ELECTRONIC TONGUES: ELECTRODE ARRAYS AND PATTERN RECOGNITION

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Received November 05, 2004. In final form June 04, 2005

Abstract

The current response of an array of different metal electrodes subjected to a train of voltage pulses can be used to classify and quantify liquid samples. The electrode array, together with proper signal evaluation and a pattern recognition method is called a voltammetric "electronic tongue". The principles of voltammetric evaluation of electrode arrays are discussed as well as the parameters in the liquid that are monitored by the method. Examples of applications of voltammetric electronic tongues are given to demonstrate their use in (industrial) processes. The examples include monitoring of water quality and an exploratory biomedical use of a miniaturized electrode. Finally some possible future developments will be speculated upon.

Resumen

La respuesta en corriente de una matriz de diferentes electrodos metálicos sujeta a un tren de pulsos de voltaje se puede emplear para clasificar y cuantificar muestras líquidas. La matriz de electrodos, conjuntamente con una correcta evaluación de la señal y con un método de reconocimiento de modelos se puede definir como una «lengua electrónica» voltamétrica. Se discuten los principios de la evaluación voltamétrica de las matrices de electrodos así también como los parámetros en el líquido que son monitoreados por el método. Se dan ejemplos de aplicaciones de lenguas electrónicas voltamétricas para demostrar su uso en procesos (industriales). Los ejemplos incluyen monitoreo de calidad de agua y un uso biomédico exploratorio de un electrodo miniaturizado. Finalmente, se especula sobre posibles desarrollos futuros.

Introduction

There is a growing interest in using multivariate signal processing on sensor signals from complex media in order to extract information. Thus, instead of using specific sensors for measuring single parameters, it is possible to get information of quality parameters, such as sample condition, state of a process or expected human perception of e.g. food. In this respect, the concept of electronic noses or electronic tongues has gained a large interest. These systems consist of an array of sensors with different selectivity patterns, a signal collecting unit and a pattern recognition software working on a computer. These systems are often referred to as artificial senses, since they function in a similar way to the human senses. One such system, the electronic nose, has gained a large interest and has been extensively studied [1, 2]. Recently similar systems have been developed for use in aqueous solutions. These systems are related to the sense of taste in a similar way as the electronic nose is to olfaction, thus, for these systems the notions “electronic tongue” or “taste sensor” have been coined [3, 4, 5, 6].

The sense of taste may have two meanings. One aspect denotes the five basic tastes of the tongue; sour, salty, bitter, sweet and “umami”. These originate from different, discrete regions in the tongue containing specific receptors called papillae. This aspect of taste is often referred to as the basic taste. The other aspect of taste is the impression obtained when food enters the mouth. The basic taste is then merged with the information from the olfactory receptor cells, when the aroma from food enters the nasal cavities via the inner passage. This merged sensory experience is referred to as the descriptive taste by sensory panels. The approach to a more specifically mimicking of the basic taste of the tongue is made by a taste sensor systems [3, 7, 8]. A taste sensor system is used to classify the different basic taste sensations. An electronic tongue on the other hand, classifies a quality of one or another kind in food, drinks, water, process fluids etc., and the results are not necessarily compared with human sensations, but with other quality properties of the sample. There is thus a difference between electronic tongues and as taste sensors. The concept of the electronic tongue and the taste sensor has developed rather fast during the last years. There are already commercial actors on the market and a number of applications have been reported [9, 10]. A voltammetric electronic tongue is developed in Sweden [11] and its applications studied together with the industry within the centre of excellence, S-SENCE, is to be described below.

The reason for the interest in electronic tongues can be summarized as follows:

- Many processes are best measured in solution,
- Complement to gas sensor systems (”electronic noses”),
- Interesting to combine different electronic senses,
- Based on well documented electrochemical methods further supported by a large industrial interest, examples of which are:
  - Paper and pulp industry: process water quality,
  - Dishwashers and washing machine producers: detergent dosage and rinsing water cleanliness,
  - Communal drinking water plants: filter quality and efficiency.

