Full Paper

A Portable Sensing System for Electronic Tongue Operations

Karen Twomey [1],*, Andreas Truemper [1] and Kilian Murphy [2]

1 Biomedical Microsystems, Tyndall National Institute, Prospect Row, Cork, Ireland;
E-mail: Karen.Twomey@Tyndall.ie; Andreas.Truemper@Tyndall.ie
2 AMT Ireland, Food Science Building, University College Cork, Ireland;
E-mail: K.Murphy@UCC.ie

* Authors to whom correspondence should be addressed; E-mail: Karen.Twomey@Tyndall.ie

Abstract: A portable, low cost sensing system is described which interfaces to an electronic tongue sensor. The sensor used is a voltammetric sensor which monitors electrochemical reactions that occur in solutions. The sensor is able to test a range of liquids with different electrochemical properties without any hardware adjustments to the system. The system can automatically adjust for the change in solution properties by performing a routine which uses an auto-ranging feature to determine a current-to-voltage conversion of the sensor data by using a binary search strategy. This eliminates the intervention of the user to modify the system each time a new solution is tested. The effectiveness of the calibration routine was tested by carrying out cyclic voltammetry in two different solutions, 0.1M sulfuric acid solution and the phosphate buffered solution of pH3. The sensor system was able to accurately acquire the sensor data for each solution.

Keywords: electronic tongue, voltammetry, working electrode, counter electrode, reference electrode, potentiostat.

1. Introduction

It has become more typical in recent years to apply a multi-sensing approach in the collection and processing of information. Instead of measuring single parameters using specific sensors, it has become, in many cases, more desirable to get information on attributes such as quality. One example would be the analysis of a complex media where a quantitive analysis is not possible or is difficult to obtain. Electronic noses (EN) and electronic tongues (ET) incorporate this multi-sensing approach.

Exact definitions of EN and ET vary but here they are regarded as consisting of an array of sensors with associated circuitry and data analysis techniques. ENs have been investigated for use in areas such as the food industry [1-4], agricultural [5], environmental [6, 7] and medical [8-10]. Sensors typically used for EN operation include metal oxide semiconductors, conducting polymers, quartz crystal microbalance and mass detection based sensors [11]. The EN mimics the human olfactory system in its ability to discriminate between varieties of odors [12]. On the other hand, the ET, as the name suggest, mimics the sense of taste. This has found application where liquids/fluids require analysis e.g. the food industry [13-16], environmental [17,18], pharmaceutical [19] and medical [20]. Different types of sensor exist to perform the liquid sensing including lipid/polymer membranes [21], arrays of glass electrodes [18], voltammetric sensors [22] and a charge-coupled device with indicators in a resin bead that change colour [23]. Research has been carried out into the combined use of EN and ET, where the EN analyses the headspace and ET is used for fluid analysis [24]. Naturally, this increases the information obtained but an improvement in the classification properties are also observed [25].

The motivation behind this work is the need for a portable sensor system that can provide continuous inline information in industrial food processes and detect many chemical and electrical properties of compounds instantly. This requires a merging of both a highly sensitive sensor array in coordination with an accurate circuit that can continuously acquire data. Traditionally, the sensors used inline in the food industry provide information on some primary variable in a production system such as temperature, pressure, flow and viscosity. The sensors do not provide the R&D department with any information on process kinetics, for example flavour changes during heating. Photometers are also used in inline food processes. However, again they tend to be tailored to provide specific information e.g. trace mercury contamination in waste water or monitoring of the cleaning procedures during the food procedures. It cannot be denied that traditional sensors play an important role in assessing food safety but they are limited in the way they provide information about quality as perceived by the consumer. Usually sensory quality of the product is assessed on the finished product by a panel of assessors, which in addition to being expensive, takes time and consequently slows down the feedback of information. The ET application will result in an improvement in the sensory quality of processed food products, an increased knowledge about process kinetics of liquid foods and also an improvement in the current control in the industry. The ET is a very promising technology for the food industry. The reason for this is not only because the product quality can be improved, but also traceability and cleanliness can possibly be assessed by these sensor systems. The ability of the ET to provide information inline is also a big advantage over a taste panel providing information on the processed product. This system will also be more suitable that the commercially available ETs for example the ASTREE electronic tongue from AlphaMos. The ASTREE is a very powerful system which finds application in many areas including the pharmaceutical and food industry. This system however, is more adequate for bench-top testing. The literature available on the ET tends to concentrate on the characterization of the electronic tongue with different liquids/solutions. In order for the ET to be successfully used in the monitoring of food procedures it is essential to provide a rugged sensor that can be inserted into various locations within the rigs and a portable system that will fully accommodate the movement of the sensor to strategic locations in the food rigs and will accurately monitor the sensor operations.

2. The Portable System

2.1 Background on the Electronic Tongue Sensor

The type of ET sensor used in this application is a voltammetric ET, see figure 1a. This sensor uses the electrochemical technique of voltammetry to obtain information on a solution/liquid that is being investigated. The ET sensor is seen to the right of the image with an array of working electrodes surrounding a central counter electrode. This type of ET was first developed by Winquist et al. [22] and has been applied in a number of different applications ranging from mold discrimination [26], detergent detection [27] to discriminating different types of tea [28]. The advantage of the ET for the food industry lies in its ability to provide a qualitative assessment of the complex liquid foods. These foods contain many electroactive species and often, it would prove too difficult to provide a quantitative assessment of all of the species using individual chemical sensors. The literature has shown the success of the ET in discriminating many different foods. These foods tend to have levels of salt which act as an ideal supporting electrolyte. However, more investigation is needed to determine how the ET will behave in reduced salt foods. The ability of the sensor to detect levels of salt down to 0.15g/l has been documented [29]. Further work is needed to determine what the minimum levels of salt are that can be detected by the ET.
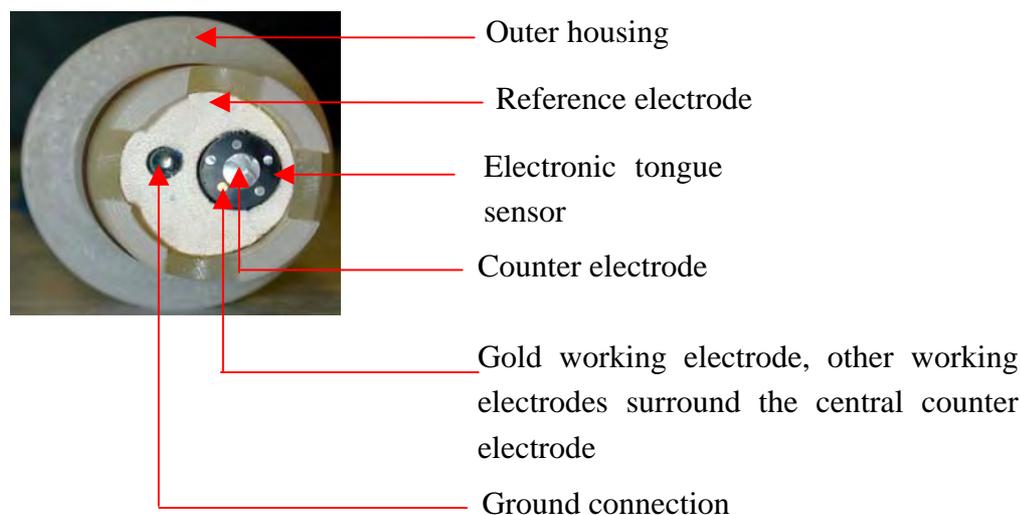

