximately 0.02 cm thickness. Each membrane possessed an electric charge due to each lipid. These are the working electrodes. The reference electrodes are made of an Ag wire whose surface was plated with Ag/AgCl, with an internal cavity filled with 3 M KCl solution and opening tube filled with 100 mM KCl and Agar. The measurement consists of a potentiometric difference between each individually coated sensor with the Ag/AgCl reference electrode. The reference electrode i.e. Ag/AgCl is the same for all application types. Electrode charge density of the lipid/polymer membrane surface and ion distribution near the surface of the membrane is changed due to taste substances. Therefore the total electrical charge on the lipid membrane gives the response membrane electric potential for the substances. Each sensor is partially selective to various chemical compounds and thus partial selectivity differs between sensors3. The cross sensitivity and selectivity of sensor arrays allow them to track any variation in the liquid matrix of samples. Thus, the electric potential response is different for chemical substances showing different taste qualities in each membrane. When experiment is carried out 50 mM KCl freshly prepared solution is used as reference solution and as rinsing fluid of electrodes after every measurement20. The measurement is carried out as follows:

1. Reference solution is measured (15 s)

2. Sample solution is measured (15 s)

3. Rinsing of electrodes with 50 mM KCl solution (120 s).

The difference between the response membrane electric potential to the sample and the reference solution gives the response potential to the sample. Each sample is analyzed three times by the rotation procedure.

Recently, nine different electrodes AU/C, OA/PEO, Pt/C, Nafion, OA/PVA, DA/PVA, RuO2, TEOS, and CNT/TEOS/Al2O3 have been produced to taste five basic qualities in human taste system and
used in the potentiometric method for application\textsuperscript{5}. All the nine sensing electrodes were produced in the laboratory at Center for Measurement Standards, Industrial Technology Research Institute, Hsinchu, 300, Taiwan, R.O.C.

**Acquisition System:**

The acquisition system establishes the communication between the sensor array and data processing system. The electrical potential responses produced at the sensor array are received by this system and it converts these electrical signals to digital signals with less distortion. An analog signal input devices, a filter mechanism and an analog to digital converter (ADC) should be present in the system as the speed of the sensor system is very slow, a low speed and high resolutions delta sigma ADC is enough to this electronic tongue system\textsuperscript{6}. The filter mechanism is necessary to provide a clean and no distortion transmission channel between the sensors and ADC. Amplifier must be present in analog signal input devices as the electrical signals from the sensors are always small. Different sensors have different impedance hence it is also necessary to have impedance match circuit at this stage.

**Data Processing System:**

Interpretation of data with multivariable such as several sensors for multiple samples required the use of statistical interpretation methods. Chemometric techniques a type of multivariate statistic used in the analytical field provide data processing, which consist of recognition, classification and identification and multivariate calibration\textsuperscript{2}. Recognition, identification and classification is mainly done by Principle Component Analysis (PCA), Discrimination factorial analysis (DFA) or by Partial least square (PLS) while multivariable calibration is undertaken with the help of PLS. Data analyses and pattern recognition depending on the study design is summarized in table 2.

**Table 2.** Perceptual recognition and its application in product development\textsuperscript{7}.
<table>
<thead>
<tr>
<th><strong>Statistical analysis</strong></th>
<th><strong>Broad use</strong></th>
<th><strong>Application</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Principal component analysis (PCA)</td>
<td>Qualification, exploration and discrimination</td>
<td>Initial formulation studies</td>
</tr>
<tr>
<td>Discrimination factorial analysis (DFA)</td>
<td>Discrimination and identification</td>
<td>Recognition of unknown sample</td>
</tr>
<tr>
<td>Soft independent modeling of class analogy (SIMCA)</td>
<td>Good/bad modeling</td>
<td>Quality control against reference product</td>
</tr>
<tr>
<td>Partial least square (PLS)</td>
<td>Quantification</td>
<td>Quantification of bitterness against sensory panel</td>
</tr>
</tbody>
</table>

{mospagebreak title=Applications of Electronic tongue}

**APPLICATIONS OF ELECTRONIC TONGUE**

1. **Foodstuffs Industry**
   - Food quality control during processing and storage (water, wine, coffee, milk, juices…)
   - Optimization of bioreactors.
   - Control of ageing process of cheese, whiskey.
   - Automatic control of taste.

2. **Medicine**
   - Non-invasive diagnostics (patient’s breath, analysis of urine, sweat, skin, odor).
· Clinical monitoring in vivo.
· Identification of unpleasant taste of pharmaceuticals.

3. Safety
· Searching for chemical/biological weapon.

· Searching for drugs, explosives.
· Friend-or-foe identification.

4. Environmental pollution monitoring
· Monitoring of agricultural and industrial pollution of air and water.

· Identification of toxic substances.
· Leak detection.

5. Chemical Industry
· Products purity.

· In the future – detection of functional groups, chiral distinction.

6. Quality control of air in buildings, closed accommodation (i.e. space station, control of ventilation systems).

7. Legal protection of inventions - digital “fingerprints” of taste and odors.

Other Analytical Applications
Taste quantification and foodstuff recognition are the main area of application of the taste sensor.
Taste sensor sensitivity was studied in aqueous solution of five basic taste substances: salty (NaCl, KCl, and KBr), sour (HCl, citric and acetic acids), bitter (quinine), sweet (sucrose), and umami (monosodium glutamate). Different patterns for chemical substances with different taste and similar patterns for substances with similar tastes were obtained by taste sensor.

Sensor sensitivity to sour and salty substances, e.g. HCl, organic acid, NaCl, KCl, KBr was approximately 50-60 mV/Px, to glutamate (umami substance) was approximately 13 mV/pX, to quinine hydrochloride (bitter substance) was approximately 50 mV/decade, to natural bitter alkaloid caffeine was only approximately 5 mV/pX, to natural sweet substances (sucrose) was very low, whereas to an artificial sweetener (aspartame) was about 40 mV/pX. For this reason an enzymatic glucose-selective sensor was used with the taste sensor when determination of the sugar concentration was crucial.

Bitterness of 18 different antibiotics and antiviral drug formulation for pediatric use were evaluated as suspension in water and in an acidic sport drink. Bitterness intensities of suspension in an acidic sport drink and in water were compared using the taste sensors. Suspension in an acidic sport drink would enhance or reduce the bitter intensity of the pediatric drug formulation compared with suspension in water; taste sensors were able to predict it.

Bitter taste suppression was studied by using sweet substances to mask the bitterness of the drug. Degree of bitterness for quinine solution and modeling was calibrated by taste sensor by using principal component regression. The bitterness of the mixed solution was predicted by use of the model. The mixed solution contained 1 mmole L⁻¹ of quinine solution and 1mmol L⁻¹ to 1moleL⁻¹ of sucrose solution and phospholipid cocktail. As the concentration of the sucrose increase to 1 mole L⁻¹ degree of bitterness estimated dropped significantly. The same experiment was repeated for artificial sweet substances-phospholipids, which is used in pharmacology to mask the bitter taste of drug.

Different kinds of commercial mineral water were classified by using the taste sensor. Mineral water was classified on the basis of the hardness of water. The tastes of 20 bottled nutritive drinks, all commercially available on the Japanese market were evaluated both in human sensory test and by using electronic tongue. The electronic tongue was able to differentiate between low price group products, middle price group products, high price group products and played important role in evaluating the palatability of bottled nutritive drinks.
Different varieties of tomato were recognized using taste sensor by measuring the crushed tomatoes\textsuperscript{27}. The taste sensor were first calibrated in canned tomato juice to which four basic taste substances, NaCl, citric acid, monosodium glutamate, and glucose were added, for quantification of tomato taste. Taste sensors also found a wide use in dairy industry. Taste sensors were found capable in discriminating between fresh and spoiled milk and to follow the deterioration of the milk quality when it was stored at room temperature. Two packaged commercial milk; the ultra high temperature (UHT) and the pasteurized milk were tested\textsuperscript{28}.