S- SENCE: Swedish Sensor Centre

The Swedish Sensor Centre is, since ten years, a centre of excellence in bio- and chemical sensor science and technology funded by the Swedish Agency for Innovation Research (VINNOVA), the industry and Linköping University. The main tasks of S-SENCE are to develop and evaluate bio and chemical sensors and sensor systems for industrial applications in close collaboration with industrial partners; to perform internationally competitive sensor research; to be a link between basic sensor research and the industry and to educate graduate students to fulfill the needs and requirements of industrial and academic employers. The present organization of S-SENCE and its science and technology basis are schematically shown in Figure 1. The figure shows the present member companies and their interest in the different research areas, denoted by gas phase applications, liquid phase applications and biosensor applications, respectively. The three application areas are supported by basic research activities as indicated in Fig. 1. Development of signal evaluation methods serves as a common platform to all application areas. The director of S-SENCE is Dr. Christina Krantz-Rülcker. The names of the senior persons responsible for the different areas are also given in the drawing.

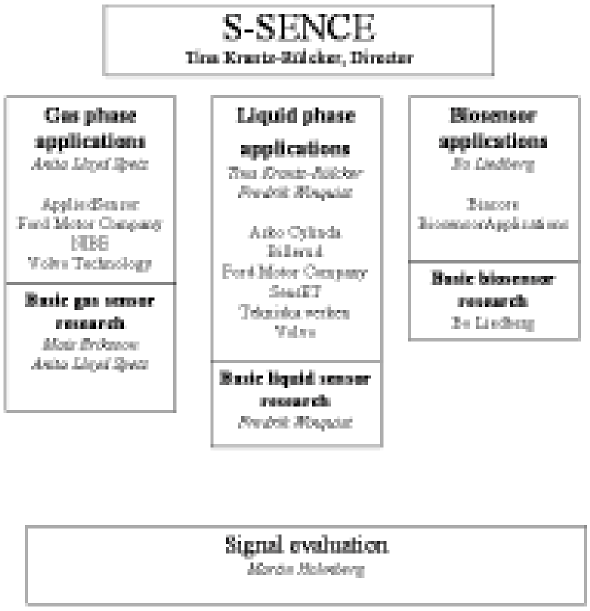

Figure 1: *Schematics of the organization of S-SENCE. The centre is located at the Division of Applied Physics, Department of Physics and Measurement Technology, Linköping University. It has its own budget supported by VINNOVA and industry, and by the university directly and indirectly through its infrastructure. Industry support is both in cash and through own labor ("in kind money")*

Voltammetric electronic tongues

The use of voltammetry in an electronic tongue has many advantages; the technique is commonly used in analytical chemistry due to its high sensitivity, versatility, simplicity and robustness. Besides, the technique offers the possibility to use and combine different analytical principles such as cyclic, stripping or pulsed voltammetry. Depending on the technique, various aspects of information can be obtained from the liquid sample studied. Normally, redox active species are being measured at a fixed potential, however, by using e.g. pulse voltammetry, transient responses when double layers are formed at the electrodes give information concerning diffusion coefficients (or mobilities) of charged species. Further information is also obtainable by the use of different types of metals as working electrodes. Three types of pulse voltammetry are commonly used, large amplitude pulse voltammetry (LAPV), small amplitude pulse voltammetry (SAPV) and differential pulse voltammetry (DPV).In large amplitude pulse voltammetry, the electrode (see Fig. 3) is held at a base

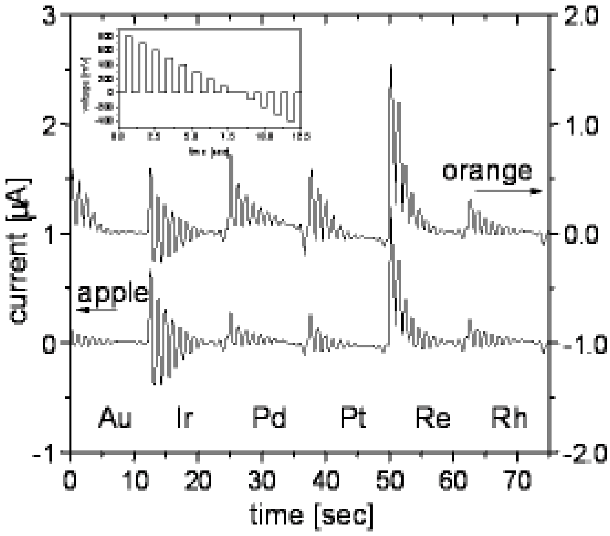

Figure 2: *Large amplitude pulse voltammetry. Current recordings from six different metal electrodes exposed to the voltage pulse train shown in the inset. Data are taken from the measurements on two different fruit juices.*