Figure 1a. A Voltammetric Electronic Tongue Sensor inserted in a Kynar housing with inbuilt reference electrode.

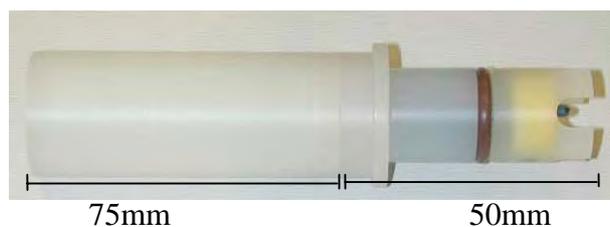

75mm   50mm

Figure 1b. Side profile of the sensor housing into which the ET slots.

This ET sensor appeals to the food industry because it can be ruggedised to withstand CIP (clean-in-place) and meet the requirements for repeatability[29]. The term ruggedised refers to the sensor being robust enough and suitable for use in the monitoring of both batch and continuous production systems. In continuous systems there is typically a constant flow of liquid food pumped through the system at high speeds, placing considerable pressure on the sensor. There is also frequent cleaning of the system. Some types of ETs contain polymer membranes, which could not withstand these harsh acid washes and would not be physically robust to withstand the pressure of the liquids. These ETs would be more suitable for bench-top testing.

2.2 Description of the Electronic Tongue used in this work

The ET sensor contains a 2mm counter electrode made of stainless steel, grade AISI 316. This grade is commonly used in the food industry. Originally, there were five working electrodes (as seen in figure 1a) including gold, iridium, platinum, rhodium and palladium. The palladium electrode was eliminated from the chosen set of working electrodes when it was seen that the electrode formed a black layer on the surface during certain electrochemical experimentation. The remaining electrodes are now used as the working electrodes. Much work was carried out on finding a suitable epoxy for the encapsulation of the ET electrodes. The epoxy had to be robust enough to withstand CIP procedures. The details of this work can be found in the literature [29].

The sensor is surrounded by an outer reference electrode of silver/silver chloride and surrounding this there is an outer housing made of Kynar. This system is suitable for the prototype work; however, the ultimate system will, more than likely, look at replacing the reference electrode. The reason for this is that many food applications place restrictions on the materials that can be used in the rigs. This particular sensor housing was supplied by the Phoenix Electrode Company see figure 1b. The 75mm cylindrical Kynar tube allows the sensor system to be connected into insertion ports in a food processing rig for example a milk pasteuriser. The 50mm section includes the in-built reference electrode, a ground connection and an opening in which to slot an external sensor (the ET). The housings are replaced on a yearly basis, although it is probable that the electrode could operate over an even longer period of time.

2.3 Description of the Sensor Electronics

The overall system consists of a laptop, electronics and the electronic tongue sensor. The laptop communicates via RS232 with the electronics. There is a software programme running on the laptop, which controls the electronics and acquires data from the sensor operations. This software was developed using MATLAB and it allows the user to run different types of voltammetry including cyclic voltammetry and pulsed voltammetry techniques, see figure 2.

Figure 3 shows a block diagram of the electronics used in the sensing system.
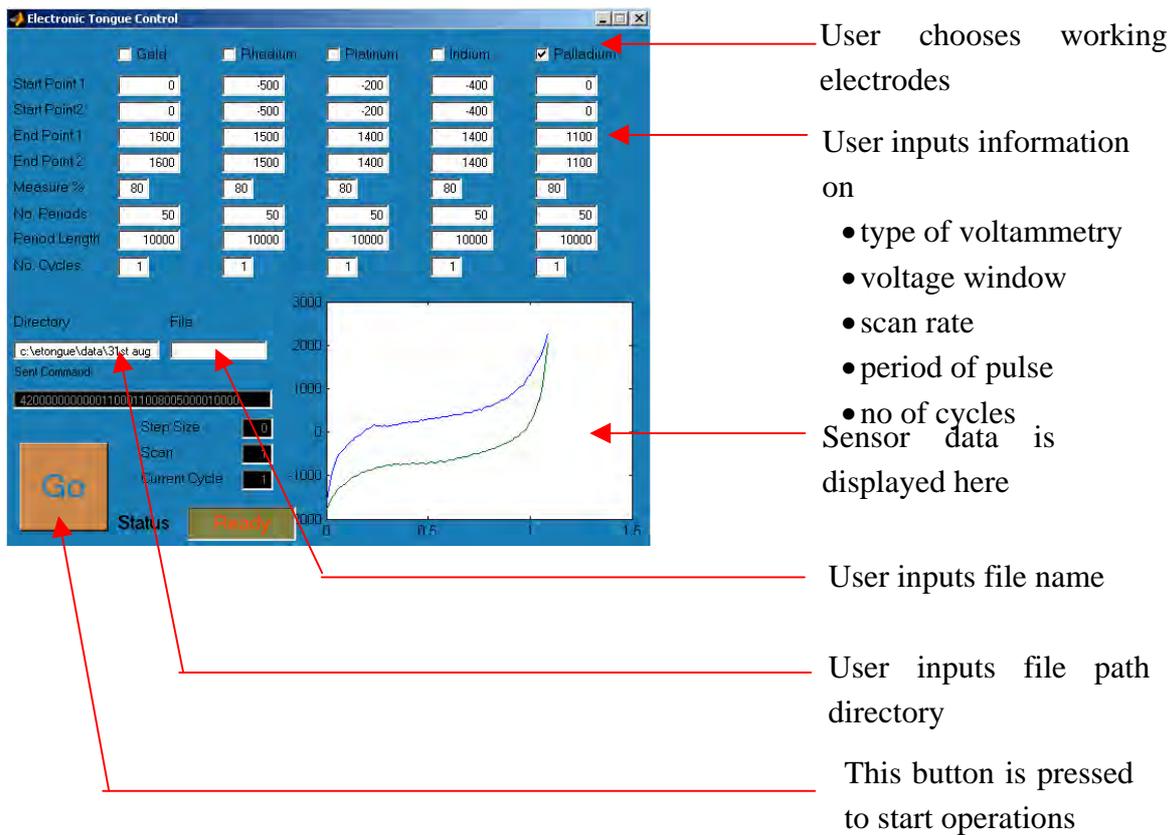
User chooses working electrodes