Ten brands of coffee of different origin (one of which was used as standard) were measured at 60°C by using taste sensors\textsuperscript{29}. Oleic acid contained in sensor was correlated with coffee acidity as perceived by tasters with a correlation coefficient of 0.98. The correlation between coffee bitterness and the response of the sensor contained dioctyl phosphate (DOP) and Trioctylmethyl ammonium chloride (TOMA) was found to be 0.94. An electronic tongue made up of micro-sensor array of three enzyme sensors had been developed for determination of glucose, urea, and triglyceride (triolein)\textsuperscript{30}. Tasting extracts of American oak (\textit{Quercus alba}) was difficult due to the variety of bitter and astringent chemical compounds that they contain. These extracts were analyzed by an array of global selectivity chemical electronic tongue sensors, which offered a simple and rapid method of analysis of oak wood extract with excellent repeatability\textsuperscript{31}. The components of medical liquids- dialysis solutions for an artificial kidney that contained Ca\textsuperscript{2+}, HCO\textsubscript{3}-, H2PO\textsubscript{4}-, Na\textsuperscript{+}, K\textsuperscript{+}, Cl\textsuperscript{-}, Mg2\textsuperscript{+}, pH were determined by quantitative performance of the electronic tongue \textsuperscript{32}. Measurement procedures were developed such that the system detects with precision of 2 % - 4 % acceptance for clinical analysis.

**CONCLUSION:**

Electronic tongues are an emerging and promising field in modern chemical sensor science. The electronic tongue proved to be a valuable tool for assessment and prediction of the taste of pharmaceuticals and related products. The system could potentially assist, or even replace, a sensory panel in certain type of routine analysis in pharmaceutical development and production. Electronic tongue measurements can be performed as often as analytically needed without the regulatory hurdles or expense of human testing. The exposure and risk of using employee to test products is greatly reduced while permitting better analytical results to quickly define the best formulation and get the product to the market. This direction of analytical chemistry and sensor is quite young and research in the area remains substantially semi-empirical. Electronic tongue
systems seem to be very useful for process monitoring and as a quality-control tool in the food industry, in clinical analysis, and in research laboratories.

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**Electronic Tongue and Neural Networks, Biologically Inspired Systems Applied to Classifying Coffee Samples**

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**ABSTRACT**

In this paper, the possibility to use an electronic tongue based on a polypyrrole sensor array in classifying coffee samples has been studied. Each sensor shows a distinguished electrochemical response when exposed to the studied solutions, providing signals with a high degree of cross-selectivity. The sensor array electrochemical response is related to the interaction of the ionic and non-ionic solution compounds and to the surface of the sensors polymeric matrix. Furthermore, the electronic tongue was used to perform an analysis on coffee samples. In this case, each sensor showed a particular response to each coffee sample. Data obtained from the registered signals were used to perform a discrimination of the samples. The analysis with neural networks of the principal components (NNPC) done on the electronic tongue response to five types of commercial coffee, allows to achieve a clear differentiation of samples.

**Keywords**: Electronic Tongue; Coffee; Electrochemical Sensors

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**1. Introduction**

In the food industry, the commercial success of a product is determined by many factors, such as appearance, aroma and flavor. The growing customers’ demand on food quality makes the inspection and approval of products more rigorous every day. In order to guarantee the quality of commercial drinks, specifically coffee, different methods of chemical, Physicochemical and sensory analysis are utilized. The first ones include a series of well-known techniques, mainly volumetric, chromatographic and spectroscopic, which are able to categorize with great accuracy the chemical composition. The goal of the second ones—sensory methods—is to evaluate the sensations produced by coffee altogether [1]. The sensorial analysis can be defined as the experimentation and analysis of the global characteristics of a product through the senses; those characteristics are known as organoleptic.

Smell and taste senses are known as chemical senses since they respond in a direct manner to stimuli produced by molecules originating a nerve reaction. Taste responds to stimuli produced by food molecules on the tongue’s taste cells. That interaction produces the sensation of taste. The taste receptor organs are located above all on the taste buds. The mechanism by which different flavors are detected and recognized are not yet determined, but it is known that taste cells respond with partial selectivity to a
series of chemical compounds; in detecting a flavor a series of electrical impulses are generated with different intensities and are transmitted to the brain, where they are compared to identify flavors [2] [3].

Smell and taste systems have produced inspiration so that from its functioning principles instruments may be developed to search for a way to emulate its capacity to classify and differentiate complex substances [4] -[6]. These biologically inspired systems are known as electronic noses and tongues. Thus, a certain analogy can be established between the human taste system and the electronic one in order to detect flavors (electronic tongues), so that some approximations can be found in its structure and functioning principles (figure 1).

Electronic systems to measure flavors or electronic tongues are some of the most promising tendencies to develop a fast, cheap and objective method to evaluate food taste. Since the development of the first prototype in 1990 by K. Toko, [7] a certain number of research groups have focused their efforts on the improvement and perfection of those systems by utilizing diverse strategies and measuring techniques. There are several types of sensors that can be utilized in electronic tongues. The most important ones are based on electrochemical techniques such as potentiometry and voltammetry. In the bibliography there are diverse papers where these types of instruments have found numerous applications [4] -[6] [8] -[11]. However, it is also possible to use sensors based on other types of transduction, such as, optical or gravimetric sensors [12] -[14].

The information given by electronic tongue instruments is analyzed through multivariate statistical techniques [15] [16]. The selection of the statistical analysis method depends on the type of study being carried out and the type of given data. The most utilized techniques to treat data from electronic tongues are different methods of recognizing patterns, such as the Principal Component Analysis (PCA), Cluster Analysis, Discriminant Analysis (DA) and so on. Undoubtedly, PCA is the most utilized chemometric method in studies made with electronic tongues because of its accessibility, simplicity in interpretation and low informatics cost. The Principal Component Analysis is a lineal method used to reduce variables or dimensions. It has been widely used in unnumbered applications. Nonetheless, being a lineal method, it is not always the most appropriate one because it generates redundancy when expressing data and it is possible to ignore important information when considering the array response as a lineal system. To solve this problem, some non-lineal PCA methods are proposed. However, many of the non-lineal methods have a constraint. The number of components to utilize should be pre-determined and an explicit order of the
components is not given. Bearing in mind that the PCA should not be utilized in non-lineal complex systems, this project proposes the use of a non-lineal adaptive system based on neural networks.

On the other hand, a new voltammetric sensor array based on polypyrrole is utilized in this work, whose signals are rich in information because its sensors’ interactions with the analyzed samples can modify the redox potential of the electrode material (polypyrrole). The polypyrrole catalytic electroactivity can ease the oxidation or reduction of compounds present in the sample, and the sensors’ response is related to the capacity to generate counterions diffusion between the matrix and the analyzed sample to keep its electroneutrality. Consequently, the given information reflects the specificities of each sample and its interaction with the electrode material, providing signals that are converted in a fingerprint of each sample that allows discrimination and classification of the samples under study. Experiments were made in this research utilizing coffee samples to test the capacity to differentiate the sensor array, and neural networks are utilized as principal components for the data treatment, thus, two biologically inspired technologies are implemented to classify coffee samples.

2. Experimental

2.1. Reagents and Samples

All reagents used had a sigma-aldrich analytical quality (pyrrole, phosphotungstic acid, potassium hexacyano-
Figure 1. Functional analogy between the human taste system and the electronic system of flavors detection.
ferrate (II), sodium salt of anthraquinone-1,5-disulfonic acid, potassium ferrocyanide (III), Sodium salt of dodecylbenzensulfonic acid and sodium salt of p-toluensulfonate) and solutions were prepared with ultra purified water with a Milli-Q quality. Coffee samples were taken from five commercial brands (La Bastilla, Córdoba, Almendra Tropical, Sello Rojo and Universal) and they were prepared according to regulation NTC 3566 (sample preparation to use in sensory analysis), 7 grams of sample were weighed and prepared in 100 ml of water. For that purpose, the water was heated in the heater up to the boiling point, 100 ml were measured and they were poured in a beaker. The infusion was decanted for 5 min, then remains were eliminated from the solution surface and the solution was cooled to room temperature.

2.2. Electronic Tongue (Measuring Instrument)

Measures on coffee samples were made with an electronic device developed in the laboratory composed by a sensor array coupled to a multichannel measuring module elaborated at LabVIEW with cards or modules for data input and output. For the acquisition of data, modules NI9263, analogous output voltage module of 16 bit and four channels, and the NI9203, input module of analogous current of 16 bit of 8 channels were used. These modules were mounted in a framework NI Compact DAQ USB especially designed for this type of cards.