potential, at which negligible electrode reactions occur. After a fixed waiting period, the potential is stepped to a final potential. A current then flows when the double layer is formed. The current falls as the double layer capacitance is charged and electroactive compounds are consumed, the diffusion limited faradaic current remains. The size and shape of the transient response reflect the amount and the diffusion coefficients of the electroactive, charged compounds, in the solution. When the electrode potential is stepped back to its starting value an opposite charging current flows. The instantaneous faradaic current at the electrode is related to the surface concentration of electroactive compounds and to the charge transfer rate constants, it depends exponentially on the difference of the electrode potential between the start value and the final potential.

In small amplitude pulsed voltammetry the applied voltage has a staircase form. In differential pulse voltammetry, a slow continuous voltage scan is applied to the electrode on top of which small amplitude voltage pulses are superimposed. The currents of the electrode are here determined by the size of the initial step in voltage and the scan rate. Large charging currents are e.g. observed only at the initial step.

A recent configuration of the electrode system is shown in Figure 3. It consists of six working electrodes, a reference electrode (calomel) and an auxiliary electrode of stainless steel. The different metals used as working electrodes are gold, iridium, palladium, platinum, rhenium and rhodium. This one and other similar electronic tongues have been used in many applications. These include several studies related to the quality of food and drinking water, to the properties of liquids used in processes in the paper and pulp industry and to the classification of microbial species (see ref. [6] and references therein). Here we give the filters in a communal plant for purification of drinking water and a recently developed mini-electrode array for elucidation of the properties of saliva.

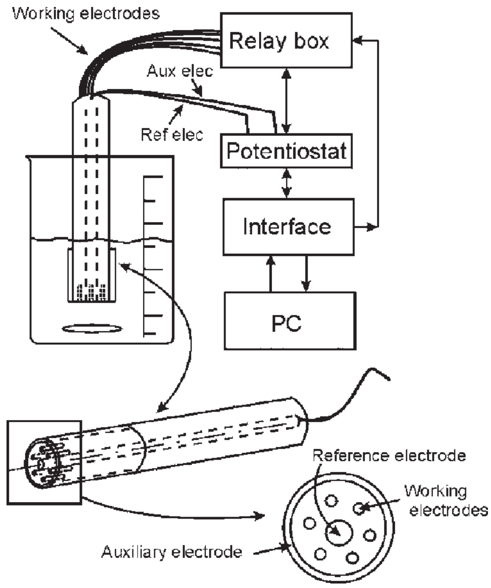

Figure 3: *Layout of a voltammetric electronic tongue with six working electrodes embedded in an insulating material, a reference electrode and an auxiliary (counter) electrode.*

Examples of applications

1. Monitoring of filters in a drinking water purification plant

The voltammetric electronic tongue has been used as a monitoring device in drinking water purification plants [12]. The layout of a drinking water purification plant is shown in Figure 4 together with a schematic drawing indicating the sampling locations of water analyzed with an electronic tongue of the design shown in Figure 3.

Water samples from eight parallel, so called slow (sand) filters, were collected and measured along with samples of raw water and water after the fast filter. The samples were analyzed with large amplitude pulse voltammetry and the resulting current, sampled every millisecond, used as the input variables for a principal component analysis. The initial findings were that the raw water samples were rather different from the samples after the slow and fast filters and those of the final drinking water, respectively. It was, however, also observed that water samples obtained after several of the slow filters cluster were similar to the samples taken immediately after the fast filter. This suggested that some of the slow filters did not work properly. The observation has been used in a study of the filters performance over several weeks in one of the production plants in Linköping. The results are shown as a PCA plot with time as an extra parameter in Figure 5. The most important conclusion from these experiments is that a voltammetric electronic tongue can be used as a “filter guard” in a drinking water sanitization plant. It is thus found that slow filters which cease to work properly, produce samples similar to those representing the water after the fast filter, and that slow filters after restoration produce samples well differentiated from those measured after the fast filters. A continuously updated PCA-plot would be very useful for a process engineer, as it can be used as an indication of disturbances in the plant.

