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Voltammetric electronic tongues – basic principles and applications

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Abstract

This review examines basic principles and applications of voltammetric electronic tongues. It is introduced by a description of the concept of electronic tongues or taste sensors followed by a general overview of electrochemical measurement principles that have been used for electronic tongues. A special emphasis is given on measurement principles for voltammetric electronic tongues, also including pulse voltammetry and variable reduction. Applications of voltammetric electronic tongue are described, such as in the food industry, environmental analysis, paper and pulp industry, household appliances and agriculture. Future developments of the concept, such as self polishing or miniaturized devices are also described. Finally, a continuous measurement system for chemical oxygen demand (COD), which has been commercialized, is depicted.

Key words
Electronic tongue; voltammetry; taste sensor; amperometry; multivariate data analysis

Introduction

Since its introduction a decade ago, the interest for the concept of the electronic tongue[1,2] or taste sensor[3,4] has grown considerably, which is due to their large application potential. Basically, they consist of an information collecting unit for use in the aqueous phase, connected to a routine for multivariate data processing. When subjected to a sample containing different compounds, they will generate an output pattern that represents a synthesis of all the components in the sample. The output pattern is given by the different selectivities of the individual sensing units and is correlated to a specific taste or quality aspect. The basis of the technique, as for all concepts of artificial senses (e.g. the electronic nose), is that although the specificity of each sensor unit is low, the combination of several specificity classes entails a very large information potential.

The sensation of taste has two meanings. One denotes the five basic tastes of the tongue: sour, salt, bitter, sweet and “umami”, originating from different regions on the tongue containing specific receptors in the taste buds. The other meaning is the sensation obtained when the food or drink enters the mouth. The basic taste will then be merged with information from the olfactory receptor cells generated from aroma passing through the inner passage to the nasal cavity. This later taste sensation is referred to what is commonly known as the descriptive taste by sensory panels.

The so called taste sensor system[5] or taste sensor is an approach to specifically mimic the five basic tastes of the tongue. The so called electronic tongue on the other hand, classifies a quality of the measured sample, and the result is not necessarily applicable to the taste sensation of a human, it can also be correlated with some other quality property of the sample. The voltammetric electronic tongue belongs to this latter class.

General measurement principles

A vast number of electronic tongues and taste sensors have been described in the literature[1,6], based on different measurement techniques, the main part being electrochemistry such as potentiometry or voltammetry. Electrochemical techniques are very well established in analytical chemistry and have found a vast range of applications, there are also a number of textbooks covering the subject[7,8]. In potentiometry, a potential across a working electrode is measured when an equilibrium state is reached, corresponding to a state where the net current is equal to zero. Various membrane materials have been developed with different specificity properties. In common analytical chemistry, these types of electrodes are widely used for measurement of a large number of ions, such as pH, calcium, sodium and phosphate, nitrate and chloride. Potentiometry offer several advantages for use in electronic tongues or taste sensors, a large number of different both specific and less specific membrane materials are available such as glass membrane, solid crystals, membranes containing ionophores and lipid membranes. The taste sensor system[5] is based on ion sensitive lipid membranes, immobilized with polyvinylchloride. Also many other electronic tongue concepts have been described based on potentiometry, using different membranes or glass electrodes[9,10].

In voltammetry, a potential is applied to a working electrode, and the resulting current obtained when redox active species are reduced or oxidized on the electrode surface, is measured. Using voltammetry entails several advantages as being sensitive, versatile, simple and robust. Compared to potentiometry, voltammetry is less influenced by electrical disturbances and will thus have a favorable signal to noise ratio. Also, voltammetry offers a number of different analytical techniques, including cyclic, stripping and pulse voltammetry. Depending on the technique, various kinds or aspects of information can be obtained. 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 use of different type of metals for the working electrode, or stripping techniques. There are thus a number of possibilities available for obtaining information using voltammetry.