The sensor array was elaborated from pyrrole electropolymerization with different doping agents. All sensors were generated by chronoamperometry in a pyrrole aqueous solution (0.2 mol L$^{-1}$) and different doping agents were utilized in each of the sensors (each at 0.1 mol L$^{-1}$): Phosphotungstic acid, potassium hexacyanidoferrate (II), sodium salt of anthraquinone-1,5-disulfonic acid, potassium ferrocyanide (III), Sodium salt of dodecylbenzensulfonic acid and sodium salt of p-toluensulfonate. For the electropolymerization, a conventional three-electrode cell was used; reference electrode Ag/AgCl (saturated); a platinum sheet as auxiliary electrode and as substrate (work electrode) for the polymerization, disk electrodes were used elaborated in laboratory. Polymerization conditions are summarized on table 1.

| Table 1. | Polymerization conditions of polypyrrole sensor array. |

2.3. Measures and Data Treatment
Coffee samples were randomly measured with the previously described instrument. After preparing samples, measures were made at room temperature, in a potential range from $-1.0 \text{ V}$ to $0.5 \text{ V}$ with a sweep rate of $0.1 \text{ V S}^{-1}$. It was necessary for each measure to primarily make 10 voltamperograms to stabilize signals, and then measures were collected to feed the system of data treatment. Seven measures were made to each sample to test the method repetitiveness. In data treatment, an algorithm for neural networks was utilized for principal components available in the Statistica V7 software. Data were analyzed with no previous treatment of signals. For data interpretation, results of first components (scores) were graphed.

3. Results and Discussion

As established in previous works with this type of research, before starting the research on differentiation of complex substances such as coffee, which is the case in this study, a preliminary test should be done to determine if the electronic tongue instrument is able to differentiate simple substances with diverse chemical and taste properties. [9] [17] [18]. In order to evaluate the discrimination capability of the sensor array, the instrument was used with a series of five simple substances whose properties are related to coffee including the specificity of basic flavors. Thus, to initially evaluate the differentiation capacity of liquids from the voltammetric and electronic tongue, measures were made on five solutions representing basic flavors related to coffee; NaCl ($0.1 \text{ mol L}^{-1}$), sucrose ($0.1 \text{ mol L}^{-1}$), citric acid ($0.1 \text{ mol L}^{-1}$), caffeine ($0.1 \text{ mol L}^{-1}$) y vainillin ($0.1 \text{ mol L}^{-1}$). On the experiments, seven replicas of each measure were made to evaluate the capacity of reproduction of signals given by the sensor array. On the different registered signals, it was observed that each sensor presents a particular response (‘fingerprint’) to a type of substance with a determined taste property, producing a sign with information on the analyzed substance. It is important to point out that with the sensor array it is possible to get voltammetric signals with well-defined peaks (with information on the analyzed method) from non-electroactive substances, differing from that obtained with the use of traditional voltammetric and metallic sensors utilized by other authors [19] [20].

The response of sensor PPy/DBS to the solutions shows a good example of the crossed selectivity from the sensors. The electrochemical behavior from the polypyrrole redox pair to the solutions is shown on figure 2. The cyclic voltammetry of the PPy/DBS electrodes in contact with NaCl (salty), citric acid (sour) and caffeine (bitter) showed two redox couples (figures 2(a)-(c)). The figure shows that the cathodic sweeps were
dominated by one sharp reduction peak (at $-0.63 \, \text{V}$, $-0.58 \, \text{V}$ and $-0.48 \, \text{V}$ for NaCl, citric acid and caffeine, respectively) and one smaller, broader peak at ca. $0.09 \, \text{V}$, $-0.08 \, \text{V}$ and $0.20 \, \text{V}$ for NaCl, citric acid and caffeine, respectively. Two redox processes were also observed in the anodic branch (at $-0.55 \, \text{V}$ and $0.08 \, \text{V}$ for NaCl, $-0.63 \, \text{V}$ and $-0.05 \, \text{V}$ for citric acid and $-0.71 \, \text{V}$ and $-0.07 \, \text{V}$ for caffeine). The CV from PPy/DBS in vanillin and sucrose (two sweet compounds) showed two redox processes. The anodic peaks appear at $-0.75 \, \text{V}$ and $-0.25 \, \text{V}$ for vanillin and $-0.69 \, \text{V}$ and $-0.15 \, \text{V}$ for sucrose. In the corresponding reverse scan, the cathodic wave of the first redox couple was not clearly observed, whereas that of the second redox process appeared at $-0.57 \, \text{V}$ and $-0.45 \, \text{V}$ for vanillin and sucrose respectively. According to the literature, these peaks can be assigned respectively to the formation of the polaron and bipolaron \cite{21}.

During the first redox process occurring at lower potentials (peak I), the doping anions remain immobilized inside the film, whereas cations are exchanged with the surrounding solution to maintain the electroneutrality. In the second process (peak II), occurring at higher voltages, the PPy film gets highly oxidized and anions from the electrolyte are inserted into the film to maintain the charge balance \cite{22} \cite{23}.

The possible mechanisms that generate the responses of the sensors can be associated with the electrochemi-
Figure 2. PPy/DBS sensor response against: (a) NaCl, (b) citric acid, (c) caffeine, (d) vanillin y (e) sucrose.

A controlled ion-exchange process. The exact nature of the ion-exchange process is not clearly deciphered, but it has been established that during the first redox process occurring at lower potentials (peak I), the doping anions remain immobilized inside the film, whereas cations are exchanged with the surrounding solution to maintain the electroneutrality. In the second process (peak II), occurring at higher voltages, the PPy film gets highly oxidized and anions from the electrolyte solution are inserted into the film to maintain the charge balance [24]. The chemical basis of the electrochemical responses can be explained as follows:

On the first reduction/oxidation process for reasons of electroneutrality, the PPy film behaves as a cation exchanger: The reduction/oxidation process leading to the second reduction/oxidation process can be formulated as follows:

In this case, the electroneutrality makes the film behave as an anion exchanger.

The PPy symbolizes a segment of the polypyrrole chain, the subscript indicates that the species is in the solution phase and is in the PPy matrix.
The above results indicate that the shape and position of the peaks depend on the nature of the doping anion. Therefore, a rich variety of sensor responses was achieved by changing the doping agent entrapped inside the polypyrrole films. On the other hand, the ability to incorporate and expel ionic species during the redox transformations for preserving the macroscopic electroneutrality of the electrode can be used to produce analytically useful signals.

In order to study the lifetime of the electrodes, they were recurrently exposed (twenty exposures per day in seven successive days) to an electrolytic solution of 0.1 mol L\(^{-1}\) NaCl. Then, the coefficients of variation (%CV) of the peak heights were calculated. The electrodes showed good stabilities up to the fifth day of exposition, with %CV values below 15%. On the seventh day, the %CV increased drastically (30% in all cases).

The voltammograms on the different solutions show a double process of oxidation/reduction typical of the polymer but in each case the sign is completely different and the potential varies from one solution to the next. The other sensors also showed crossed selectivity, that is, they showed a particular behavior to each substance. Besides, each sensor responds differently to a unique type of substance. Thereby, it is evident that each sensor shows a characteristic response to each solution. These changes are mainly due to variation on forms, positions of redox peaks and relative intensities. This way, the matrix data built from the intensity values of the signals given by the sensor array allowed to make the work of differentiating the substances through an NNPC analysis.

In order to evaluate the discrimination capabilities of the voltammetric sensors, NNPC analysis was conducted by combining the information obtained from the PPy electrodes system. Then, the array of electrodes was immersed in the samples and seven replicates of each sample were registered. Because the voltammograms comprise a large amount of information with a large number of current–potential pairs and since a CV is a bi-valuated curve, the anodic scan was selected to build the matrix used for the pattern recognition techniques.

Figure 3 shows results obtained from the NNPC analysis. This representation of the primary three principal components shows a clear differentiation of the five studied substances (with different taste properties). The three principal components represented in the figure present a variance (information) of 87.5%, as expected, the first component (C.P.1) has the maximum information (54.0%); the second principal component (C.P. 2) contains 20.3% and the third principal component (C.P.3) only 12.8%.
Having tested the differentiation capacity of the electronic tongue, the instrument was used to analyze coffee samples. Samples were commercially acquired and represent five out of the most popular brands in Colombia. Each sample was analyzed with the sensor array and seven replicas were made for measuring. On the sensors’ response it could be observed that each sensor showed a particular response when exposed to each coffee sample. The response variety of the sensors, which reflects the high crossed selectivity of the array, is represented on figure 4. This response variety is due to interactions that take place among the different sensors and the sample compounds. Responses from each sensor vary from one coffee brand to the next. As for the case of simple substances with different analyzed taste properties in the preliminary assays, these differences are detected mainly by changes in the peak’s position and the variations in its relative intensities. This way, the data given by the electrochemical signals from the sensor array can be utilized to differentiate and classify coffee samples with no need to analyze its particular components.