2. Physiological measurements with a small electrode array

A miniaturized electronic tongue, based on pulsed voltammetry has also been developed. It consists of three types of working electrodes (gold, platinum and rhodium) and a counter electrode. In this case no reference electrode is used, which means that the exact potentials of the working electrodes are not known. For practical measurements this is not a limitation. The area of the counter electrode should, however, be large enough in order not to limit the currents flowing at any of the voltage pulses. The working electrodes, two of each type, are inserted inside the counter electrode, which consists of a platinum tube. A schematic of the mini-tongue is shown as an inset in Figure 6. Here we like to describe two possible applications of the mini-tongue, demonstrating some of its advantages, like measurements on small sample volumes and in-situ measurements in narrow places.

For measurements of heavy metals in small sample volumes, a drop of the samples, of 5 µL, is applied on top of the mini tongue. A voltage of –0.9 V is applied during 5 sec to the electrodes for deposition of the metal ions. The metal is then stripped off by successive pulses of increasing amplitudes in steps of 0.1V, each 100 ms long. Typical current spectra are shown in Figure 6.

For studies of saliva in mouth, the mini-tongue was carefully placed and fixed under the real tongue of a volunteer, in such a way that the edge of the mini-tongue was close to the opening of a saliva gland. Typical current responses are shown in Figure 7. Measurements were also performed every 10 seconds to follow changes during the exercise of the volunteer. Initially, the collaborator sat relaxed in a chair, and the currents were recorded six different times (i.e. during 60 seconds), then the volunteer made knee-bending exercises during two minutes, during which time pulse and breath rate increased substantially, thereafter, he was allowed to relax back again during seven minutes. A PCA-plot from the mini-tongue data (i.e. responses similar to those in Figure 7) is shown in Figure 8. The exercise starts around point 6 in the diagram, and ends at around point 18. Obviously, the change in the properties of the saliva, as followed by the mini-tongue, may be partially explained by the exercise, if we take into account that a certain delay is expected before the increased stress influences the saliva. It should, however, be stated, that this experiment could be carried out in a much more planed and careful way with experimental conditions better controlled. The experiment described was mainly made to illustrate the feasibility of the mini-tongue for the registration of changes in physiological parameters related to the properties of saliva.

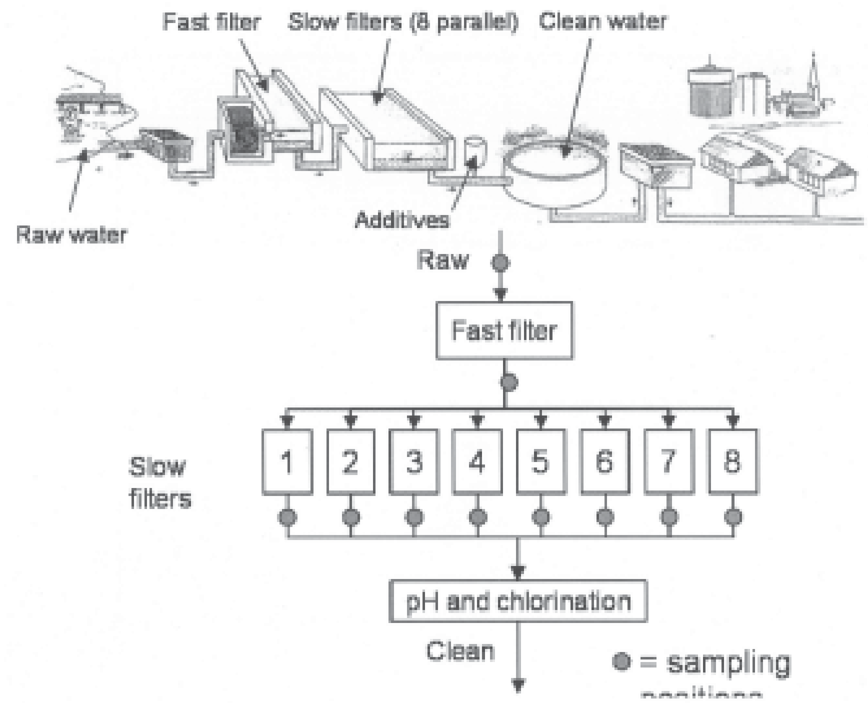

Figure 4: *Layout of a drinking water purification plant (upper drawing) and a schematic drawing showing the different sampling points used to test the performance of the plant with a voltammetric electronic tongue (lower drawing).*