User inputs information on
- type of voltammetry
- voltage window
- scan rate
- period of pulse
- no of cycles

Sensor data is displayed here

User inputs file name

User inputs file path directory

This button is pressed to start operations

Figure 2. The MATLAB user interface that is used to carry out the voltammetry techniques for the electronic tongue sensor operations.
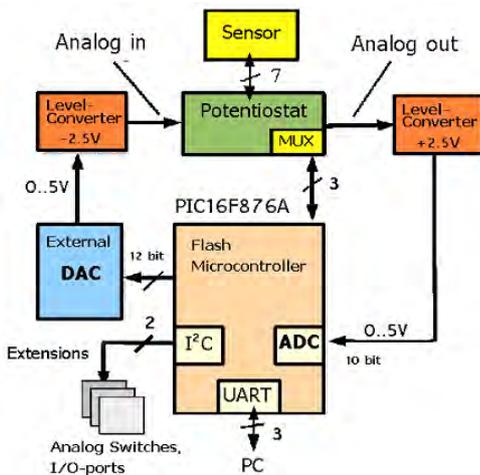

Figure 3. Block diagram of the electronics for the electronic tongue sensor.

The electronics are powered from the mains power supply; therefore, there is a power conversion board (not shown) which powers the different components in the interface circuitry: ±8V for the opamps and ±5V for the remaining IC's on the board. A type of circuit called a potentiostat is

connected to the sensor, see figure 4. Vsim denotes the voltages that are generated by the system and applied to the sensor. The method of voltage generation is described in detail in section 2.4.
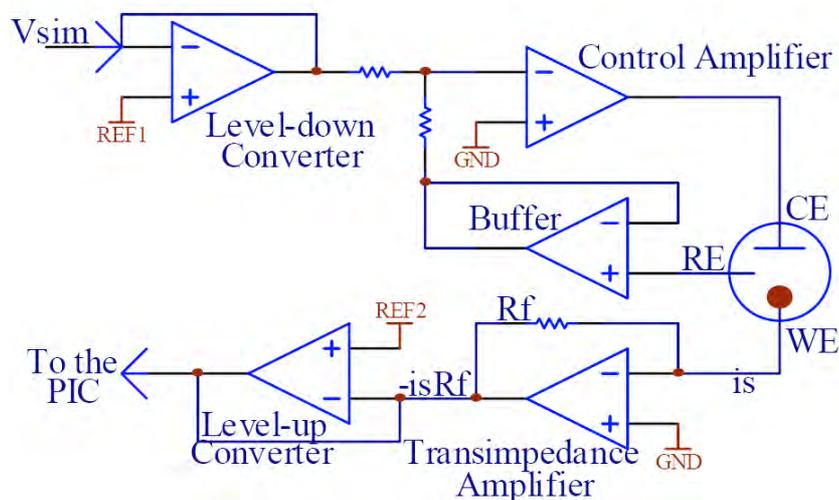

Figure 4. The potentiostat circuit with level-up and level-down converters shown, REF1 = REF2 = 2.5 V.

It is of interest to monitor the voltage that develops at each working electrode when the ET is in operation in the solution under investigation. This voltage can only be measured relative to another electrode. The voltage of this other electrode must be constant. A reference electrode has a stable voltage. By connecting the reference electrode to a buffer amplifier, which will have an infinite input impedance, it will ensure that no current is drawn through the reference electrode, thus maintaining the constant voltage. The reference electrode used is a commercial Ag/AgCl electrode. The aim of the potentiostat is to control the voltage difference between the working electrode and the reference electrode. This control is implemented by forcing current through the counter electrode via the control amplifier. In this way the current that develops at the interface between each electrode and the solution under investigation (commonly called the electrolyte in electrochemical terms) can be monitored. This total current is made up of two current amplitudes, the current that develops due to a double layer capacitance and a Faradaic current [30]. The Faradaic current contains important information on the electrolyte and it is this current that is acquired by the electronics. A transimpedance amplifier or current-to-voltage converter converts this current into a corresponding voltage. A network of resistors is available which can connect across the amplifier to perform the conversion, designated by Rf in figure 4. An auto-ranging feature is described in a later section, which determines the appropriate resistor(s) to be switched into the circuit. The potentiostat circuit needs to be matched to the ADC (analog-to-digital converter) and DAC (digital to analog converter). For this, a level-down (-2.5V) converter is connected between the DAC and the potentiostat and a level-up (+2.5V) converter is connected between the potentiostat and the ADC.

2.4 Description of the Waveform Generation for the Voltammetry Techniques

A microcontroller is necessary to perform the waveform generation (the different voltammetry techniques), the data acquisition and initial data analysis. A PIC microcontroller PIC16F84A from