From the registered signals, a data matrix was built which allowed classifying the coffee samples through an NNPC analysis. Figure 5 shows the resultant graph from the NNPC analysis done from the obtained data. The three primary and principal components summarize 87.0% of information; the first component collects a 53.9%, the second one a 23.6% and the third 9.7%. As observed, each of the clusters resulting from the analyzed sample are perfectly differentiated, consequently the sensor array allows to clearly classify the analyzed coffee samples. These results demonstrate that the developed electronic tongue instrument with polymeric sensors can be utilized to perform experiments on classifying coffee samples.

**4. Conclusion**

An electronic tongue elaborated from a polymeric sensors array was used to classifying coffee samples. The electrochemical responses to the analyzed samples were collected through an electronic instrument of multichannel measures (multi-potentiostat) which was able to differentiate a group of substances with different taste
Figure 3. NNPC analysis based on signals matrix obtained from substances with basic taste properties.
Figure 4. Electronic tongue registered signals against Córdoba coffee: (a) PPy/ AQDS, (b) PPy/DBS, (c) PPy/FCN, (d) PPy/HCF, (e) PPy/PWA y (f) PPy/PTS.
Figure 5. NNPC Analysis based on the electronic tongue response against commercial coffee samples.

properties. The classification of the substances was made through an NNPC analysis and the resultant graphic shows an excellent separation of clusters representing each studied sample. In addition, when this device was used with coffee samples, it showed signals that were converted to a samples’ fingerprint since each sensor provides a particular curve that can be used to differentiate the samples using NNPC. This opens the possibility of using these devices as the sensing units of an electronic tongue in the analysis of other beverages and sample types (water, drugs, beer, etc.).

Acknowledgements

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Quality Detection of Soybean Oil with Voltammetric Electronic Tongue

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Keywords: Soybean oil; Voltammetric electronic tongue; Kernel principal component analysis; Factor analysis; Partial least square.

Abstract. This paper proposes a reasonable methodology applied in classification and quantification techniques based on the voltammetric electronic tongue. We designed voltammetric electronic tongue oil sample pretreatment system with petroleum ether organic solvent. Through three-electrode system and cyclic voltammetry method processing blending soybean oil sample to get waveform output. Extracting crest methods as its feature extraction Pattern recognition use kernel principal component analysis and factor analysis blending on a different level of soybean oil. Partial Least Square (PLS) techniques was applied for data management and prediction models building, the prediction models are the blending ratio, the results show that voltammetric electron tongue can distinguish the quality of soybean oil.

Introduction

In recent years, the issue of food safety has increasingly become the focus attention, because food security influences our attention of the whole society [1]. Adulteration of food is very harmful for people’s health and this is a serious illegal behavior. During food adulteration, edible oil adulteration problem is very prominent that "waste oil" frequently appeared in China. Even more serious is recent reports found the new “waste oil”. Inferior oil seriously harms the interests of consumers. The soybean oil with soybeans as its materials have a large proportion in edible oil in China, therefore the soybean oil detection is very necessary. Voltammetric electronic has the advantages of simply operation, strong adaptability, high sensitivity and large amount of information. Now its has been widely applied in food engineering, biomedical, pharmaceutical, environmental measurements, and especially in the field of food testing has been applied to the green tea [2], milk [2], honey [4], eggs [5] detection field.

Experimental

The soybean oil sample brands are Jiansu oil and Jinlong oil, which was produced in Heilongjiang and Guangdong of China, brought them in Jilin supermarket, inferior oil was bulk and brought in Jilin wholesale market, the old oil is fried soybean oil. Each soybean oil select five samples for repeated measurement, mixing oil is made of high quality Jiansu soybean oil and bulk inferior oil with the proportion of 60%, 80%, 100%, 0%, 20%, 40%.

Structure of Electronic Tongue. The electronic tongue system is composed of the sensor array, electrochemical workstation, personal computer (PC), which is shown in (Fig.1).

The proposed method has three stages, skin segmentation to detect the hand, edge tracking for feature extraction, and particle filter for hand tracking. The overall diagram of our method is given in (Fig. 1).
The sense of smell known as olfaction is the largest gene family in the body, it has over 3% of the genes in the body dedicated to it. More than sight, sound, and taste put together The sense of smell is an electrical process, and together with the haptic sense of feeling the is an electro-sense in the body. The sense of smell is NOT directly wired to our verbal minds, but to our body electric.
SHARK SENSES ELECTRICITY
by Mary Ann Badavi & Stephanie Parker

A shark’s ampullae of Lorenzini are able to feel electric currents at short ranges.

All living things emit a small electrical current, a shark can feel it from 0-8 Hz.

The electro-sense in humans has evolved into the Olfaction shape detection sense. Voltammetric shape readings of various homeopaths are used to measure the Electro-Physiological-Reactivity (EPR) of patients.

The Electro-Sense is part of the Olfaction smell sense and it is not part of the Rectiulr Activating System, so the Electro Sense is Unconscious (non-verbal) and part of the subtle unconscious body electric beneath awareness.

Everybody has an Electro-sense It’s just not wired to the verbal mind.

Thalamus
Pineal Gland
Pons
Reticular Formation
Medulla Oblongata
Spinal Cord
Somatic Sensory Impulses (from nociceptors
Proprioceptors

The Bonnethead Shark has an electrosense that is five million times greater than the electro-sense of humans.

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11 Jan 2012
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**Communication: Alkaline phosphatase enzymatic signal amplification for fast, sensitive impedimetric DNA detection**
Miriam Kaatz, Holger Schulze, Ilenia Ciani, Fred Lisdat, Andrew R. Mount and Till T. Bachmann; *Analyst*, 2012, 137, 59-63
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APPARATUS FOR VOLTAMMETRIC ANALYSIS

The invention relates to apparatus for voltammetric analysis.

Voltammetric analysis is a widely used electroanalytical technique. The art of this technique has been well described in many publications [1,2]. Voltammetric analysis can be carried out using various waveforms, for example, linear, pulse, square and AC or using various operation modes, for example cyclic voltammetry and stripping voltammetry [3].


Saloheimo et al [7] introduced ultrasonic vibration during pre-electrolysis in stripping voltammetry. Other researchers have designed special electrodes for anodic stripping voltammetry [8-10].

Kissinger [11] predicted the future of electroanalytical instrumentation as being computerization, miniaturization and automation. Computers have been used to collect electrochemical signals [12], to acquire data and control experiments [13] and to modify waveforms [14]. Computerised voltammetric instruments are now commercially available from many instrument manufacturers.

However, computerised voltammetric instruments are generally large in size and costly. Small polarographic or voltammetric analysers are available for specific analytes, such as aldehyde [15] and lead [16]. Multi-element analysis using this type of equipment can be achieved by using multichannel selection [17] or multi-electrodes [18]. However, the number of elements that can be analysed is physically limited.

In addition, the process of voltammetric analysis often involves many decision making steps. Although computerised voltameters can run analysis automatically it is still necessary for the supporting electrolytes, calibration standards and experimental conditions, such as initial potential, final potential, scan rate and current range, to be chosen by an operator before the analysis commences. During analysis, voltammograms with peak currents or peak areas need to be acquired, and after analysis, the data requires processing and the results reported. These decision making steps require trained personnel with knowledge and experience.
Although they can be simplified into a computer program as demonstrated by De kreuk et al. [19] in an automatic stripping voltammetric method, as indicated by some researchers [20], automation of voltammetric instrument is a more complicated task than that of other electroanalytical techniques. Hence, automation is often at the level of operation rather than the decision making process.

Therefore, even computerized and highly automated systems still require skilled and experienced personnel to operate them.

In addition, conventional electrodes for voltammetry have the problem that it is difficult to ensure good electrical contact between the electrode and the electrical wire coupling the electrode to the analyzing equipment. In particular, with some types of electrode, such as glassy carbon, it is not possible to solder the electrical wire to the electrode.

Accordingly, conventional methods of electrically contacting the wire to the electrode include using mercury to bond the wire to the electrode or using conductive glue. Mercury has the disadvantage that it is toxic and the conductive glue has the disadvantage that it is not easy to disconnect the conductor from the electrodes.

