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Communication

Miniaturised multi-channel system of electrochemical measurements for an electronic tongue for milk samples

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Abstract: The development of a multi-channel system is described for electrochemical measurements as part of an electronic tongue fabricated using Programmable System on Chip (PSoC) technology. The purpose of this development is to offer the dairy sector a portable device that can perform the analysis of milk *in situ*. To obtain signals from a liquid substance, the acquisition circuitry acquires the signal using a variety of sensors, followed by the application of a technique known as cyclic voltammetry, which provides a characteristic pattern for each substance. During the testing, the system uses multivariate statistical methods to clearly differentiate between the characteristics of three types of milk, i.e. whole milk, semi-skimmed milk and lactose-free semi-skimmed milk.

Keywords: PSoC technology, electronic tongue, multi-potentiostat, milk analysis, electrochemical measurement

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INTRODUCTION

Due to the growing demand, the food industry has expanded its search for methods to aid in the quality control of food products. Among the technological alternatives that have emerged, the development of bio-inspired devices, such as electronic noses and tongues, is of particular interest [1-7]. One of the most reliable methods used for gustatory food inspection is the tasting panel, where the features (or organoleptic characteristics) that affect the sense organs are evaluated [8].

However, tasting panels are costly in terms of time and money and are potentially risky if the item being tested is unsafe.

An alternative is to use equipment to facilitate the gustatory evaluation of food products. However, this equipment is often based on laboratory instruments and is therefore difficult to transport to the field. The equipment employs electrochemical techniques for the acquisition of signals, which are then treated and processed by the computer, where the tested substances can be differentiated according to taste. Cyclic voltammetry is a very common technique used for the acquisition of signals in electronic tongues, in which a voltage that varies in the form of a ramp with respect to time is applied to a substance while the currents produced during the reaction are recorded. Plots of these currents with respect to the ramp potential are known as voltammograms. The signals that are acquired by this equipment are essential for recognising the taste, and the taste characteristics of the analysed substances in combination with the sensor material used to acquire the signals cause the captured signals to form unique patterns.

The equipment developed to provide these functions must also have the ability to apply cyclic voltammetry using various sensors with different chemical properties. This ability allows the resulting voltammograms to provide a larger amount of information about the analysed substance. In the literature these types of devices have been constructed from data acquisition cards for the analysis of coffee [9]. However, the process of designing and implementing miniaturised equipment such as this is complex. In contrast, the system discussed in this work is based on programmable system on chip (PSoC) technology, which consists of microcontrollers that include a range of reconfigurable analogue and digital blocks on a single chip [10]. These characteristics facilitate the straightforward implementation of complex circuits in a small space and differentiate the PSoC from other families of microcontrollers on the market [11]. There are several examples of successful implementation described in the literature [10, 12-17]. With this technology, our intention is to develop a portable electronic tongue for conducting electrochemical measurements of liquid substances using cyclic voltammetry techniques. The design incorporates multiple channels connected to a sensor array and serves as the signal processing stage for the electronic tongue.

MATERIALS AND METHODS

The electronic tongue we developed consists of an array of electrochemical sensors, a signal acquisition and conditioning stage, and a data processing stage for pattern recognition. The samples under analysis consisted of three milk samples: two commercial samples (semi-skimmed and lactose-free) and one of raw milk.

This work focuses on the development of a multi-channel system used for electrochemical measurements, which is part of the signal acquisition and conditioning stage. As mentioned previously, the multi-channel equipment applies the cyclic voltammetry technique to a substance through several channels connected to an array of electrochemical sensors. This process is explained below.

Multi-Potentiostat Circuit

The cyclic voltammetry technique can be implemented using a potentiostat, as shown in Figure 1. In the Figure, the technique is applied to a substance via three electrodes: the counter electrode, reference electrode and working electrode.