Microchip [31] is used. Due to the real time requirements, the controller program is written in assembly language. This allows reduction of possible high-level language overhead and yields the highest possible performance at a low clock speed. A flow chart of the routines that happen once the MATLAB software is initiated are shown in figure 5.
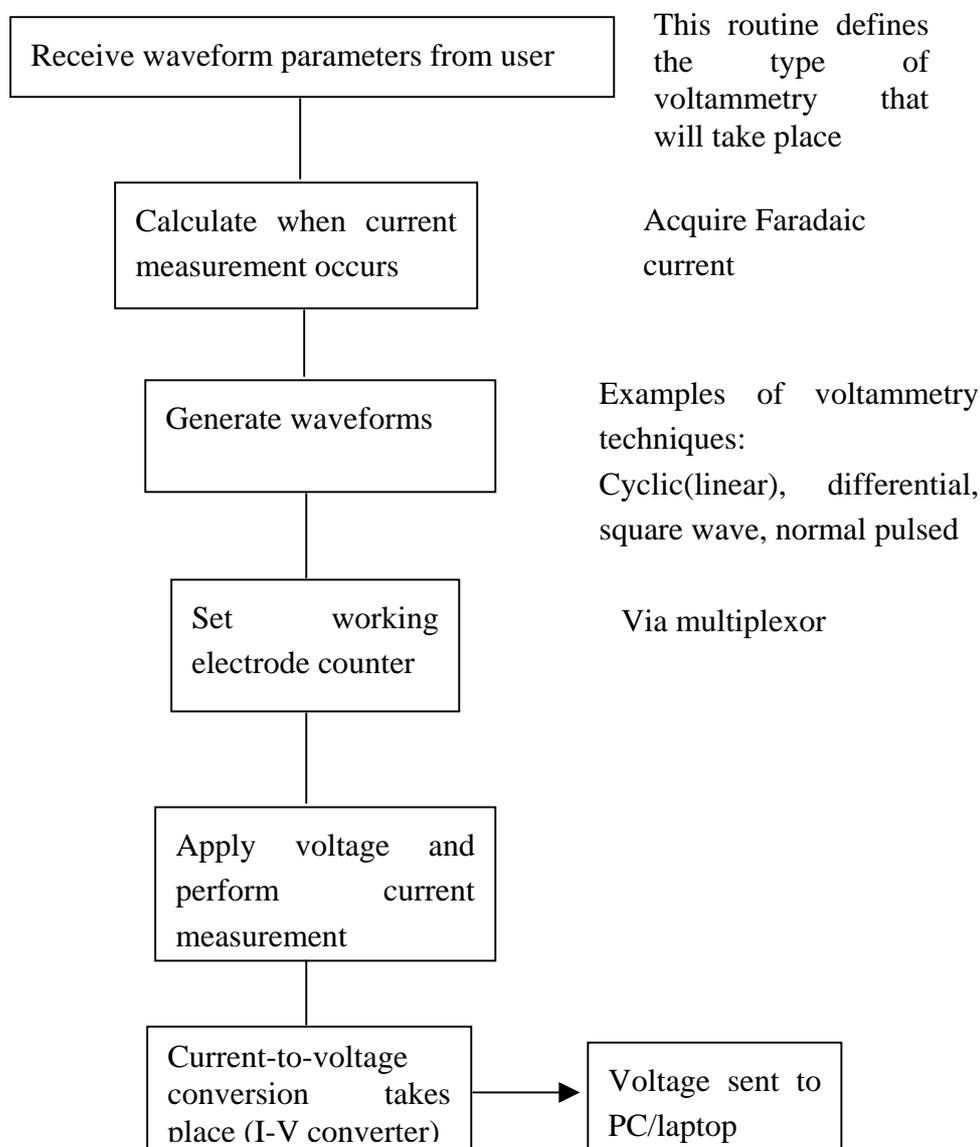
```
┌─────────────────────────────────────┐     This routine defines
│  Receive waveform parameters from    │     the   type   of
│  user                                │     voltammetry   that
└─────────────────────────────────────┘     will take place

        ┌──────────────────────────┐         Acquire Faradaic
        │  Calculate when current  │         current
        │  measurement occurs      │
        └──────────────────────────┘

          ┌──────────────────────┐           Examples of voltammetry
          │  Generate waveforms  │           techniques:
          └──────────────────────┘           Cyclic(linear),    differential,
                                             square wave, normal pulsed

          ┌──────────────────────┐            Via multiplexor
          │  Set        working  │
          │  electrode counter   │
          └──────────────────────┘

          ┌──────────────────────┐
          │  Apply  voltage  and │
          │  perform     current │
          │  measurement         │
          └──────────────────────┘

        ┌──────────────────────┐   ┌──────────────────┐
        │  Current-to-voltage  │──▶│  Voltage sent to │
        │  conversion   takes  │   │  PC/laptop       │
        │  place (I-V converter)│  └──────────────────┘
        └──────────────────────┘
```

Figure 5. A flow diagram showing the routines that occur when the user initiates the MATLAB software

Once the user defines the type of voltammetry to be carried out the parameters are sent to the PIC microcontroller. A calculation is carried out to determine when the current from each electrode should be acquired. The waveforms are generated and the chosen working electrodes are connected into the circuit via a software controlled multiplexor. These waveforms are sent to each electrode one after the other and the current measurements take place. This current is converted to a voltage, which is then sent to the laptop and both displayed on a current versus voltage plot and stored in an excel file format for further data analysis.

The different waveforms that are applied to the sensor are implemented though a combination of assembly routines. Both linear and pulse waveforms can be generated. An advantage to using the pulse

techniques is that it can eliminate any migratory effects that are common when successively monitoring the electrochemical properties of liquids and beverages. The waveforms are generated as follows: two straight lines are defined as boundaries for the generated waveform. Starting points (SP) and end points (EP) are defined in Volts. By setting these values different wave shapes are set. SP1 and EP1 define one line and SP2 and EP2 define another line. The period of the waveforms is set by the user using the number of periods and period length. The waveform is generated between the two lines.

Figure 6 illustrates some of the waveforms that can be generated by setting different values for the start and end points.

For example to generate a square wave voltammogram the user could set SP1=0, EP1=2V and SP2=-2V and EP2=1V to generate two parallel lines. A command block will be sent to the microprocessor and it will then generate a waveform according to the user specifications. Other voltammetry techniques include normal pulse and differential. With normal pulse voltammetry pulses of increasing amplitude are applied. The current resulting from these pulses is compared with the current at a constant baseline voltage. With differential voltammetry, a series of pulses are superimposed on a linearly changing voltage. The current is monitored just before a pulse has been applied and again towards the end of the pulse. The difference between the current values is plotted. This technique differs from the normal pulse voltammetry by the fact that the baseline voltage is constantly changing.