In accordance with a first aspect of the present invention, apparatus for voltammetric analysis comprises a processor; a first memory device coupled to the processor, the first memory device comprising a programmable read only memory and storing a number of electrochemical cell control programs; an output device coupled to the processor; an input device coupled to the processor; a second memory device coupled to the processor; an electrochemical cell controller coupled to the processor, the cell controller being adapted to be coupled to an electrochemical cell; the processing device, in response to an analyte input signal entered via the input device, retrieving a corresponding electrochemical cell control program, and instructing the cell controller to apply a scanning voltage to an electrochemical cell coupled to the cell controller in use, in accordance with the retrieved control program, and processing output signals received by the cell controller from the electrochemical cell, in response to the applied scanning voltage, to obtain an indication of the concentration of an analyte, corresponding to the analyte input signal, in the electrochemical cell, and outputting the indication to the output device.

Preferably, the programmable read only memory is an electrically erasable programmable read only memory (EEPROM).

Preferably, the output device comprises a display device, such as a liquid crystal display (LCD). However, alternatively or in addition, the output device may comprise an interface device which permits the processor to communicate with another processing device, such as a computer, or with a storage device, such as a magnetic disk or tape drive.

Preferably, the cell controller includes a potentiostat and a signal processor.

Preferably, the apparatus is for stripping voltammetric analysis of an analyte in an electrochemical cell.
In accordance with a second aspect of the present invention, an electrochemical cell comprises a container comprising a bottom portion, an upper portion and an opening to permit a liquid to be analysed to be introduced into the container; a stirring device depending from the upper portion into the bottom portion of the container; and a counter electrode and a working electrode depending from the upper portion into the bottom portion of the container.

Preferably, the axis of rotation of the stirring device is substantially co-axial with the central vertical axis of the container and the counter and working electrodes are arranged around the stirring device.

Typically, the upper portion of the container, may be separated from the bottom portion of the container to permit liquid to be inserted into the container prior to engagement of the upper portion with the bottom portion.

Typically, the bottom portion may be in the form of a jar or other liquid containing device and the upper portion may form a lid for the jar or containing device.

Preferably, the electrochemical cell further comprises a reference electrode which also depends from the upper portion of the container such that the reference electrode is adjacent the stirring device and located between the counter and the working electrodes.

Preferably, the electrochemical cell is adapted to be used with the apparatus in accordance with the first aspect of the invention.

In accordance with a third aspect of the present invention, a coupling device for electrically coupling a conductor to an electrode for an electrochemical cell comprises a first conducting member; a second conducting member, electrically coupled and movably coupled to the first conducting member; and a biasing device to bias the first and the second member away from each other; the first conducting member being adapted to be coupled to an electrical conductor and the second member having an engagement portion adapted to engage with and electrically couple the second member an electrode for an electrochemical cell.

Preferably, one of the first and the second members is slidably located within the other of the first and the second members such that the engagement portion of the second portion is biassed away from the first member by the biasing device.

Typically, the second member is slidably located within the first member.

Preferably, the engagement surface of the second member is of a material which provides a low electrical contact resistance with the material of the electrode with which the engagement surface is to be engaged. For example, the material of the engagement portion may be a material which is harder than the material of the electrode, such as titanium or iridium, or a material which has a low susceptibility to oxidation, such as gold.
Typically, the first member may include an aperture in the first member adapted to receive a generally cylindrical electrically conducting member such that the conducting member when inserted into the aperture is electrically coupled to the first member.

An example of apparatus for voltammetric analysis in accordance with the invention will now be described with reference to the accompanying drawings, in which: Figure 1 is a schematic diagram of apparatus for voltammetric analysis; Figure 2 is a side view of an electrochemical cell for use in the apparatus of Figure 1; Figure 3 is a cross-sectional view of an upper portion of the electrochemical cell shown in Figure 2; Figure 4 is a front view of the upper portion shown in Figure 3; Figure 5 is a cross-sectional view of an electrode for use in the cell shown in Figures 2 to 4; Figure 6 shows the apparatus of Figure 1 incorporated into a handheld voltammetric analyser; Figure 7 shows the apparatus of Figure 1 incorporated into an on-line voltammetric analyser; Figure 8 is a flow diagram illustrating the operation of a diagnostic program for use with the apparatus shown in Figures 1, 6 and 7; and, Figure 9 is a graph showing calibration results and test results obtained using the analyser shown in Figure 6.

Figure 1 is a block diagram of voltammetric analysis apparatus 1 which includes a microprocessor 2, an electrically erasable programmable read only memory (EEPROM) 3, a display device 4 such as a liquid crystal display device, a memory device 5 which may be a random access memory (RAM), an interface device 6 such as an RS 232, a potentiostat 7, a cell controller 8, a signal processor 9, and an input device, such as a keypad 10.

The cell controller 8 is adapted to be coupled to an electrochemical cell 11 which is generally in the form of a container with electrodes 14, 15, 16 and a stirrer 17. An example of an electrochemical cell 11 suitable for use with the apparatus shown in Figure 1 is shown in more detail in Figures 2 to 4.

The interface device 6 permits the apparatus 1 to be linked to a computer, for example, to permit programming of the EEPROM 3 or to permit downloading of the memory 5 to a more permanent storage device in the form of for example, magnetic media such as a magnetic disk or tape.

The potentiostat 7 is coupled to the microprocessor 2 and generates a scanning potential which is modified with various waveforms such as DC, AC, square wave or differential pulse, in accordance with a chosen program downloaded from the EEPROM 3 to the microprocessor 2.

The cell controller 8 is coupled to the microprocessor 2 and contains a group of switches. According to the chosen program it will switch on or off the electrochemical cell 11 to allow potential generated by the potentiostat 7 to be applied to the electrodes 14, 15, 16 and to allow signals detected by the electrodes 14, 15, 16 to be received by the signal processor 9. It also turns on and off the stirrer 17.

The signal processor 9 is coupled to the microprocessor 2. In accordance with the chosen program it will receive signals from the cell 11, process the signals, convert them into digital information, and pass them to the microprocessor 2 to be stored by the microprocessor 2 in the memory 5.
As shown in Figure 2, the electrochemical cell 11 includes a container comprising a vessel 12 and an electrode holder 13 in the form of a lid for the vessel 12. The lid 13 supports a working electrode 14, a reference electrode 15 and a counter electrode 16 as well as the stirring device 17. The stirring device 17 comprises an electric motor 18 mounted on top of the lid 13, a drive shaft 19 extending through the lid 13 into the vessel 12 and a rotor 20 located at the end of the drive shaft 19 and adjacent to lower ends of the electrodes 14,15,16.

Typically, the stirrer 17 is a 0.1W stirrer and the vessel 12 is a glass bottle with a volume of approximately 20ml. The working electrode 14 may be a 3mm diameter disc glassy carbon electrode, the counter electrode 16 may be a 3mm x 3mm platinum electrode and the reference electrode 15 may be a Ag/AgCl electrode.

The reference electrode 15 has a conventional reference electrode construction. A cross-sectional view of the electrode construction for the working and counter electrodes 14,16 is shown in Figure 5. As shown in Figure 5, each of the electrodes 14,16 comprise an electrode sensing material 50 held in an electrode body 51. In the electrodes 14,16 the sensing material 50 is glassy carbon and platinum, respectively. The body 51 encloses a coupling device which comprises an outer casing 52, a contact pin 53 slidably mounted within the casing 52 and a biassing device 54 within the casing 52. The biassing device 54 acts to bias the pin 53 to an extended position in which a contact point 55 of the pin 53 is biassed against the sensing material 50 to make electrical contact with the sensing material 50. The pin 53, biassing device 54 and casing 52 are all electrically conducting and the end of the casing 52, opposite to the end from which the pin 53 extends, is electrically coupled to a wire 56 which couples the sensing material 50 to the controller 8.

In order to ensure a good electrical contact between the contact point 55 and the sensing material 50, the pin 53, or at least the contact point 55, is formed from a material which is harder than the sensing material 50. This helps ensure a good electrical contact as the contact point 55 “bites” into the sensing material 50. For example, the pin 53 could be manufactured from titanium or iridium.