Measurement principles for voltammetric electronic tongues

In voltammetry, a potential is applied to a working electrode. The resulting current due to reduction or oxidation of a target analyte is then a measure of its concentration. Thus, if a red-ox active specie is reduced at the electrode surface, the reaction can be written:

$$\text{Ox} + \quad ne^- \quad \longrightarrow \quad \text{Red}^- \qquad (1)$$

where Ox is the oxidized form and Red is the reduced form of the analyte. At standard conditions, this redox reaction has the standard potential E_o. The potential of the electrode at equilibrium, $E_{electrode}$ can be used to establish a correlation between the concentration of the oxidized (C_o) and the reduced form (C_r) of the analyte, according to the Nernst relation:

$$E_{electrode} = E_o + RT/nF \ (\ln(C_o / C_r)) \qquad (2)$$

At the onset of a voltage pulse at the electrode, charged species and oriented dipoles will arrange next to the surface of the working electrode, forming a Helmholtz double layer[6,7]. Thus, a charging current will initially flow as the layer builds up which then exponentially decays until reaching the level for the redox current. This current flow, i_c, is similar to the charging of a capacitor in series with a resistor, and follows an equation of the form:

$$i_c = E{*}e^{(-t/Rs*B)}/ Rs \qquad (3)$$

where Rs is the resistance of the circuit (=solution), E is the applied potential, t is the time, and B is an electrode related equivalent capacitance constant.

The redox current, i_r, from electroactive species behaves in a similar way, initially a large current pulse is generated when compounds close to the electrode surface are oxidized or reduced, but decays with time. The current follows the Cottrell equation for a planar electrode[16-18]:

$$i_r = nFADC/(\pi Dt)^{1/2} \qquad (4)$$

where A is the area of the working electrode, D is the diffusion constant and C is the concentration of analyte. At constant concentration, the equation is simplified to:

$$i_r = K\,(1/t)^{1/2} \qquad (5)$$

K is a constant.

For voltammetric electronic tongues, pulsed voltammetry is often used. Most commonly used are large amplitude pulse voltammetry (LAPV) and small amplitude pulse voltammetry (SAPV), but also staircase voltammetry has been used. In large amplitude pulsed voltammetry, (LAPV), potential pulses are applied to the working electrode, with a zero potential in between. At the onset of the pulse current will flow to the electrode surface, initially sharp when the Helmholtz double layer is formed. The current will then decay until the diffusion limited faradic current remains, as depicted by the equations (3) and (5) and shown in Figure 1. The size and shape of the transient response reflect the amount and diffusion coefficients of both electroactive and charged compounds in the solution. At the onset of zero electrode potential, similar but opposite reactions occur, omitting the faradic current. In normal LAPV, successive potential pulses of gradually changing amplitude, between which the base potential are applied to the working electrode. A typical LAPV is shown in Figure 2.

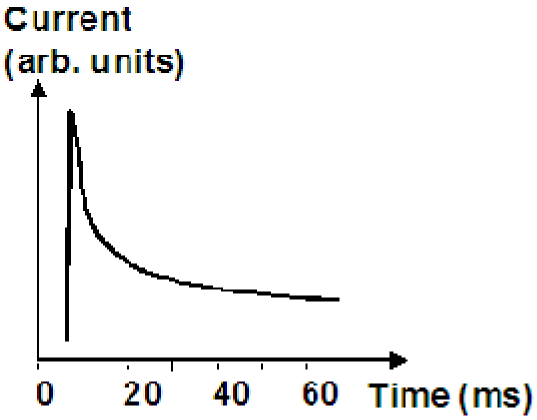

Figure 1: By the onset of a potential step, a current pulse will be formed due to migration of charged species to the electrode surface, thereby creating a Helmholtz double layer. The current will then decay until the diffusion limited faradic current remains.

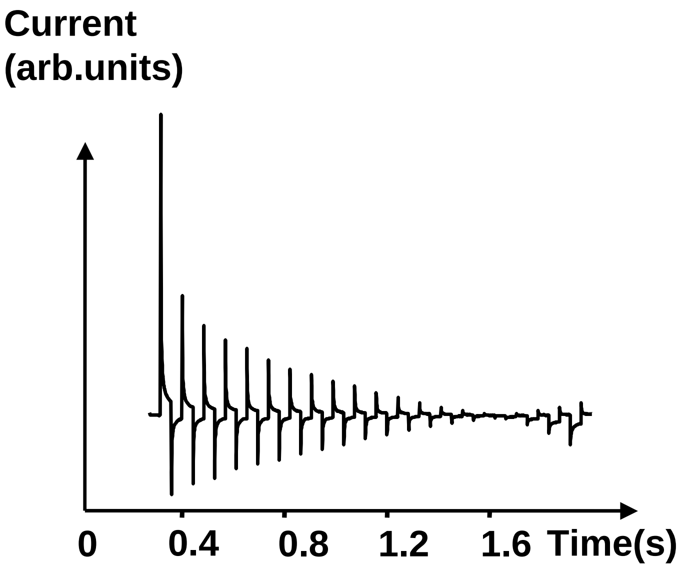

Figure 2: Recordings from large amplitude pulsed voltammetry (LAPV), in which potential pulses are applied to a working electrode, with a zero potential in between.