2.5 The Auto-Ranging Feature

An important feature of the circuit is the auto-ranging function that is operational when data acquisition occurs. In some basic commercial potentiostats the current-to-voltage conversion is carried out by connection of an appropriate external resistor. The problem with this particular set-up is that it is probable that the resistor value needs to be changed for different electrodes and different test solutions. This is tedious and time-consuming and in some cases a trial-and-error approach is necessary to determine the most appropriate resistor. The alternative to this is to use a top-of-the-range potentiostat e.g. CHInstruments Model 600C, which will automatically carry out a current to voltage conversion. This equipment tends to be more suitable for bench-top testing and is quite expensive. In this paper, we concentrate on a more cost-effective system, which is also suitable to use in a portable system. In the circuit described here a 16-resistor network and two multiplexor chips (Linear Technology LTC1380) controlled by a software routine are used for the auto-ranging capability. 16 different resistances can be switched across the current-to-voltage converter. The different working electrodes are also connected into the circuit via LTC1380 chip, see figure 7.

There is a software routine that determines which resistor combination should be connected into the circuit when the current-to-voltage conversion is taking place. The routine determines where the acquired current is located from a total of 16 current ranges. Ranges 0-7 are controlled by one multiplexor and ranges 8-16 are controlled by another multiplexor. The ranges correspond to the following current values: Range 0: ±12mA, Range 1: ±6mA, Range 2: ±34mA,……Range 14: ±1uA and Range 15: ±0.5uA. Figures 8a and b illustrates how the feature is implemented in software.
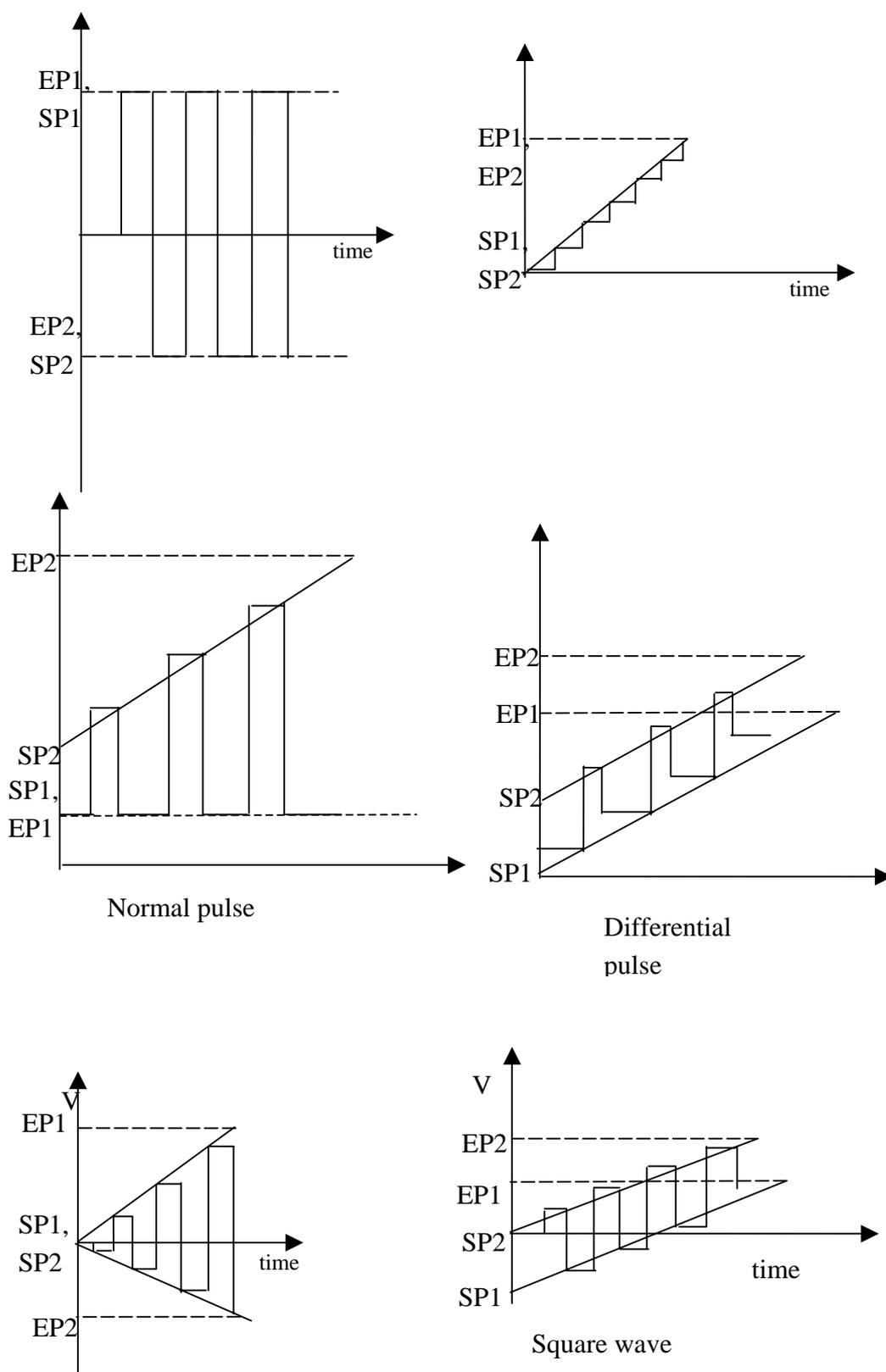
Figure 6. Diagrams showing how different waveforms are generated by the PIC microcontroller for the pulsed voltammetry techniques.
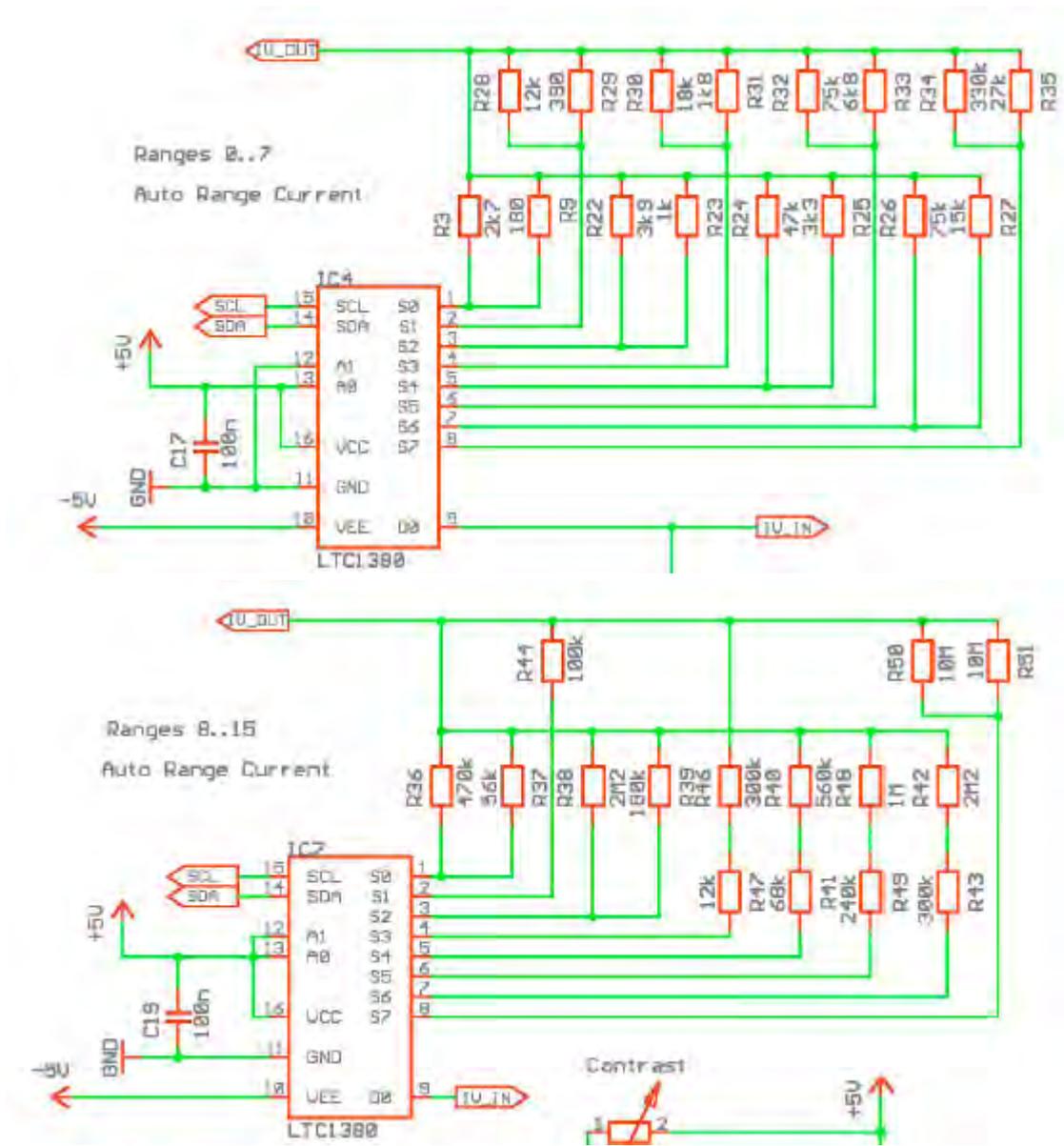
Figure 7. The Hardware used to implement the Autoranging Routine.