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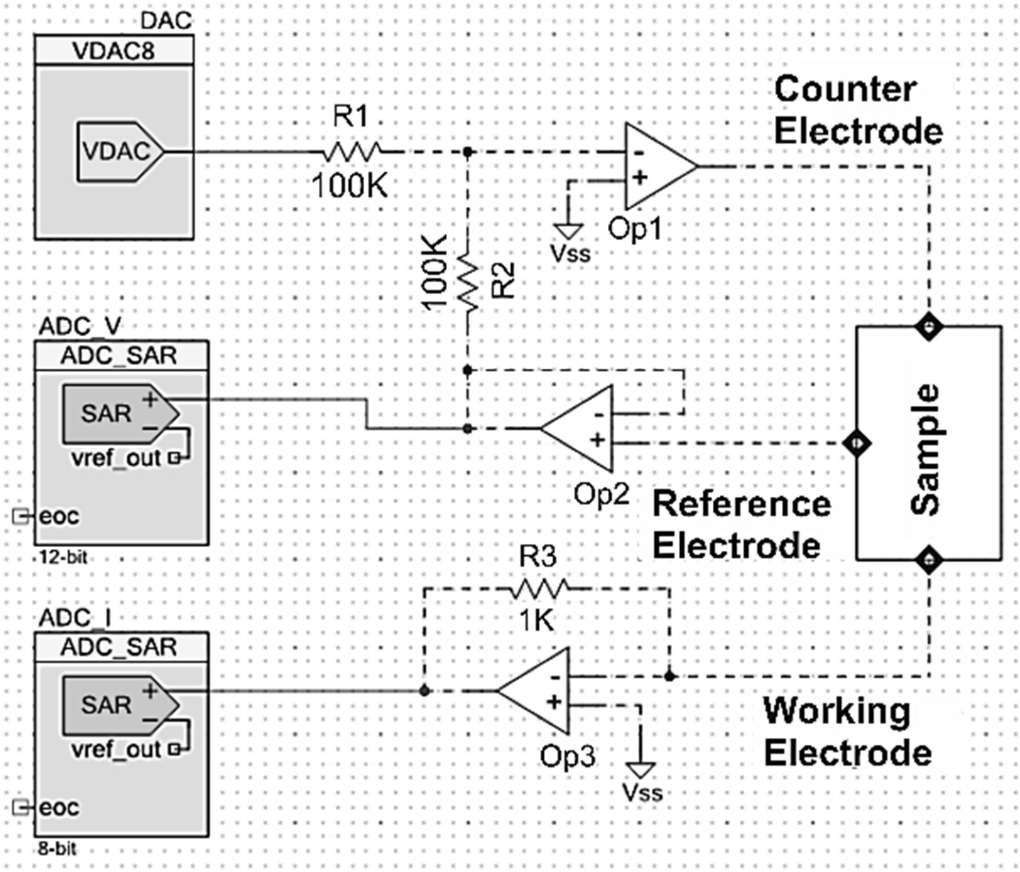

Figure 1. Simple potentiostat circuit

In the circuit of Figure 1, the potential difference between the reference and working electrodes is controlled from the auxiliary electrode. An array of closed-loop operational amplifiers is used to generate a potential between the reference and working electrodes that is equal to the input potential. This potential is a ramp that is generated from a digital-to-analogue converter (DAC), which generates a reaction that can be described by the currents flowing through the working electrode. Because microcontrollers are designed to accommodate voltage signals and not current signals, it is necessary to incorporate a block that transforms the current signals of the working electrode to voltage signals. This is the function performed by operational amplifier Op 3 and resistor R3 (1 KΩ). The output voltage of the Op-3 block is equal to the current of the working electrode divided by the resistor R3. The analogue voltage from Op 3 is acquired by the ADC_I component in order to process the current from the working electrode, and the analogue voltage from Op 2 is acquired by the ADC_V component in order to obtain the voltage signal from the reference electrode. The material of the working electrode causes the pattern of the output voltage to vary if a reaction occurs. Consequently, increasing the number of working electrodes and varying the materials used extract more information from the sample. In order to apply the cyclic voltammetry technique using multiple sensors, the signal acquisition equipment must support multiple channels. Figure 2 shows the proposed signal acquisition and conditioning scheme.

As shown in the Figure, the three working electrodes are connected to an analogue multiplexer with three inputs and one output "AMux". The latter is controlled by a software, and its function is to connect one of its inputs to its output. By sequentially selecting each multiplexer input, the different sensor signals can be sampled.