In small amplitude pulsed voltammetry (SAPV), a slow continuous DC scan is applied to the electrode on to which small amplitude voltage pulses are superimposed. This DC scan causes a change in the concentration profile of the electroactive species at the surface. Since only small pulse changes in the electrode potential are considered, this will result in small perturbations in the surface concentration from its original value prior to the application of the small amplitude excitation. Normally for SAPV, 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. This differential measurement gives a peaked output, rather than the usually obtained wavelike responses, and is often used in classic electroanalysis, called differential pulse voltammetry (DPV).

Variable reduction

During the signal analysis, a large amount of variables are collected to be able to correctly describe the shape of the current. For each pulse, up to 50 variables may be collected, and for a complete measurement series using up to 100 pulses applied to four electrodes, a total amount of up to 20000 discrete values can be collected. Most of them are redundant having a low level of information.

The shape of the current responses for LAPV follows in principal equation (3) and (5). This means that constants can be calculated that express the current response. In a first attempt, constants fitting equation (5) was calculated, and for a given application for classification of different teas, PCA showed that a better separation was obtained using these constants compared with original data[10].

It is also possible to use multivariate approaches, i.e. when PCA or PLS scores are used as descriptors in further multivariate data analysis. In hierarchical PCA, a large data set is divided into meaningful blocks, which is followed by a PCA to extract score values[11]. These are in turn combined to a new data set and PCA is the performed again.

Data compression of voltammograms obtained from amperometric sensors have also been achieved by employing discrete wavelet transform (DWT) followed by artificial neural networks (ANNs) [12, 13].

General applications and developments

The voltammetric electronic tongue was first described in 1997[14]. It consisted of a double working electrode (platinum and gold), an auxiliary and a reference electrode onto which both LAPV and SAPV were applied. In the first study, samples of different juices, milk and phosphate buffer were studied, and a PCA plot performed on the data showed good separation between the samples

After this first set-up, the voltammetric electronic tongue was further developed. A common configuration is shown in Figure 3, consisting of five working electrodes (gold, iridium, palladium, platinum and rhodium), a reference electrode and an auxiliary electrode of stainless steel. The working electrodes were embedded in a dental material in a stainless steel tubing. The wires from the working electrode were connected via a relay box to a potentiostat and a computer. Different types of pulsed voltammetry have been applied, LAPV, SAPV and staircase. In Figure 2, typical voltage pulses and corresponding current responses are shown.