If one considers figure 8a which shows data that is located in range 3. Initially, the search will begin in the middle range, range 7. If data resides in the upper half the up arrow is chosen. If there is no data point within the range then a down arrow is chosen. Therefore, to determine the correct measurement if data resides in range 3 will take 5 steps. Consider if data resides in range 14. Again, the search will commence in range 7. This time the data resides in the lower ranges. A search of the lower interval will be carried out (depicted by the down arrow) and continues until range 14 is reached. This takes four data steps. Once the appropriate range is determined the resistor combination is chosen and the current-to-voltage conversion takes place. This voltage can be represented by the equation:

$$U_A = -R_{IV} \cdot I_{IN} \quad \text{(voltage from the current-to-voltage converter)} \quad (1.1)$$

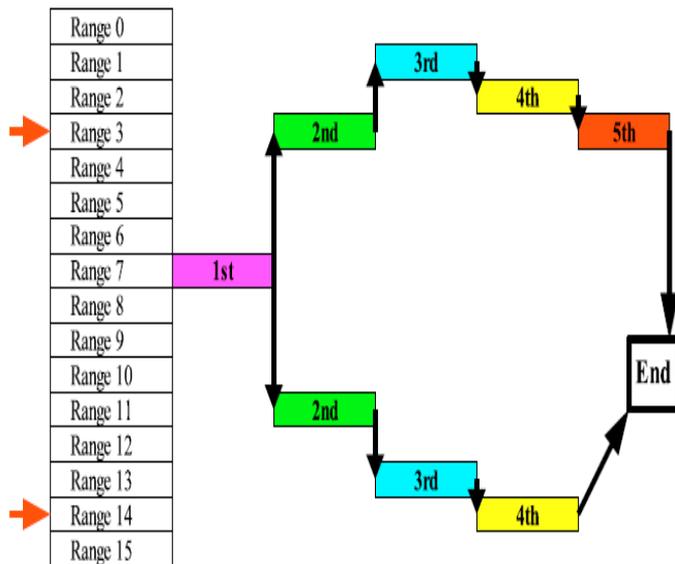where I_{IN} is the current acquired from the sensor electrode.

Figure 8a. Auto-Ranging Feature to Determine Location of Sensor Data.

Range:=7;
PerformMeasurement;
If (data is in second half)
                Range:=Range-4;
else
                Range:=Range+4;

PerformMeasurement;
If (data is in second half)
Range:=Range-2;
else
Range:=Range+2;
PerformMeasurement;
If (data is in second half)
Range:=Range-1;
else
Range:=Range+1;
PerformMeasurement;
If(data is in second half)
Keep this range;
else
Range:=Range+1;

Figure 8b. A software representation of how the autoranging is implemented.

As was previously mentioned, there is a level-up converter between the ADC and the current-to-voltage converter therefore, the voltage after it has passed through the level-up converter is

$$U_{AD} = A(gain) - gain \cdot U_A, where: A(gain) = 2.5 \cdot gain \tag{1.2}$$

Therefore,

$$U_{AD} = 2.5 \cdot gain + gain \cdot R_{IV} \cdot I_{IN} \tag{1.3}$$

Solving for I_{IN} yields

$$I_{IN} = \frac{U_{AD} - 2.5 \cdot gain}{R_{IV} \cdot gain} \tag{1.4}$$

The ADC has a 10-bit resolution the voltage can be quantised as follows (FS=full scale of the voltage, n=number of ADC bits),

$$U_{AD}(number) = \frac{FS}{2^n} \cdot number \tag{1.5}$$

Thus I_{IN} can be rewritten,

$$I_{IN}(number)[nA] = \frac{\dfrac{FS}{2^n} \cdot number - 2.5 \cdot gain}{R_{IV} \cdot gain} \cdot 10^9 \tag{1.6}$$

and

$$number = (\frac{I_{IN}[nA] \cdot gain \cdot R_{IV}}{10^9} + 2.5 \cdot gain) \cdot \frac{2^n}{FS} \tag{1.7}$$