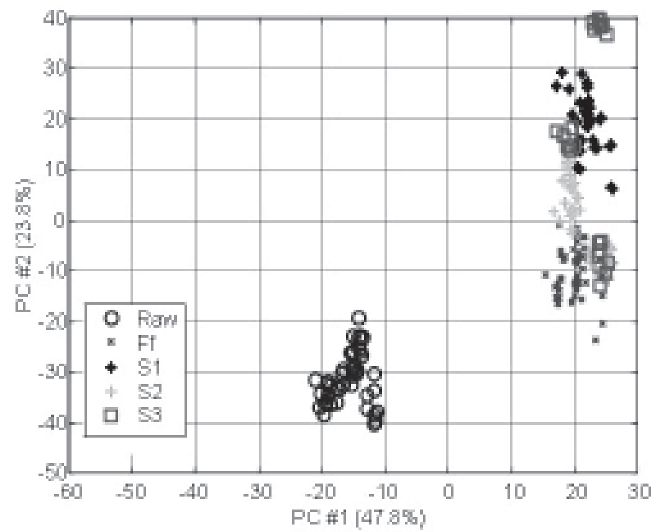

Figure 5: *PCA plot of water samples from a drinking water purification plant taken over a period of five weeks. Notations: Raw: raw water. Ff: water after the fast filter. S1, S2 and S3: water after three different slow filters. S1 represents a slow filter which was stable during the measurement period, S2 a slow filter, which drifted towards the cluster representing the water after the fast filter, and S3 a slow filter, which was initially not working well (cluster of squares close to the x's) and therefore restored during the measurement period (cluster of squares at the top: immediately after restoration, in the middle: at the end of the measurement period).*

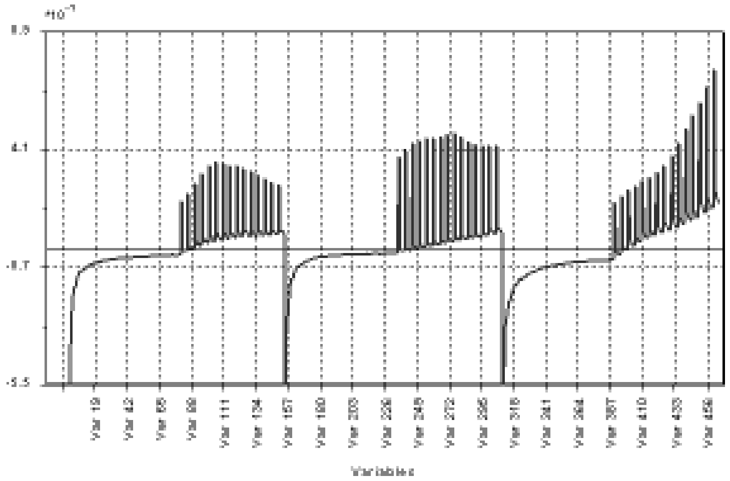

Figure 6: *Current spectra from a stripping experiment of cadmium. The y-axis shows the current in mA. The x-axis is the time, where 100 variables correspond to 7 seconds. One variable corresponds to one measurement of the value of the current. Wires of the three working electrodes (diameter 0.25 mm) are imbedded in a dental material in such a way that only the ends of the working electrodes are exposed. The opposite ends of the electrodes are connected by electrical leads to a potentiostat built at S-SENCE. The working electrode arrangement is inserted in the counter electrode, which consists of a platinum tube, 2 mm diameter and 4 mm long. The platinum tube is in turn inserted into a silicon tubing (2 mm diameter) covering the electrical connections and about 1 mm of the platinum tube.*