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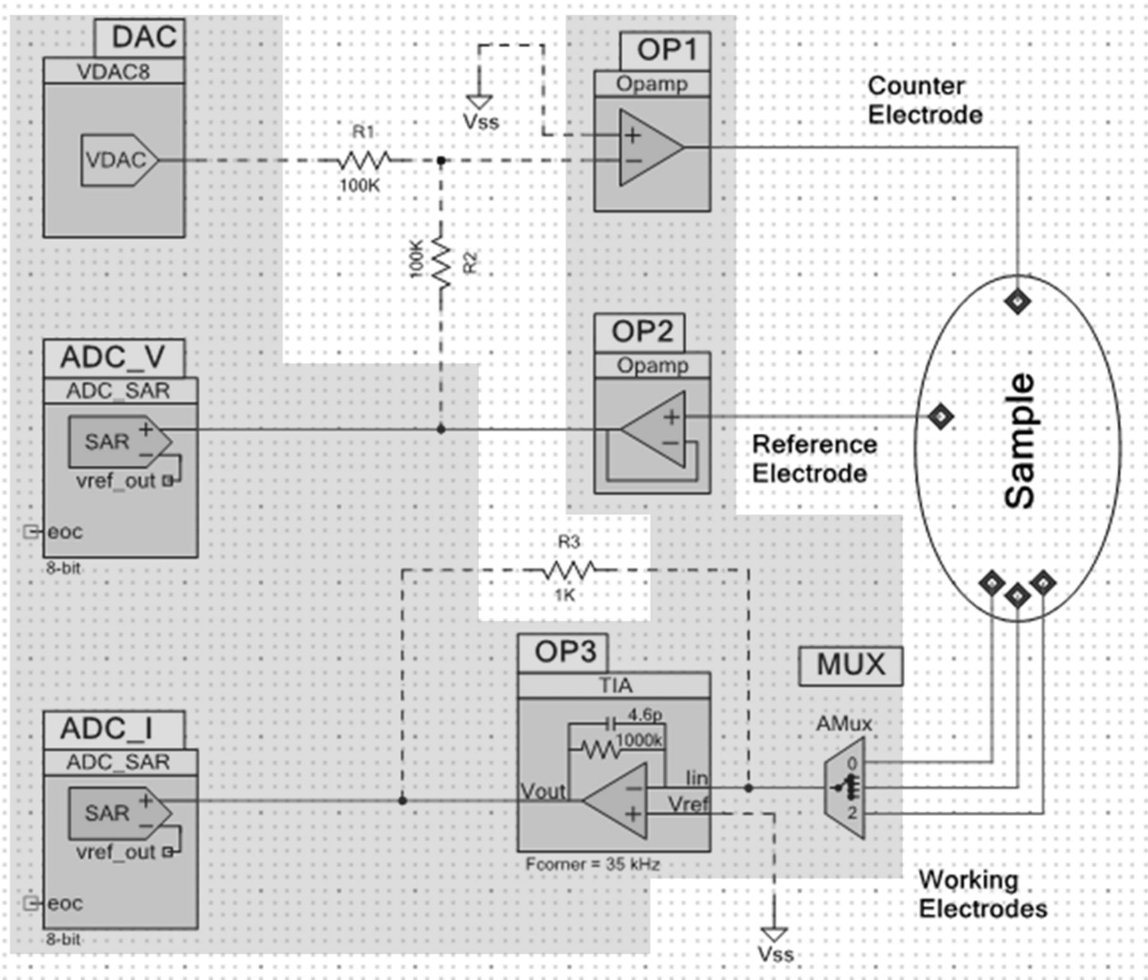

Figure 2. Multi-potentiostat circuit with PSoC blocks (shaded area)

Signal Acquisition

As also shown in the Figure, two analogue-to-digital converters, 'ADC_V' and 'ADC_I', were used to acquire and communicate with the voltammetric signals. These were connected to the multi-potentiostat to acquire the voltage at the reference electrode and the current at the working electrode.

Registration and Data Processing

The block (not shown in Figure 2) used for processing the data obtained from the potentiostat is briefly described. A software program was developed to connect to the circuit via Bluetooth and graphically plot the acquired current versus voltage value to generate the voltammetric signals representing the information about the analysed substance.

The program was designed to store all data in a "txt" file format that can then be opened using a mathematical processing software. Finally, an algorithm was designed based on a statistical method known as principal component analysis, which is used in pattern recognition. The result is that the system is able to compare two sets of sample data and discriminate between them according to their chemical and organoleptic characteristics.

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RESULTS AND DISCUSSION

The multi-channel system developed in this work incorporated three sensors, each of which consisted of three electrodes, namely the counter electrode, reference electrode and working electrode. Each working electrode was electrochemically modified to give it the ability to provide more information about the analysed substances. Initially, the sensors used were inorganic working electrodes (platinum). Then the electrodes were modified using a technique known as chronoamperometry, in which polypyrrole (PPy) was electrodeposited on the surface of the working electrode for a pre-determined time. The surface modification was made with PPy and different doping agents in an aqueous medium. The dopants used were lithium perchlorate (PL), lithium sulfate (SL) and sodium dodecylbenzenesulfonate (DBS). The modified sensors consisted of PPy/PL, PPy/SL or PPy/DBS, depending on the dopant used. In addition, three commercial milk samples were used: whole milk, semi-skimmed milk and lactose-free semi-skimmed milk. The assembly scheme used for the collection and processing of data is shown in Figure 3.