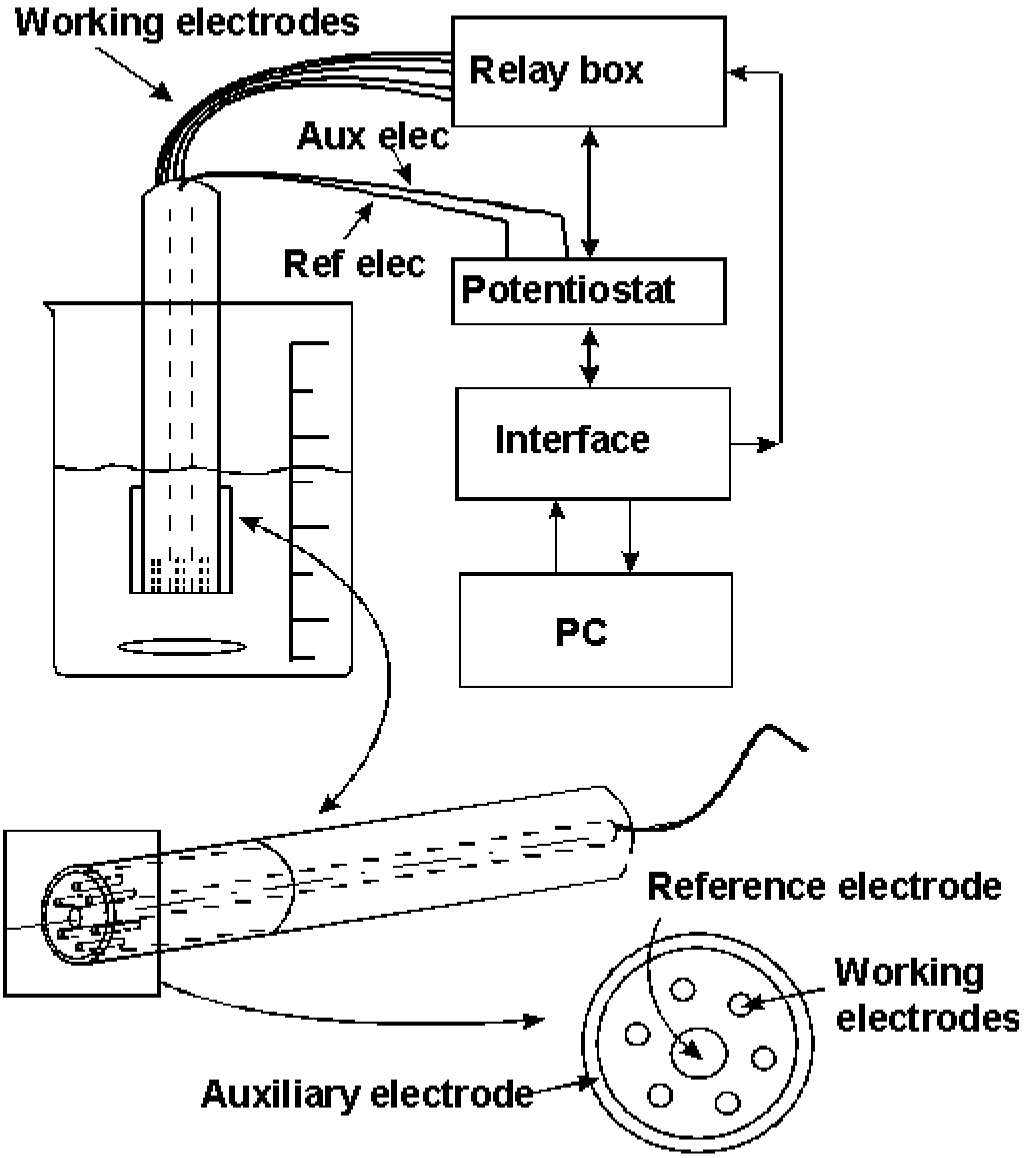

Figure 3: A common configuration of the voltammetric electronic tongue, consisting of five working electrodes a reference electrode and an auxiliary electrode of stainless steel. The electronic tongue is connected to a computer via a relay box and a potentiostat.

The voltammetric electronic tongue has been used for a large number of applications. Thus, the detoriation of milk due to microbial growth have been followed and correlated with colony forming units (CFU)[15]. Various types of teas could be separated[16], as well as different detergents[17]. The voltammetric electronic tongue has also been used for monitoring of drinking water quality, and a review has been published[18].

A voltammetric electronic tongue was used to discriminate between red wines aged in oak barrels and red wine matured in steel tanks in contact with oak wood chips[19]. The quality of the wine was also determined using conventional analytical methods. In another study, it was possible to successfully detect fraudulent red wines, obtained by adding a range of forbidden adulterants to red wine samples[20]. Studies have been performed on the aminoacids tryptophane, cysteine and tyrosine, with applications on direct measurement of these amino acids in animal feed samples[12,13]

A novel electrochemical method, multifrequency large amplitude pulse voltammetry (MLAPV) for electronic tongue has been employed[21]. The applied waveform of MLAPV comprised three individual frequency segments, 1 Hz, 10 Hz and 100 Hz. The electronic tongue was based on several metallic working electrodes, such as platinum, gold, titanium, nickel, palladium, a Ag/AgCl ref. electrode and a pillar platinum electrode as counter electrode for std. three-electrode systems. Six Chinese spirits and seven Longjing teas were successfully discriminated at different frequency segments.

The usefulness of modified electrodes were demonstrated in a system with two traditional Pt and Au electrodes, while the 3rd one was modified with poly(3,4-ethylenedioxythiophene) conducting polymer[22]

A Chinese yellow wine classification method was described based on chemometric analysis of voltammograms from a copper electrode in strong alkaline solution[23]. Six Chinese wine samples could be classified.

If the number of information sources is increased, also the quality of information will increase. This was demonstrated by the hybrid electronic tongue[24], based on the combination of the measurement techniques potentiometry, voltammetry and conductivity. It was used for classification of different types of fermented milk. The sensors in the system consisted of ion selective electrodes for pH, carbon dioxide and chloride ion, a conductivity meter and a voltammetric electronic tongue. The data obtained from the measurements were treated with multivariate data analysis based on PCA and an artificial neural net. Using individual information from either the ion selective electrode or conductivity meter, or from the electronic tongue, all but two of the fermented milk samples could be separated, but when merging all sensordata, all six different types of fermented milks could be clearly separated. Also, the composition of the microorganisms of the different fermentations was reflected in the PCA.