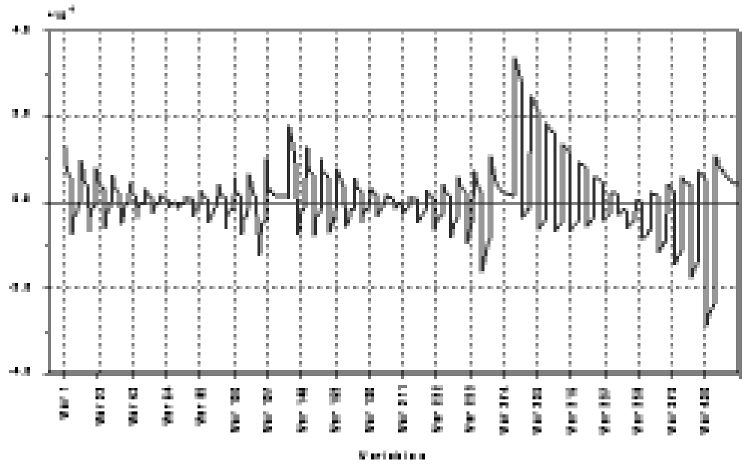

Figure 7: *Typical current spectra for saliva measurements. The y-axis shows the current in mA. The x-axis is the time, where 100 variables corresponds to xx seconds. One variable corresponds to one measurement of the value of the current. The spectra were measured with large amplitude pulse voltammetry (from a base line voltage of 0.8V to –0.5V, in steps of –0.1V, each pulse 10 ms long) for the three different electrodes used in the mini electronic tongue.*

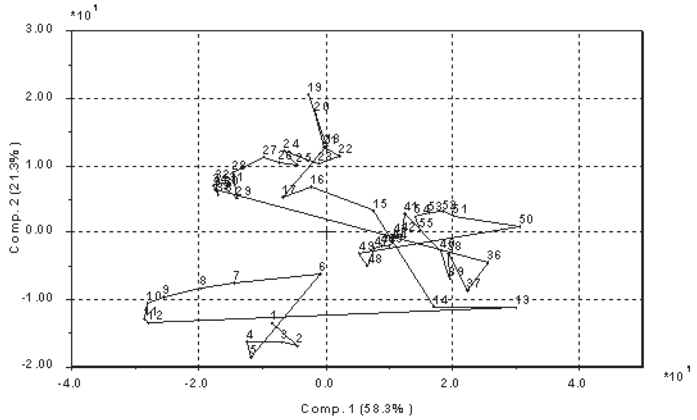

Figure 8: *Time dependent PCA plot of data from a mini electronic tongue placed in the mouth of a person making knee-bending exercises. One data collection was made each 10 seconds. During the 6 first measurements the test person rested. Knee-bending movements occurred during the next 12 measurements (i.e. for 2 minutes).*

Discussion

We have described the use of arrays of metal electrodes interrogated by voltammetry for the elucidation of the quality and performance of processes and products. One interesting observation is that (pulse) voltammetry is a well established technique and that the electrode arrays generate large data sets, suitable for modern pattern recognition models. Only two application examples were given. It should be stressed again that there are many more application areas for the electronic tongue [6]. A miniaturized electrode array was described in some detail. It was shown that a useful array can be made in a very simple way. The performance of this mini-tongue (Figure 6) compared to a conventional one (Figure 3) is equal, or even better if taken into account the small sample volume required and the possibility to measure at places normally not available with a conventional electronic tongue. This development opens up possibilities for measurements on saliva or tears with possible medical applications. Although not treated in this contribution, micro- and nano- sized electrode arrays are possible to be built not only of small sizes but also with new and interesting electrochemical properties, e.g. making measurements on less conducting systems, such as oils, fats and food stuff, possible. This is one area in which S-SENCE is presently engaged.

With nature as a model, electronic noses and electronic tongues represent biomimetic measurement methods. The biomimetic aspect should, however, not be taken too literally. The human senses are strongly connected in the brain and give rise to associations based on integrated previous experience. Also, in many cases, the sensor arrays do not even respond to the same molecules, which give rise to the human sensation. In many applications the sensor signal patterns contain themselves the information needed without any comparison with human sensory data. The examples given above are of that kind, where the output from the sensor array is compared directly with specific properties or correlated with particular states of a process or system. In such cases the electronic nose or tongue is calibrated with standard analytical techniques or through general diagnostic methods. In the development of biomimetic measurement methods, new achievements in both hard- and software will act together to improve the performance of sensor arrays. Also, for some of the techniques used, a very large number of data is produced, in most cases with a large redundancy. An efficient data evaluation method is therefore necessary in order to utilize the measurements in an optimal way. Further development of algorithms is therefore an important task especially for sensor arrays based on simple, but well investigated, individual sensors, like the different electrodes used in a voltammetric electronic tongue.

Acknowledgements

This work was done in the Swedish Sensor Centre, S-SENCE funded by the Swedish Agency for Innovation Systems (VINNOVA), Industry and Linköping University.

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