The lid 13 of the cell 11 is shown in more detail in Figure 3 which shows a cross-sectional view of the lid 13 and Figure 4 which shows a top view of the lid 13. The lid includes a central through bore 21 through which the drive shaft 19 extends and four side through bores 22,23,24,25. The working electrode 14 extends through the bore 23, the reference electrode 15 extends through the bore 24 and the counter electrode 16 extends through the bore 25. The bore 22 is left empty and may be used for introduction of analyte and/or electrolyte into the vessel 12.

Due to the relative simplicity of the apparatus 1, the apparatus can be incorporated into a relatively small handheld analyser 30 as shown in Figure 6. The typical dimensions of the handheld analyser 30 are 40mm x 100mm x 200mm and the overall weight is typically approximately 0.5kg.

The handheld voltammetric analyser 30 incorporates the apparatus shown in Figure 1 with the exception of the electrochemical cell 11. In particular, the handheld voltammetric analyser 30 includes the LCD display 4, the keypad 10, the communication interface 6 and a port 31 which permits the analyser 30 be connected to an external power supply.
However, as an alternative to, or in addition to, the external power supply, the handheld analyser 30 may be powered by an internal battery, such as any form of suitable conventional rechargeable battery. Typically, the battery may be recharged by the external power supply via the port 31 when necessary.

The remainder of the components, including the microprocessor 2, the EEPROM 3, the RAM 5, the potentiostat 7, the cell controller 8 and the signal processor 9 are contained within the housing of the analyser 30.

The handheld analyser 30 also has a communication port 33 which is coupled to the electrochemical cell 11 in use and is coupled internally to the cell controller 8. This permits the cell controller 8 to control the scanning voltage applied to the electrochemical cell and to receive the output signals from the electrochemical cell in response to the applied scanning voltage. In addition, the handheld analyser 30 may optionally be connected through the interface 6 to a remote computer, for example, to transfer data to the remote computer and/or to be remotely controlled by the remote computer.

In addition, the apparatus shown in Figure 1 can be incorporated into an on-line voltammetric analyser 60 as shown in Figure 7. The on-line analyser 60 is coupled via the interface 6, local controller 34 and interface 35, to a remote computer 36 which is used to remotely control the analyser 60.

The analyser 60 and the local controller 34 are powered by a power supply 32 which may be battery operated or powered by a mains power supply 37. In the analyser 60, the key board 10 is omitted, as instructions may be entered into the analyser 60 via the remote computer 36. However, apart from the omission of the key board 10, the analyser 60 is identical to the handheld analyser 30, described above and shown in Figure 6. The on-line analyser 60 is coupled via cable 61 and connection port 33 to the electrochemical cell 11 and to metering pumps 62,63,64,65,66 which can be operated to pump liquid from reagent reservoirs 67,68,69, a sampling valve 70 and a rinsing water valve 71, respectively into the electrochemical cell 11. In addition, a vent valve 72 in the electrochemical cell 11 can also be controlled by the remote computer 36 or by local controller 34.

The liquid containing the sample to be analysed is connected to the sampling valve 70, clean water is connected to the rinsing valve 71 and standard reagents are stored in the reagent reservoirs 67,68,69. The vent valve 72 is used to empty the electrochemical cell 11 of liquid.

In use, the handheld analyser 30 and the on-line analyser 60 are set up by programming into the EEPROM 3 digital information corresponding to the configuration of the electrochemical cell 11 to be used with the analyser 30,60.

Such information includes details of the working electrode, reference electrode, stirrer and vessel. For example, typical information may be that the cell contains a 3mm diameter disc glassy carbon electrode, a 3mm by 3mm platinum counter electrode, a Ag/AgCl reference electrode, a O. 1W stirrer, a 20ml vessel and an electrode holder to fix each electrode position.
The second step is to formulate a reagent with a known composition as a testing media and convert it into digital information. The formulated reagent will contain a standard analyte, a buffer, a masking agent, a supporting electrolyte, a preservative and a performance enhancer. The standard analyte with known concentration is used to calibrate the cell. The concentration range is typically from 1 ppb to 1000 ppm. The buffer is used to control pH and usually contains a salt and an acid or a base. The masking agent is used to reduce interference from samples, which may be a complex agent, an organic solvent, a precipitation agent, a redox agent, a salt, etc. The supporting electrolyte is an ionic compound to provide conductivity. The preservative prolongs shelf life of the reagent. The performance enhancer can increase selectivity and sensitivity of the reagent.

A voltammetric analysis is then performed under fixed experimental conditions such as scan waveform, initial potential, scan rate, final potential, current range, etc.

This arrangement makes a voltammetric response position (potential) easily identifiable. The conditions can be obtained according to published papers, previous experience and expert knowledge. All data is converted into digital information.

Voltammetric response is searched for automatically by the analyser. The voltammetric response potential is determined for the highest current reading in a certain time period while voltammetric response current is calculated by subtracting background current from current reading. This procedure is programmed into the EEPROM.

System testing is then performed using the standard reagent.

As cell configuration, testing media and experimental conditions are fixed, voltammetric response to the analyte in the testing media should be a constant. Any significant changes of response potential or current will indicate system errors such as reference electrode failure or working electrode fouling. The purpose of the system testing step is to find and display these errors by comparing measured values with pre-set values. This procedure is programmed into the EEPROM.

The electrodes are then calibrated automatically.

Voltammetric analysis of the standard reagent is carried out in the testing media. The response potential and current is stored. This procedure makes sure that the electrodes are calibrated just before sample analysis so that the electrode surface condition remains unchanged. This calibration procedure is programmed into the EEPROM.

A test sample is then analysed. This is performed by voltammetric analysis of a test sample by mixing a known volume of the test sample with a known volume of the standard reagent. The response potential and current is compared with stored response for the standard reagent and the result is calculated and reported. This procedure is also programmed into the EEPROM.

The EEPROM also includes a diagnostic program which is illustrated schematically in the flow diagram shown in Figure 8. In particular, the diagnostic program checks the results of the
analysis to ensure that a peak current is detected in the voltammetric analysis. If the peak current is not detected, the microprocessor displays an error message in the LCD and stops the analysis. The diagnostic program also uses the reference potential value range stored in the data in the EEPROM and compares this with the peak current response at maximum intensity to check the reference electrode status. If the reference potential value is out of range, the analyser outputs an error message to the operator and stops the analysis. The diagnostic program also uses the reference current data in the EEPROM and compares this with the maximum response intensity obtained during analysis to check gain and working electrode status.

If the maximum response intensity detected is out of range of the reference current data, the diagnostic program causes the microprocessor to instruct the signal processor to change to a more suitable gain level and the analysis is continued.

If the diagnostic program detects that no gain is available, the microprocessor outputs an error message to the operator and stops the analysis. This permits the diagnostic program to optimise the signal collection potential range and current range which is stored in the memory.

In addition, the diagnostic program uses the reference data stored in the EEPROM which is compared with the actual peak current response obtained from the standard reagent to determine whether the peak current obtained from standard reagent corresponds to the peak current expected from the standard reagent. In the event that the peak current obtained is outside a certain deviation from the expected peak current, the microprocessor will output an error or warning message to the operator.

After programming of the EEPROM, the analyser can be used in conjunction with the cell to run a voltammetric analysis on a particular analyte. Initially, an operator turns on the analyser being used and enters the analyte to be analysed and the concentration of interest. The operator then formulates a standard reagent for the analyte of interest and adds this to the electrochemical cell through the aperture.

The analyser then conducts a test on the reagent to check the conditions of the system automatically.

After this test, electrode status and instrument readiness will be reported and some analysis conditions such as gain and peak position will be set automatically. Any system errors detected by the diagnostic program will stop analysis with correction instructions. This enhances the performance and reliability of the apparatus.

As soon as the instrument is ready, the system is calibrated automatically. During the calibration process, the system collects and processes raw data and stores a response which represents a known concentration of the analyte to be tested for in the memory.

After the calibration process, a fixed volume of the test sample is added into the cell and mixed with a fixed volume of the standard reagent. The system then collects and processes the voltammetric raw data again. The response which represents the concentration of the standard
plus the sample is stored in the memory. The microprocessor 2 performs a calculation to determine the concentration of the analyte in the test sample using the information from the calibration sample and the result will be reported and displayed.

An example of use of the analyser 30 and cell 11 to analyse the concentration of Cu2+ in a waste water sample will now be described. However, the analyser 60 could be used in the same manner to perform the analysis.