An integrated electronic tongue device has been developed[25], including a multiple light-addressable potentiometric sensor (MLAPS) and two groups of electrodes. The MLAPS was based on chalcogenide thin film for the simultaneous detection of Fe(III) and Cr(VI) while the electrodes detect other heavy metals using stripping voltammetry (SV). Applications include detection of heavy metal in wastewater or seawater

The voltammetric electronic tongue has also been used in measurement system, based on flow injection analysis (FIA)[26]. Thus, a reference solution was continuously pumped through a cell with the electronic tongue, and test samples were injected into the flow stream. FIA technique offers several advantages, the system is less influenced by sensor baseline drift, calibration samples can be injected within a measurement series, and the system is well adapted for automatization. The system was evaluated by repeated analyses of standard solutions of H_2O_2, KCl, $CuNO_3$, $K_4[Fe(CN)_6]$ and NaCl, and principal component analysis performed showed that electrode drift was considerably decreased. The set-up was also used for classification of different orange juices. This system has also been used for characterization and prediction of conductivity, pH and chemical oxygen demand (COD) of waste water coming from the paper mill industries[27]

Systems based on sequential injection analysis (SIA), have been described[28,29], based on three different enzymatic glucose oxidase electrodes and metallic catalysts electrodes. It was used for simultaneous determination of glucose and ascorbic acid. A similar (SIA) system based on 3 working electrodes, platinum, gold and epoxy-graphite disks were used for the quantification of ascorbic acid, uric acid and paracetamol.

A miniaturized electronic tongue, based on pulsed voltammetry has also been developed. It consists of three types of working electrodes (gold, platinum and rhodium) inserted in a platinum tube, acting as a counter electrode. The size of the miniaturized electronic tongue is 2 mm diameter and 4 mm length. Initial experiments on this miniaturized electronic tongue prototype have been performed for the determination of trace amount of cadmium and lead (in the μM range). Furthermore, the miniature electronic tongue has also been placed under the real tongue of a volunteer to follow the saliva composition during exercise.

A general problem using either potentiometric or amperometric electrodes are fouling. If the measured sample is relatively clean, such as drinking water, this causes no problem, but for measurements in more complex media, such as milk or process water from the paper and pulp industry, this will lead to fouling of the electrode surfaces, which in turn causes drift and eventually loss of sensitivity. Thus, electrodes must be cleaned and calibrated regularly, which especially for the process industry is time consuming and expensive. This is one reason why potentiometric and amperometric electrodes are not so frequently used. One way to surmount the fouling problem is to wash the electrode within the measurement cycles, an example of this is to use the voltammetric electronic tongue in a dishing and washing machine. The other way is to polish the electrode surface regularly.

Thus, self polishing voltammetric electronic tongues have been designed and built, either polishing the electrode surface continuously or at regular time intervals[30]. Studies of a number of samples, containing varying degree or purity, showed large improved performance. In principle, a self cleaning voltammetric electronic tongue is completely maintenance free, since a new surface is regularly created.

When combining the electronic tongue with stripping voltammetry, measurements of e.g. heavy metals can be made extremely sensitive. Thus, the concentration of cadmium could be determined down to a concentration of 1µg/L (corresponding to 9nM). This measurement procedure has been automatized in a FIA configuration, also equipped with a self polishing unit. With this system, cadmium concentrations have been determined in soil and flour samples.

The state of the art of the electrochemical sensors of the electronic tongue was recently revised[31], with a special attention to two families of compounds, the phthalocyanines and the conducting polymers.

Applications for the industry

The construction of the voltammetric electronic tongue is very robust, which is another reason that makes it suitable many in different areas of industrial applications. This quality is of especial importance in the food industry where the use of sensors made of glass, for example, is normally not accepted.

In the pulp and paper industry, an increased need of control of the wet-end chemistry of the paper machine is needed, due to the increased machine speed and system closure of the papermaking process. In this respect, the voltammetric electronic tongue has been used for evaluation on pulp samples concerning five reference parameters – pH, conductivity, COD, cationic demand, zeta potential[32]. The results also showed that the electronic tongue had very promising features as a general tool for wet-end control, due to flexibility, fast response and wide sensitivity spectra.