I_{IN} can also be written as:

$$I_{IN}[nA] = \frac{FS \cdot 10^9}{2^n \cdot gain \cdot R_{IV}} \cdot number - \frac{2.5}{R_{IV}} \cdot 10^9 \tag{1.8}$$

To implement the autoranging feature, the value of R_{IV} must be changeable. The coefficient with the number term can be calculated separately for each R_{IV} value in addition to the constant offset term. The values of R_{IV} are obtained by knowing the maximum allowed output for the current-to-voltage converter is ±2.5V and choosing the desired current range. As an example, for range 0 (±12Ma), a resistance value that could be used is calculated as:

$$R_{IV} = \frac{2.5V}{0.012A} = 208.3\Omega \tag{1.9}$$

Table 1 summarises the current ranges and the resistor values. The values for the coefficient and offset term for each resistor is also shown, assuming a gain of one, a 10 bit ADC and a full scale value of 5V.

It should be noted that the average resistance of a closed switch within the LTC1380 of 40Ω has to be subtracted from the calculated resistance value. Therefore, the appropriate resistance is

$$R_{IV} = \frac{2.5V}{0.012A} - 40\Omega = 168.3\Omega \tag{1.10}$$

Table 1. The Current Ranges, Resistor Values, coefficients and offsets for the ranges used in the auto-ranging feature.

Range	Maximum Current	R9(Ω)	Coefficient	Offset
0	±12mA	208	23475	-12019231
1	±6mA	417	11709	-5995204
2	±3mA	833	5862	-3001200
3	±1.5mA	1667	2929	-1499700
4	±800uA	3125	1563	-800000
5	±400uA	6250	781.25	-400000
6	±200uA	12500	390.625	-200000
7	±100uA	25000	195.3125	-100000
8	±50uA	50000	97.65625	-50000
9	±25uA	100000	48.828125	-25000
10	±15uA	166667	29.2968	-15000
11	±8uA	312.5k	15.625	-8000
12	±4uA	625k	7.8125	-4000
13	±2uA	1.25M	3.90625	-2000
14	±1uA	2.5M	1.953125	-1000
15	±500nA	5M	0.97655625	-500

The resistance values for the remaining current ranges are calculated in a similar fashion and composed by either a parallel or a series resistor network as close as possible to the required resistor value. For example to obtain a resistance of 168.3Ω, a 180Ω resistor in parallel with a 2.7kΩ resistor would give a total resistance of 168.75Ω. The resistor values are matched as closely as possible to what is required for the appropriate current-to-voltage conversion.

3. Results and Discussion

The sensor system was validated by carrying out cyclic voltammetry in different chemical solutions from Sigma Aldrich. Firstly cyclic voltammetry was carried out on each electrode in 0.1M sulfuric acid solution. The operation of the gold and platinum electrodes in this solution are well-documented in the literature [32-36]. The appropriate potential range to be applied to the electrodes was determined and a scan rate of 0.2V/s was used. When all the parameters are entered into the MATLAB user interface the program is started and the electrochemical data is obtained from the sensor in the sulfuric acid solution. The resulting voltammograms are shown in figure 9 and compare well with the literature.
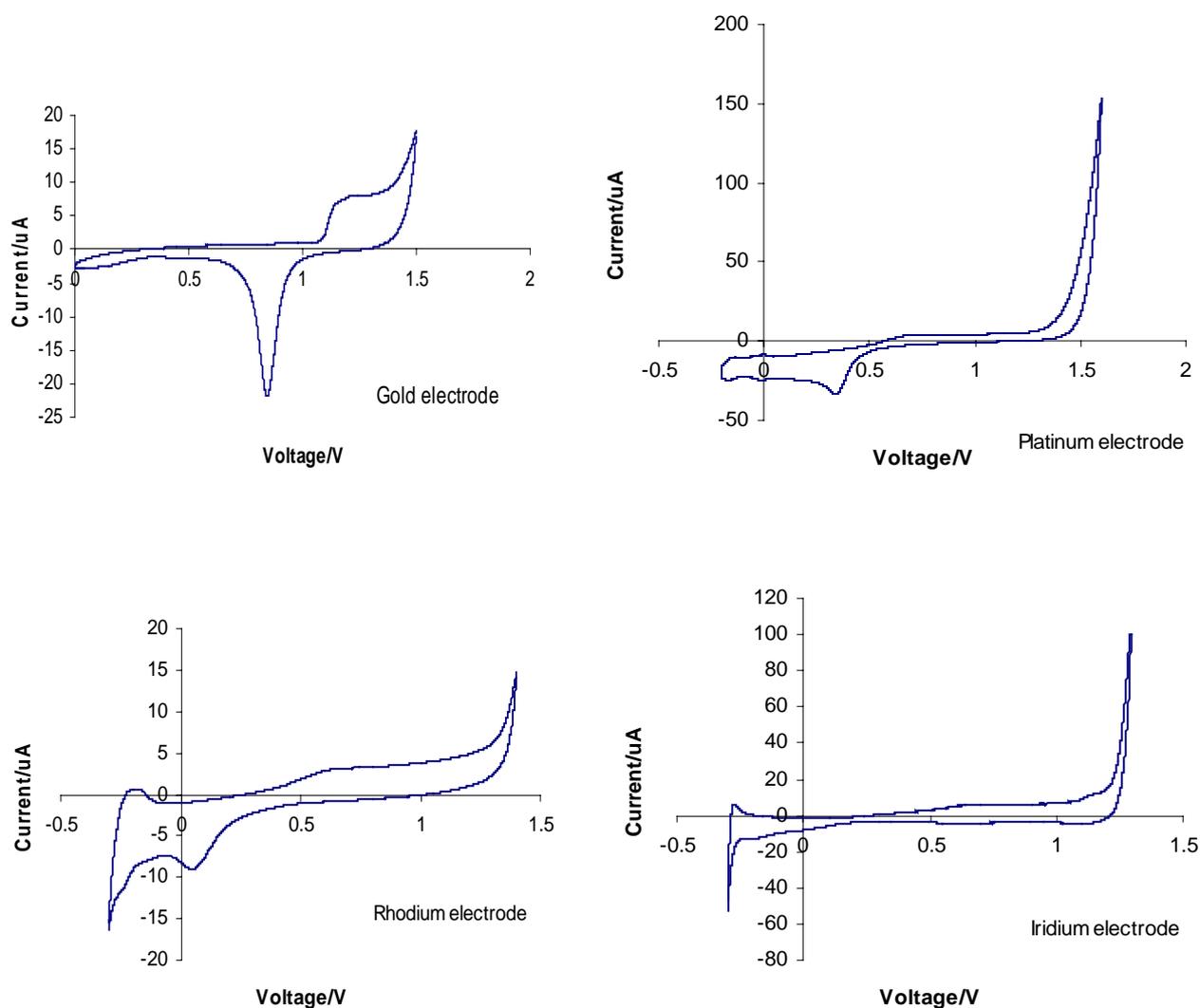
Figure 9. Voltammograms obtained for the working electrodes of the ET sensor in operation in 0.1M sulfuric acid solution at a scan rate of 0.2V/s.