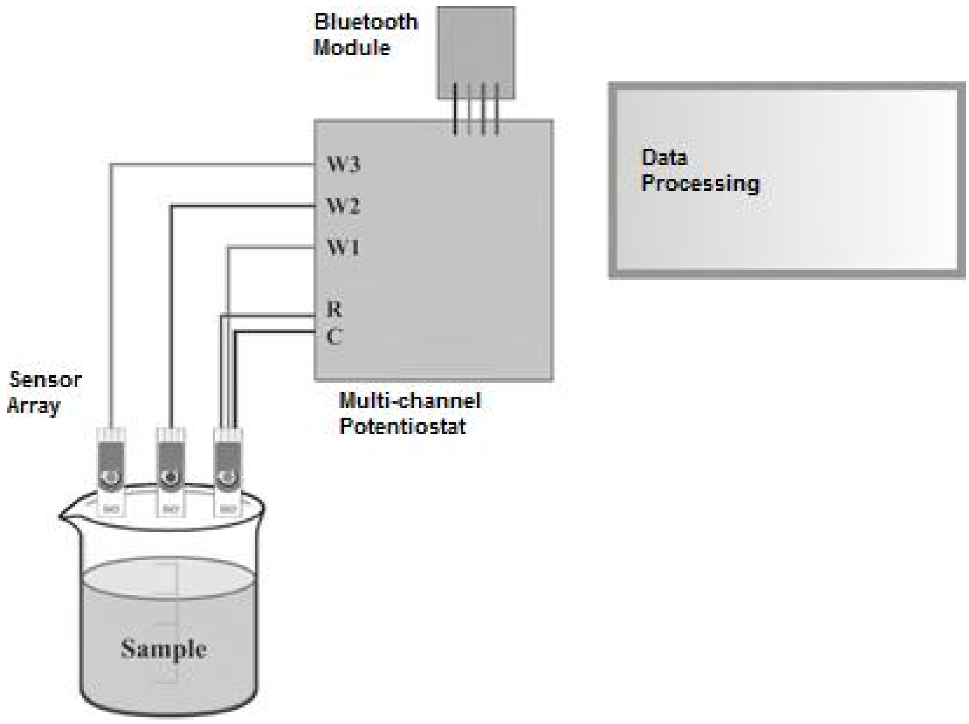

Figure 3. Mounting system for data collection

As can be seen in Figure 3, two of the sensors are connected via only their working electrodes W2 and W3, while the remaining sensor was connected through all three electrodes (working electrode W1, reference electrode R and counter electrode C). This configuration was used to obtain the voltammetric signals that corresponded to the studied milk samples. Figure 4 shows the different voltammograms obtained by one of the sensors that was modified with PPy / DBS for the different samples. The measurements were made in the milk samples without any type of pre-treatment. Registered voltammograms show the redox electrochemical processes that occur in the sensors and that reflect the interaction of the sensors and the milk samples.

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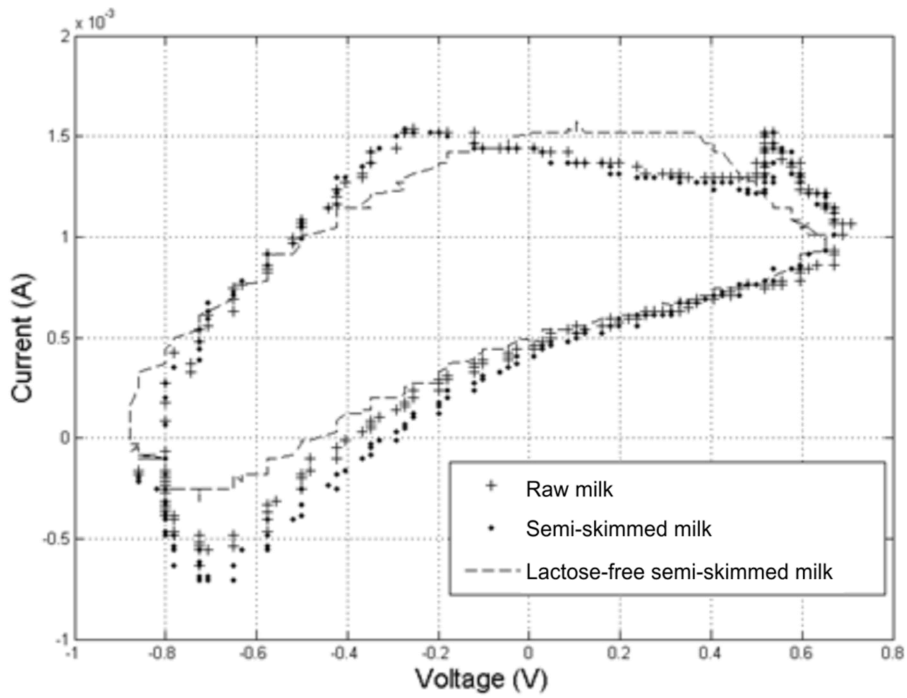