In household appliances like dishwashers and washing machines, informations concerning water quality, type of soil loaded and when the rinse water is free from detergents are very important for optimization of the dishing and washing efficiency, which thereby also will minimize water consumption. The voltammetric electronic tongue has shown useful for distinguishing between different standardized soil types, also at high levels of detergents added to the solutions[17]. It has also been used to follow the rinsing process in a washing machine[33].

An important industrial application for electronic tongues is as a monitoring device in drinking water production plants[1,6,18]. The quality of drinking water varies due to the origin and quality of the raw water and with efficiency variations in the drinking water purification process. A voltammetric electronic tongue was thus used for quality estimations of water samples from three parallel sand filters in a drinking water production plant. A PCA plot for the samples is shown in Figure 4. The raw water samples are well separated from the treated water samples in the plot. As can be seen from the plot, three of the slow filters work well, whereas one filter obviously starts to malfunction. Samples were collected and measured each week and the drift in filter 3 is clearly observed. Shortly afterwards, this filter was taken out of use for regeneration.

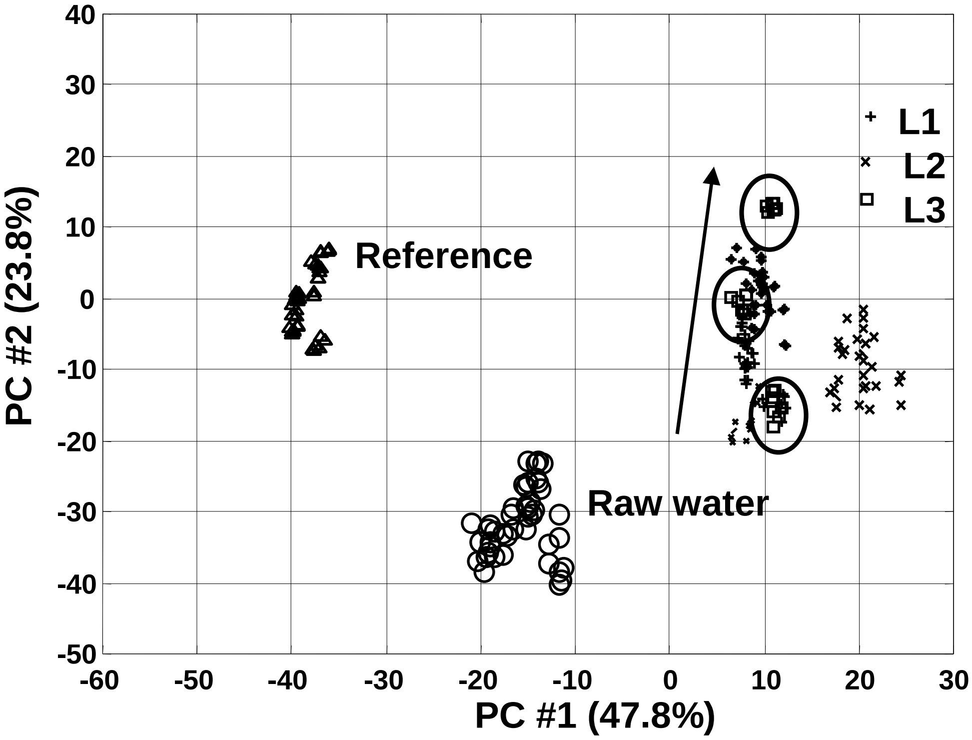

Figure 4: PCA plots from quality estimations of water samples from three parallel sand filters (denoted L1, L2 and L3) in a drinking water production plant using a voltammetric electronic tongue. As can be seen from the plot, the filter L3 (marked with squares) starts to malfunction. Samples were taken at three occasions with one week in between.

The voltammetric electronic tongue has also been used in the dairy industry. One application has been to follow the fermentation process in yoghurt fabrication[34]. In an other application, the electronic tongue was used to follow the dishing and cleaning process[35]. This is an important process in a dairy industry, since the inner wall of the stainless steel tubes transporting milk will be covered with proteins from the milk, which will have to be removed. This is especially important in the heat exchanger in the Pasteurization process. The dishing and cleaning process is performed by pumping hot (90^{o}C) acid followed by alkaline solution, also containing detergents, through the tubes. The cleaning efficiency was evaluated continuously by the electronic tongue, with an excellent performance during more than 6 months, free of maintenance. The reason for this good result is due to the robustness of the system and that the electrode surfaces of the electronic tongue continuously were cleaned by the hot dishing and washing solutions.