A standard reagent containing 2 ppm copper nitrate, 0.5 M acetic acid, 0.5 M sodium acetate and 20 ppm mercury chloride was prepared. The formulation of the reagent was digitally coded and entered into the EEPROM 3. In addition, a linear anodic stripping voltammetry scan was also programmed into the EEPROM 3 with the following conditions: (i) An initial potential of -0.8V; (ii) Pre-electrolysis for 30s; (iii) A scan rate of 100mVs⁻¹; (iv) A final potential of +0.5V; and (v) An electrode cleaning time of 20s at +0.5V.

10ml of the reagent was then introduced into the vessel 12 through the aperture 22 as a standard and the voltammetric analysis process was started using the keypad 10. When started the microprocessor 2 prompts a user via the display 4 to enter the analyte to be tested for. The operator in response to this enters "copper". The microprocessor 2 then prompts a user via display 4 for the concentration of interest and the user enters "1ppm" using the keypad 10. In response to this information, the microprocessor 2 selects the appropriate program stored in the EEPROM 3 for an analyte of copper with a concentration of interest of 1ppm and this is downloaded from the EEPROM into the microprocessor 2. The microprocessor 2 then runs the chosen program and in response to the program the microprocessor 2 generates control signals to control the output from the potentiostat 7 to the cell controller 8 and the signal processor 9 and the cell controller 8 directly. By causing the cell controller 8 to apply the pre-programmed linear anodic stripping voltammetric conditions (i) to (v) listed above which form part of the program downloaded from the EEPROM 3 into the microprocessor 2. The microprocessor 2 then analyses the test results and stores the results as a calibration.

After the calibration is completed, the microprocessor 2 prompts a user via the display 4 to add the actual test sample. At this point, the user replaces the 10ml of the standard calibration reagent with 5ml of the calibration reagent and 5ml of the waste water sample to be analysed. The operator then informs the analyser 30 using the keypad 10 that the cell 11 contains the sample to be tested and the analyser repeats the linear anodic stripping voltammetry scan under the same conditions as that conducted for the standard calibration sample.

The microprocessor 2 then compares the results of the test sample with the calibration sample and outputs the concentration of Cu2+ found in the test sample by means of the display 4.

In addition, an operator can subsequently or simultaneously download the results to the computer 36 for permanent storage and/or for graphical display and/or printing of the results.

A typical graphical display obtained from the analyser 30 is shown in Figure 9 for the above example. The graph shows the applied voltage versus the sensed current for the calibration...
sample (A) containing 1ppm Cu2+ ions and the waste water sample (B). It can be seen from the graph that sample B has a peak which is approximately 1.5 times greater than the calibration sample A indicating that the concentration of Cu2+ ions in the waste water sample B is approximately 2.2ppm. It should be noted that the same graphical display would be obtained using the analyser 60 for the analysis instead of the analyser 30.

In addition to copper, the apparatus 1 and electrochemical cell 11 can be used to detect concentrations of most ions.

Examples of typical ions that can be detected are ions of titanium, vanadium, chromium, manganese, iron, cobalt, nickel, zinc, gallium, germanium, arsenic, silver, cadmium, indium, tin, antimony, tungsten, platinum, gold, mercury, thallium, lead and bismuth, as well as organic compounds such as aromatics, aldehydes, alcohols, ketones, ethers, quinones, halides, heterocyclics, nitrocompounds, amines, phenols, organic acids and organic metallics.

In fact the apparatus 1 and the cell 11 can be used to detect any ion which can be detected using conventional voltammetry.

Concentrations that can be detected can be any concentration which can be detected using conventional voltammetric analysis, and typically any concentration in the range from approximately lppb to 1000ppm.

Inventors:
Dubounet, Desire’
Sirbu C.P.

Plaque It!

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OSIM Of Romania
M/11506
Publication Date:
Filing Date:
10/17/2006
View Patent Images:
Export Citation:
Assignee:
SCIO International, Oradea, Romania
Primary Class:
44: Service Medicale

QUANTUM QUALITY CONTROL
DOUBLE Q C
QQC (trademarked)
A DEVICE FOR TESTING THE TRIVECTOR ELECTRICAL SIGNATURE OF HOMEOPATHIC ITEMS

By Eclosion Kft, Budapest, licensed to SCIO International, Romania

Description of Device:

Thus device is designed to capture a polographic or voltammetric electrical signature pattern of a liquid compound. Electro chemical analysis of compounds is a tried and tested method of analysis. A review article is contained in the appendix.

The International Journal of the Medical Science of Homeopathy has published a series of articles on this technique. First the early process of analysis was heralded in 1997, and later reviewed in the 2005 volume. Copies of these articles are in the appendix.

The device uses a set of electrodes made of different metals. The different metals invoke an electro-potential. This variant electro potentials will vary the displaced electrons to reflect the electro potential variations to reflect the substance changes.

The device will send a low level variant current thru a substance to be tested. The changes in the potential are then measured thru this scale. A second pass will vary voltage and measure current variations.

Changes in the magnetic or inductance field will be measured. And changes in the dielectric or static field will be reflected in the measurement.

Thus an electro-magnetic-static picture will evolve from the test. Thus three dimensional reflection of the liquid crystal structure of the substance will be measured. This three dimensional field is termed the Trivector (trademarked).

The Trivector field reflects the electro-signature of any item tested.

Potential of measurement:

The system operates in a range of Voltages distributed from zero to four volts. The amperage current ranges from zero thru 4 milliamps. The system is designed to test substances not for patient testing.

Potential for Homeopathic Enhancement:

The QQC system can run an energy into a homeopathic substance to measure the electrical trivector voltammetric field or the energetic signature. The energy of the measure effects the tested entity and alters it. The QQC system can be used thus alter or improve a homeopathic. This is called the enhancement of the product. The zeta flickering rate of the water is effected, and the trivector field can be stabilized for use.

Portray of System
Atoms all have Protons and possibly Neutrons in the center with Electrons around the large Electrical-Magnetic-Static Charge they have that repels each other.

Atoms join to make Molecules by the need to fill the Outer Quantic Valant Shell. If they have low energy electrons in the outer shell they make simple IONIC bonds such as in the Mineral Kingdom. The Electrons of each atom making up a Molecule never touch each other because they repel each other.

What holds together the atoms and the molecules are Quantic Valant Attraction forces and Electro-Magnetic-Static fields. There is undeniably inarguably an energetic field around all Atoms and Molecules.

All Molecules interact with each other through their fields. The outer Electrons never touch, they repel to each other. All of biology is a study in field interaction. This is a basic scientific fact.

Voltammetry (Electro-Analytical-Chemistry) is the study the nature of the field of a substance and the shape of the interactive field.

Field lines of the van der Waals force between two atoms or molecules.

The van der Waals force usually causes things to stick; the force is attractive; and it acts only across short ranges.

This is a basic universally accepted form of science.

The Body Electric has many global important measures. These include Volts, Aamps, Resistance, Hydration, Oxidation, and Proton and Electron pressure. There are oscillatory norms of these values as well. The electrical vital signs. These are all easily measured and easily corrected in a cybernetic biofeedback loop. By interfacing with the body electric thru stimulus, response, correction and re-stimulation, we can try to normalize and stabilize the body electric. If we can reduce the causes of disease with behavioral medicine, provide good nutrition to supply needed homeostasis, repair the damage to organs, and unblock the blockages to energy flow, we have the start of a good truly modern medicine. Selye has proved that by reducing stress and the stressors we can advert the early progression of disease, and dramatically reduce degenerative disease. But this is drugless and threatening to the profits of the drug companies. We need to prefer people over profit.

The over emphasis on drugs (SNIthetic drugs) and surgery and the under emphasis on lifestyle has created a monster. The regulatory bodies, FDA, let Big Tobacco, Big Sugar, Big Pharma, run rampant while spending time and money on attacking safe, scientific, tested and effective natural medicines. This is a tragedy of modern times and profit corporations out of control.

We were all taught in Grade School that all things are made of atoms. They used the Rods and Balls analogy to teach us, but there are definitely no rods and no balls, just quantic energy states.