Figure 4. Voltammograms obtained for different milk samples using PPy / DBS sensor

The three voltammograms obtained by this sensor demonstrate the ability of the system to provide different curves for substances with different taste properties. Figure 4 shows the response of the PPy/DBS sensor to the three different milk samples, and a distinct sensor response for each sample can be seen. Multivariate statistical methods can then be employed to determine patterns that can be used for discriminating between them.

To evaluate the discriminating ability of the system for the milk samples, five replicas of each measurement were created. The resulting data matrix was treated by principal component analysis to reduce the number of variables. The result is presented in Figure 5.

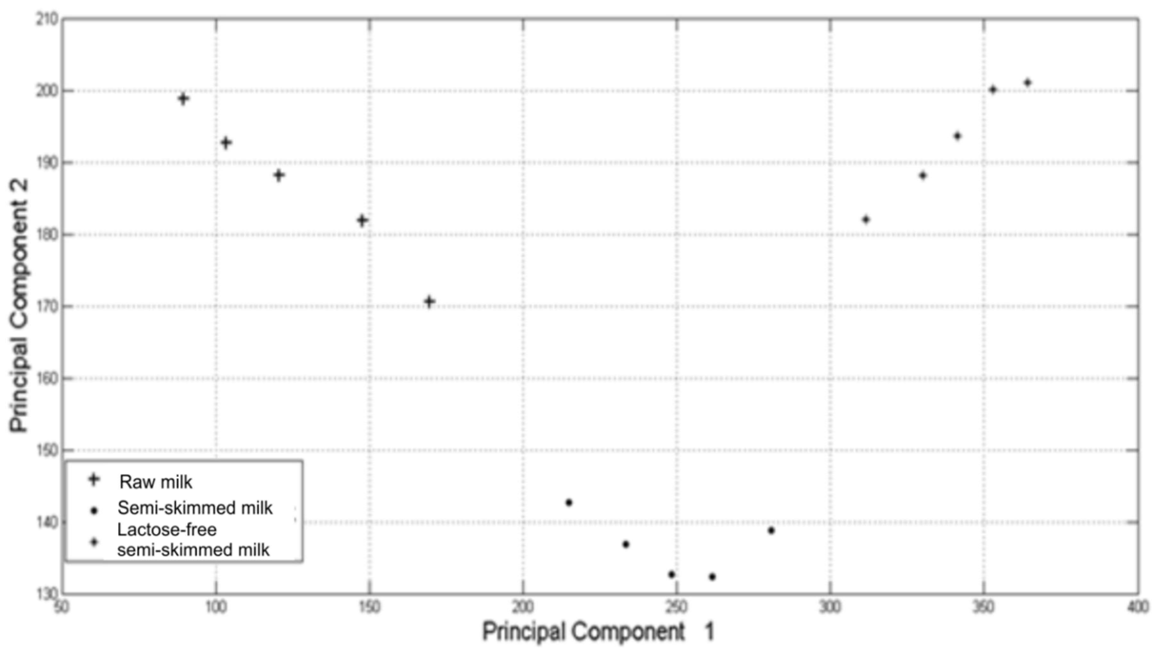

Figure 5. Principal component analysis of data matrices of milk samples

As shown in Figure 5, the electronic tongue is able to differentiate between the milk samples based on their different chemical characteristics. These results demonstrate that this device meets requirements that are essential for quality control in this industry. In addition, the small size and high performance of the device means that it has the potential of being used in the field to inspect milk quality.

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