Other application areas are the use of the electronic tongue for detection of microbial activity [15,36,37], which is of especial importance for the food industry, either as unwanted microbial occurrence like pathogenic bacteria or mould or wanted microbial growth like for example in fermented foods. It has been shown that the voltammetric electronic tongue could follow growth of mould and bacteria, and also to separate between different strains of moulds. Similar results have been obtained from water from the paper and pulp industry, the detection limit was found to be 2 bacteria/100mL[39].

Commercialization

A company SensET AB[38] was founded in 2001 to commercialize the voltammetric electronic tongue. This company now offers a continuous measurement system for chemical oxygen demand (COD), which is an important environmental parameter. The main customers have been the paper and pulp industry, and systems have been in use for several years, giving correct predictions each fifth min of the COD concentration.

Conclusions

Since its introduction some ten years ago, the voltammetric electronic tongue has proven very valuable in a large number of applications in many industrial fields, as described in this contribution. Commercial systems for COD predictions have been used in the paper and pulp industry for several years. Although the technique is well established, it still has many development possibilities. Interesting areas include miniaturization, use of microelectrodes, development of continuous measurement system for heavy metal (e.g. Cd, Hg, Pb) directly on soil samples for the agriculture, measurement system for microbial activity and water quality.

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References

[1] Winquist F, Krantz-Rülcker C, Lundström I (2004) Electronic tongues, MRS Bulletin 29:726.

[2] Legin A, Rudnitskaya A, Vlasov Y, Di Natale C, Davide F, D'Amico A (1996) Tasting of beverages using an electronic tongue based on potentiometric sensor array, Tech Digest of Eurosensors X, Leuven, Belgium 427.

[3] Toko K, Hayashi K, Yamanaka Y, Yamafuji K (1990) Multichannel taste sensor with lipid membranes, Tech Digest 9th Sens Symp. 193.

[4] Hayashi K, Toko K, Yamanaka Y, Yamafuji K (1990) Multichannel taste sensor using lipid membranes", Sens Actuat B2:205.

[5] Toko K, (1996) Taste sensor with global selectivity, Mat Sci Eng C4:69.

[6] Bard A J, Faulkner L R (1980) Electrochemical Methods – Fundamentals and Applications, John Wiley & Sons, Inc.

[7] Wang J, (1994) Analytical Electrochemistry, Wiley-VCH.

[8] Legin A, Rudnitskaya A, Vlasov Y, Di Natale C, Mazzone E, D'Amico A (1999) Application of Electronic tongue for quantitative analysis of mineral water and wine, Electroanal 11: 814.

[9] Di Natale C, Macagnano A, Davide F, D'Amico A, Legin A, Vlasov Y, Rudnitskaya A, Selezenev B L (1997) Multicomponent analysis on polluted water by means of an electronic tongue, Sens Actuat B44:423.

[10] Artursson T, Spångeus P, Holmberg M, (2002) Variable reduction on electronic tongue data Anal Chim Acta 452:255.

[11] Holmin S, Spångeus P, Krantz-Rülcker C, Winquist F (2001) Compression of electronic tongue data based on voltammetry – a comparative study, Sens Actuat B76:455.

[12] Moreno-Baron L, Cartas R, Merkoci A, Alegret S, Gutierrez J, Leija L, Hernandez P, Muñoz R, del Valle M (2005) Data Compression for a Voltammetric Electronic Tongue Modelled with Artificial Neural Networks, Anal Lett 38:2189.

[13] Moreno-Baron L, Cartas R, Merkoci A, Alegret S, del Valle M, Leija L, Hernandez P R, Muñoz R (2006) Application of the wavelet transform coupled with artificial neural networks for quantification purposes in a voltammetric electronic tongue, Sens Actuat B113:499.

[14] Winquist F, Wide P, Lundström I (1997) An electronic tongue based on voltammetry, Anal Chim Acta 357:21.

[15] Söderström C, Boren H, Winquist F, Krantz-Rülcker C (2003) Use of an electronic tongue to analyze mold growth in liquid media, Int J Food Microbiol 83:253.

[16] Ivarsson P, Holmin S, Höjer N-E, Krantz-Rülcker C, Lundström I, Winquist F (2001) Discrimination of tea by means of a voltammetric

electronic tongue and different applied potential modes, Sens Actuat B76:449.