THERE ARE ENERGIES THAT HOLDS TOGETHER ALL SUBSTANCES

EVERYTHING IS MADE MOSTLY OF ELECTRONS AND PROTONS

THIS EVERYTHING HAS AN ELECTRICAL NATURE

Inside an atom

This computer-generated graphic shows how electronic charges are distributed across the surface of a molecule made of two cobalt atoms

Ionic Weak Bond

NaCl

Stronger Co-Valent

Sigma Bond

Empty space is not empty, but is filled with the quantum vacuum, with endless virtual processes. The energy of the quantum vacuum, the zero-point energy is infinite according to our present theories. Clearly, this infinity is an artifact - it would make the electromagnetic field infinitely massive, because energy and mass are related according to Einstein’s E=mc\(^2\). The empty electromagnetic field would collapse under the weight of its own gravity. Some unknown mechanism beyond quantum electromagnetism must regularize the infinity of the electromagnetic vacuum energy. Nevertheless, the zero-point energy results in perfectly finite and experimentally confirmed facts, for example the Casimir force.
We are taught chemistry with a poor rod and ball analogy. There are no Rods and no Balls, there are quantic energy fields. The Rods and Balls faulty analogy misleads us into a perception of how Synthetic Chemistry can assemble new molecules. The energy state of these molecules is different in nature than in the synthetic world. The Angel discovered this in 1982 and published the first book on Quantum Biology the Promorphes proving the incompatibility of the Synthetic Chemicals in Biology.

There are no Rods and no Balls!!!
Just energy fields

The Angel discovered that Quantum Electro Dynamics ability to describe the photon electron and proton interaction, means that the energy state of a natural made substance is different from the petrochemical SINthetic Chemistry of the Drug Co.

Modern science has de-emphasized the energy states of the electrons in glucose and the QED connection largely because it refutes the idea of SINthetic chemistry but the Angel noted the hypocrisy and has made a new medicine to help people. For this, the Drug Co. have attacked her.

Plants take in water, carbon dioxide, nutrients and photonic energy (light). They give off organic material and oxygen.

Animals take in the organic material and oxygen. They give off fertilizer nutrients carbon dioxide, water and photonic energy (body heat)

The Photosynthetic Organism can use the energy of sunlight to take electrons to higher energy states.

Sunlight + H₂O + CO₂ + Nutrients → Body Heat CH₂O₁ + O₂

Water Carbon Dioxide Nitrate NO₃ Phosphate PO₄

Iron Silicic

Organic Oxygen matter

The Sunlight comes in at wavelength of 400 to 700 nm and the body gives off heat radiation at wavelength 50 to 75 nm. The difference is the energy used for life. DNA gives off radiation and receives radiation in the infrared and visible light with just a touch of UV.

Desire used this advanced science for good.
To Make Medicine Safer the Angel has Made

The Quantum Quality Control

Electro-Chemistry Analyzer for the Analysis of the Trivector electrical signature of a biological or anti-biological substance.

Everything is made up of atoms with mostly electrons and protons. Everything has an electrical field and an electrical interaction with its environment. This 3D interaction can be measured with Voltammetry.

John Edward Brough Randles gave Desi inspiration and advice on the VoltAmmetric QQC
**Desire' Dubounet Patents**

- Irish Patent #S1995/0437. Grant# S67328 “Apparatus and method for detecting the reaction of a subject to a plurality of substances.”
- Irish Patent #S1994/0228. Grant# S60784 a homeopathic medicine
- Irish Patent# S1994/0084. Grant# S64087 a method for testing a homeopathic pharmaceutical
- Irish Patent# S1993/0215. Grant# S58223 a homeopathic medicine.

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**Clinical Review:**


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Selected publications


More publications

**Patents**


**Family list**

- 5 application(s) for: EP1636575 (A1)

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<th>VOLTAMMETRIC DETECTION OF METABOLITES IN PHYSIOLOGICAL FLUIDS</th>
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<td>LEE-DAVEY JON [GB] ; MALECHA MICHAEL MARKUS [GB] (+2)</td>
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<td><strong>Applicant:</strong></td>
<td>UNIV CRANFIELD [GB]</td>
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Invited Publications


Patents

• **Presentations**


  *53. “SECM Imaging with the TPM-Impedance (TPMZ) Mode,” David O. Wipf at the 4th Workshop on Scanning Electrochemical Microscopy (SECM) at Falcade, Italy September 3 - 6, 2006.


  *51. “Chemical Imaging Possibilities with Scanning Electrochemical Microscopy,” David O. Wipf at the South Dakota School of Mines and Technology, Rapid City, SD, June 20, 2005. *(Invited)*


  *47. “Multidimensional Imaging with Scanning Electrochemical Microscopy,” David O. Wipf at the University of Southampton, Southampton, UK, June 1, 2005. *(Invited)*


  *45. “New Imaging Possibilities with Fast-Scan Cyclic Voltammetry Scanning Electrochemical Microscopy,”David O. Wipf, M. Alpuche-Aviles (Mississippi State University), and L. Diaz-Ballote at the 205th Meeting of the Electrochemical Society, San Antonio, TX, May 9-14, 2004. *(Invited)*


• #*32.”Microscale Surface Chemistry with the Scanning Electrochemical Microscope,” David O. Wipf, at the XIV National Congress of the Mexican Electrochemical Society, August 24-28, 1999, Mérida, Yucatan, Mexico. (Invited)
• #*25. Local Modification of Electrode Surfaces by the Scanning Electrochemical Microscope,” D. O. Wipf, University of South Dakota, November 18, 1996. (Invited)
• #*24. Local Modification of Electrode Surfaces by the Scanning Electrochemical Microscope,” D. O. Wipf, University of Wisconsin - Eau Claire, November 15, 1996. (Invited)
• #*23. Local Modification of Electrode Surfaces by the Scanning Electrochemical Microscope,” D. O. Wipf, University of Southern Mississippi, October 25, 1996. (Invited)
• #*20. Local Modification and Imaging of Surfaces by the Scanning Electrochemical Microscope,” D. O. Wipf, April 4, 1996, presented at the University of Alabama, Tuscaloosa. (Invited)
• #*19. Local Modification and Imaging of Surfaces by the Scanning Electrochemical Microscope,” D. O. Wipf, March 8, 1996 presented at Illinois State University, Normal, IL. (Invited)
• #*13. Scanning Electrochemical Microscopy”, D. O. Wipf, Oct. 6, 1995 presented at Tennessee Technological University, Cookeville TN. (Invited)
• #*10. Initiation and Study of Localized Corrosion with the Scanning Electrochemical Microscope,” David O. Wipf, October 21, 1994, presented at Jackson State University, Jackson MS. (Invited)
• #*7. Scanning Electrochemical Microscopy” David O. Wipf, presented at the University of Mississippi, Oxford, MS, January 21, 1994. (Invited)


- Student and Collaborator Presentations


*39. “Visualization of the Electrochemical Activity of Silicon Carbide Particles in Aluminum Composites by Scanning Electrochemical Microscopy,” L. Diaz-Ballote,


*6. UV/Ozone Treatment to Activate Carbon Electrodes,” J. Zhou and D. O. Wipf, 47th Southeast / 51st Southwest Joint Regional Meeting of the American Chemical Society, Nov. 29-Dec. 1, 1995 Memphis, TN, No. 84

*5. Chemical Activation of Carbon Electrodes,” L. H. Bluhm+ and David O. Wipf, presented at the 27th Annual Southeast Regional American Chemical Society Conference of Undergraduate Student Chemists, Clemson, SC, March 16-17, 1995


• Theses and Dissertations


Declaration of Conformity of EU Class 1 regulations for Maitreya for QQC device

Address of Declaration: Kalvaria ter #2
Product: QQC voltammetry device
Identification: Model number: QQC model 0022
Device type: Voltammetry device to measure voltammetric signatures of remedies
Rating: 10mA
Safety rating: Class 1
Contact Person: Desire Dubounet

The above described product is made and tested to ISO quality standards for safety and efficacy in the European Union.
We at Maitreya declare that the product QQC 0022 is made to all European Requirements of safety and efficacy of voltammetry devices. All technical file details have been reviewed and observed.

January 2006

Signature: Desire Dubounet
Declaration of Conformity of EU Class 1 regulations for Eclosion for QQC device

Address of Declaration: Kalvaria ter #2
Product: QQC voltammetry device
Identification: Model number: QQC model 0022
Device type: Voltammetry device to measure voltammetric signatures of remedies
Rating: 10mA
Safety rating: Class 1
Contact Person: Desire’ Dubounet

The above described product is made and tested to ISO quality standards for safety and efficacy in the European Union. We at Maitreya declare that the product QQC 0022 is made to all European Requirements of safety and efficacy of voltammetry devices. All technical file details have been reviewed and observed.

January 2011

Signature: Desire’ Dubounet