The sensor system was also tested for the response at pH3, which is the typical pH of fruit juices. Phosphate buffer solution was prepared to give a pH solution of 3. The appropriate voltage ranges were determined for each electrode and the experiments were carried out at a scan rate of 0.2V/s, see figure 10 for the obtained voltammograms. Well-defined peaks were observed for gold and platinum. For the gold electrode an oxidation peak is observed at 1.2V and a corresponding reduction peak is observed at 0.5V. For the platinum electrode an oxidation peak is observed at 1.4V and the reduction peak at 0.9V. In relation to this, little redox behaviour is observed for the rhodium and iridium electrodes. The obtained voltammograms illustrate that the circuit can operate reliably in the various test solutions.
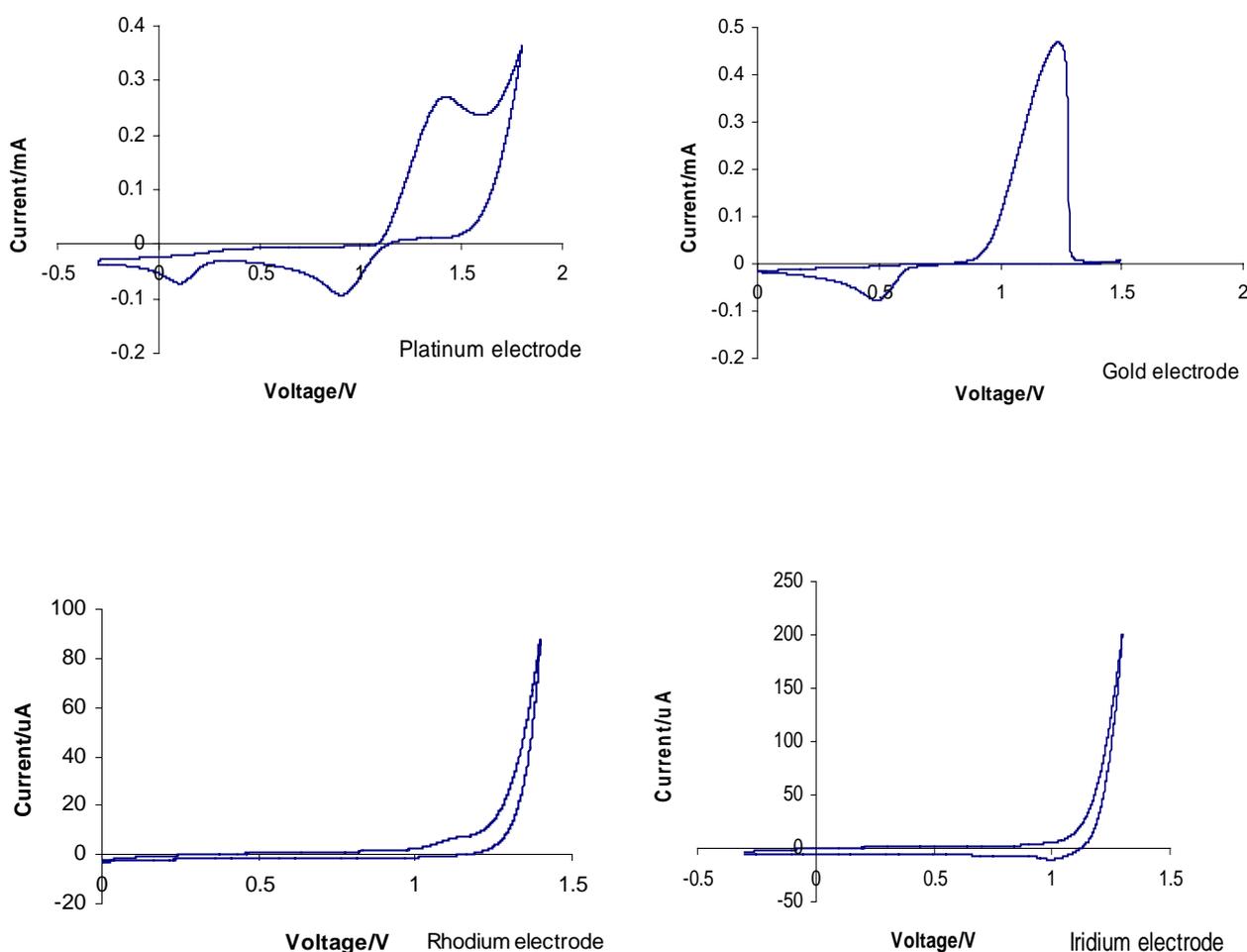
Figure 10. Voltammograms obtained for the working electrodes of the ET sensor in operation in phosphate buffer solution at a pH of 3 and a scan rate of 0.2V/s.

Future work will concentrate on minimizing the electronics to make the system smaller than it's present dimensions of 10x12cm. The resistor network will be optimized to include digital potentiometers, which will reduce the number of resistors required. This in turn will make the system more accurate because the issue of resistor tolerances will be reduced. Low power versions of the electronic components will be investigated to enable a battery powered version to be developed which will be able to run over an acceptable period of time without the need for frequent battery replacement. Some modifications to the software will be carried out to ensure all types of pulsed voltammetry techniques can be performed using the system. At present, much thought is needed to determine what input parameters are needed to generate the required pulses. A more user friendly approach would be more suitable and will be investigated. Work will also be carried out on the replacement of the reference electrode to address the restrictions that the food industry places on the materials that can be used.

Acknowledgements

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