[17] Ivarsson P, Kikkawa Y, Winquist F, Krantz-Rülcker C, Höjer N-E, Hayashi K, Toko K, Lundström I (2001) Comparison of a voltammetric electronic tongue and a lipid membrane taste sensor, Anal Chim Acta 449:59.

[18] Krantz-Rülcker C, Stenberg M, Winquist F, Lundström I (2001) Electronic tongues for environmental monitoring based on sensor arrays and pattern recognition: A review, Anal Chim Acta 426:226.

[19] Apetrei C, Apetrei I M, Nevares I, Del Alamo M, Parra V, Rodriguez-Mendez M L, De Saja J A (2007) Using an e-tongue based on voltammetric electrodes to discriminate among red wines aged in oak barrels or aged using alternative methods, Electrochim Acta 52:2588.

[20] Parra V, Arrieta A A, Fernandez-Escudero J-A, Rodriguez-Mendez M L, De Saja J (2006) Electronic tongue based on chemically modified electrodes and voltammetry for the detection of adulterations in wines, Sens Actuat B118:448.

[21] Tian SY, Deng S P, Chen ZX (2007) Multifrequency large amplitude pulse voltammetry: A novel electrochemical method for electronic tongue, Sens Actuat B123:1049.

[22] Martina V, Ionescu K, Pigani L, Terzi F, Ulrici A, Zanardi C, Seeber R (2007) Development of an electronic tongue based on a PEDOT-modified voltammetric sensor, Anal Bioanal Chem 387:2110.

[23] Wu J, Liu J, Fu M, Li G, Lou Z (2005) Classification of Chinese yellow wines by chemometric analysis of cyclic voltammogram of copper electrode, Sensors 5:529.

[24] Winquist F, Holmin S, Krantz-Rülcker C, Wide P, Lundström I (2000) A hybride electronic tongue, Anal Chim Acta 406:157.

[25] Men H, Zou S, Li Y, Wang Y, Ye X, Wang P (2005) A novel electronic tongue combined MLAPS with stripping voltammetry for environmental detection, Sens Actuat B110:350.

[26] Winquist F, Rydberg E, Holmin S, Krantz-Rülcker C, Lundström I (2002) Flow injection analysis applied to a voltammetric electronic tongue, Anal Chim Acta 471:172.

[27] Gutes A, Cespedes F, del Valle M, Louthander D, Krantz-Rülcker C, Winquist F (2006) A flow injection voltammetric electronic tongue applied to paper mill industrial waters, Sens Actuat B115:395.

[28] Gutes A, Calvo D, Céspedes F, del Valle M (2007), Automatic sequential injection analysis electronic tongue with integrated reference electrode for the determination of ascorbic acid, uric acid and paracetamol, Microchim Acta 157(1-2).

[29] Gutes A, Ibañez A B, del Valle M, Cespedes F (2006) Automated SIA e-tongue employing a voltammetric biosensor array for the simultaneous determination of glucose and ascorbic acid, Electroanal 18:88.

[30] Olsson J, Winquist F, Lundstrom I (2006) A self polishing electronic tongue, Sens Actuat B118:461.

[31] Rodriguez-Mendez M L, de Saja J (2004) Voltammetric sensors as sensing units of an electronic tongue, Trends in Electrochemistry and Corrosion at the Beginning of the 21st Century, 475.

[32] Carlsson A, Krantz-Rülcker C, Winquist F (2001) An electronic tongue as a tool for wet-end monitoring, Nordic Pulp & Paper Res J 16:319.

[33] Ivarsson P, Johansson M, Höjer N-E, Krantz-Rülcker C, Winquist F, Lundström I (2005) Supervision of rinses in a washing machine by a voltammetric electronic tongue, Sens Actuat B108:851.

[34] Koller U Licentiate Thesis no. 859, (2000) “The electronic tongue in Dairy industry”, Linköping University.

[35] Winquist F, Bjorklund R, Krantz-Rülcker C, Lundström I, Östergren K, Skoglund T (2005) An electronic tongue in the dairy industry, Sens Actuat B112:299.

[36] Söderström C, Winquist F, Krantz-Rulcker C (2003) Recognition of six microbial species with an electronic tongue, Sens Actuat B: Chemical B89:248.

[37] Johnson H, Karlsson O, Winquist F, Krantz-Rülcker C, Ekedahl L-G (2003) Predicting microbial growth in pulp using an electronic tongue, Nordic Pulp & Paper Res J 18:134.

[38] SensET AB, Linköping Sweden, www.senset.se