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Anodic Stripping Voltammetry using EVAL-ADICUP 3029

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Anodic Stripping Voltammetry using EVAL-ADICUP 3029

by

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DEDICATION

I dedicate this creative component to my beloved parents, Lakshmi Narayanan and Shobaa, without whose constant love, support and encouragement, I would not have been in a position to complete this work.

I also dedicate this to my sister, Preetha and brother in-law, Balaji who helped me sail through the high tides of graduate student life.

"Thank you Amma, Appa, Preetha and Balaji!"

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Finally, I thank my friend Raghav Ram for being a pillar of moral support and offering encouragement at all times.

ABSTRACT

Anodic Stripping Voltammetry (ASV) is a voltammetric method used to quantitatively determine the amount of ionic species in an analyte of interest. ASV has grown rapidly over the past few years owing mainly to the fact that it is a method used to simultaneously determine several elements with a wide range of concentration levels.

In this creative component, we propose a method to perform ASV using an evaluation board – ADICUP3029, designed by Analog Devices, thus eliminating the traditional method of performing ASV using an electrochemical workstation.

CHAPTER 1. INTRODUCTION:

Electroanalytical methods are a branch of analytical chemistry which is used to study an analyte as a function of voltage and current within an electrochemical cell. Depending on which aspect of the cell is controlled and measured, we can further classify electroanalytical methods into the following: 1) Potentiometry 2) Coloumetry 3) Voltammetry.

We focus on voltammetry for this creative component. Voltammetry is also classified into many types and our focus is on Anodic stripping voltammetry (ASV). It is a type of electrochemical stripping analysis which is used for the detection of heavy metal ions within an analyte of interest. It makes use of three electrodes, namely, working electrode, counter electrode and reference electrode. ASV primarily consists of the following steps: 1) A deposition step where in the analyte of interest is electroplated on the electrodes. 2) A voltage is applied to the electrodes during which the metal gets stripped off and dissolves into the analyte. 3) A voltage is swept, and the corresponding current is measured.

EVAL-ADICUP 3029

The EVAL-ADICUP3029 is an Arduino-like development platform based on the ADUCM3029 ultra low power microcontroller (MCU) with integrated power management for processing, control, and connectivity. The MCU system is based on the ARM Cortex-M3 processor, a collection of digital peripherals, embedded SRAM and flash memory, and an analog subsystem which provides clocking, reset, and power management capability in addition to an analog-to-digital converter (ADC) subsystem.

The ADUCM3029 has industry leading ultra-low power which makes it ideal for Internet of Things (IoT) applications. The platform has an Arduino Uno form factor, two

PMOD connectors, and an I2C Grove style connector for easy to connect sensors and signal conditioning add on modules [1]

The EVAL-ADICUP3029 base board consists of two basic blocks:

- An ultra low power, 32-bit ARM Cortex™-M3 processor, on a single chip ADuCM3029 microcontroller.
- An on-board serial wire download (SWD) interface, which is implemented with the Freescale's MK20DX128 microcontroller. This block allows the Freescale device to act as an on board debugger, so you don't need additional external hardware to program or debug your ADuCM3029 applications[3]

AD5940

The AD5940 is a high precision, ultra-low power, analog front end (AFE) system designed to excite and measure the current, voltage, or impedance response of a sensor. The AD5940 is specifically designed for high precision analysis of electrochemical cells. The hardware used is the AD5940 evaluation kit, which includes the EVAL-ADICUP3029 Arm Cortex™-M3 microcontroller-based Arduino Uno form factor and the EVAL-AD5940ARDZ.[2]

Goal

The major goal of this creative component is to interface EVALADICUP-3029 with EVAL-AD5940 and perform anodic stripping voltammetry, thus replacing traditional methods of performing ASV.

CHAPTER 2.   AD5940- IN DETAIL

The AD5940 is specifically designed for high precision analysis of electrochemical cells. Evaluation kit AD5940 consists of the following:

1. EVAL-ADICUP3029 Arm Cortex™-M3 microcontroller-based Arduino Uno form factor
2. the EVALAD5940ARDZ evaluation board
3. the AD5940Sens2 daughter card

The interface of the above mentioned hardware is as shown:

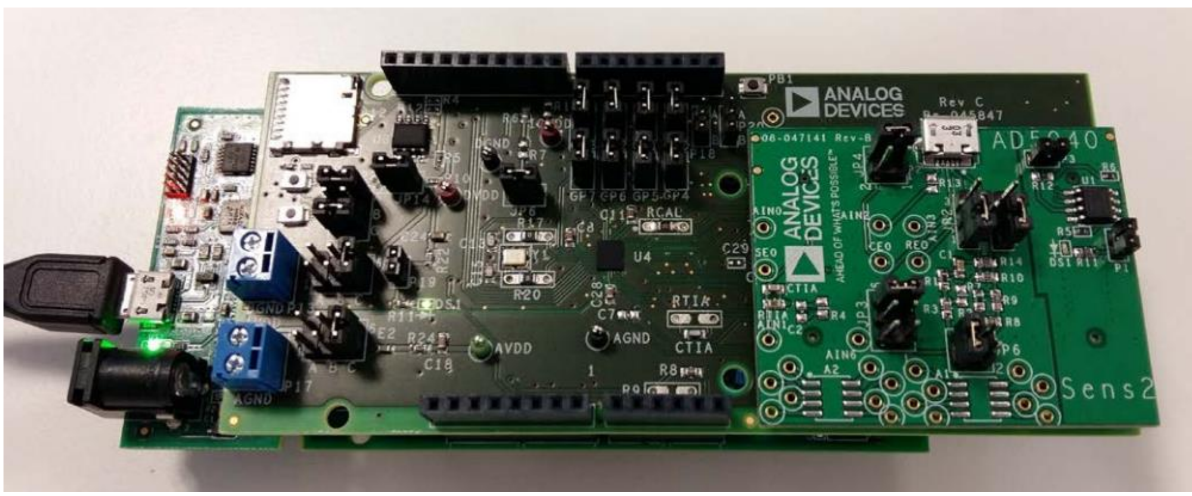

Figure 1 : Hardware setup

AD5940 MEASUREMENT LOOP

The AD5940 data acquisition loop consists of a low bandwidth loop, a high bandwidth loop, a high precision analog-to-digital converter (ADC), and a programmable switch matrix.

The low bandwidth loop consists of the following:

• Low power, dual output digital-to-analog converter (LPDAC) that generates VZERO and VBIAS.

• Low power trans-impedance amplifier (LPTIA) used to convert current to voltage. The LPTIA ensures that the dc voltage in the sensor is zero when the dc voltage of the digital-to-analog (DAC) and the LPTIA bias voltage are equal.

The high bandwidth loop consists of the following:

• High speed DAC (HSDAC) and excitation amplifier designed to generate a high frequency ac excitation signal when making impedance measurements.

• High speed TIA (HSTIA) designed to convert high bandwidth current signals up to 200 kHz into voltages to be measured by the ADC.

The switch matrix consists of the following:

• A series of programmable switches that allows connection of external pins to the high speed DAC excitation amplifier and to the HSTIA inverting input.

• A series of programmable switches that allow calibration of unknown sensor impedance vs. an external known resistor connected to the RCAL0 pin and the RCAL1 pin.

• A series of programmable switches that allows connection of an external TIA gain resistor (RTIA).

Electrochemical/potentiostat Measurement Theory

Electrochemical measurements are measurements carried out on an electrochemical cell. Common examples of electrochemical cells are electrochemical gas sensors, blood glucose strips, and continuous glucose monitoring devices. An electrochemical cell typically has three electrodes: the counter electrode, the reference electrode, and the sense electrode (sometimes known as the working electrode). Two electrode and four electrode variants also exist, though they are less common. In normal operation, a voltage is applied between the reference electrode and the sense electrode. This voltage is known as the bias voltage of the sensor. Electrochemical reactions occur at the sense electrode where a current is generated and measured. A potentiostat circuit is required to maintain the sensor bias voltage and sink or source current as it is required when the electrochemical reactions take place. The current is sink or sourced through the counter electrode. Figure 2 shows a typical electrochemical cell connected to the potentiostat amplifier (PA) circuit of the AD5940.[2]

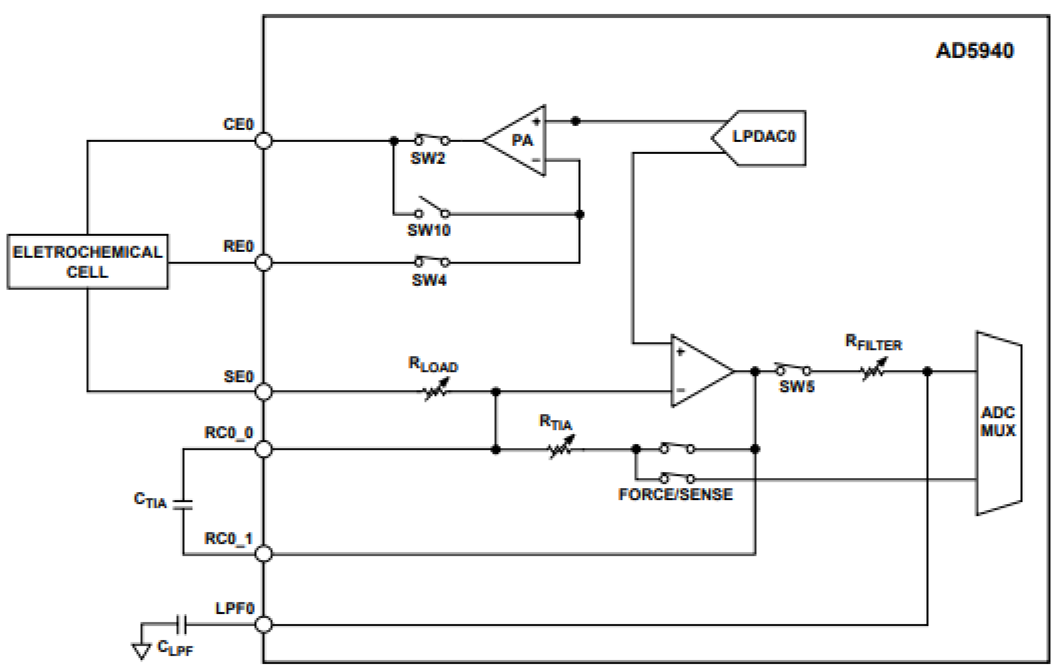

Figure 2: Electrochemical Cell Connected to the AD5940

AD5940 – Schematics

The following schematics help us to get an understanding of the internal operation of EVAL-AD5940.

Test points

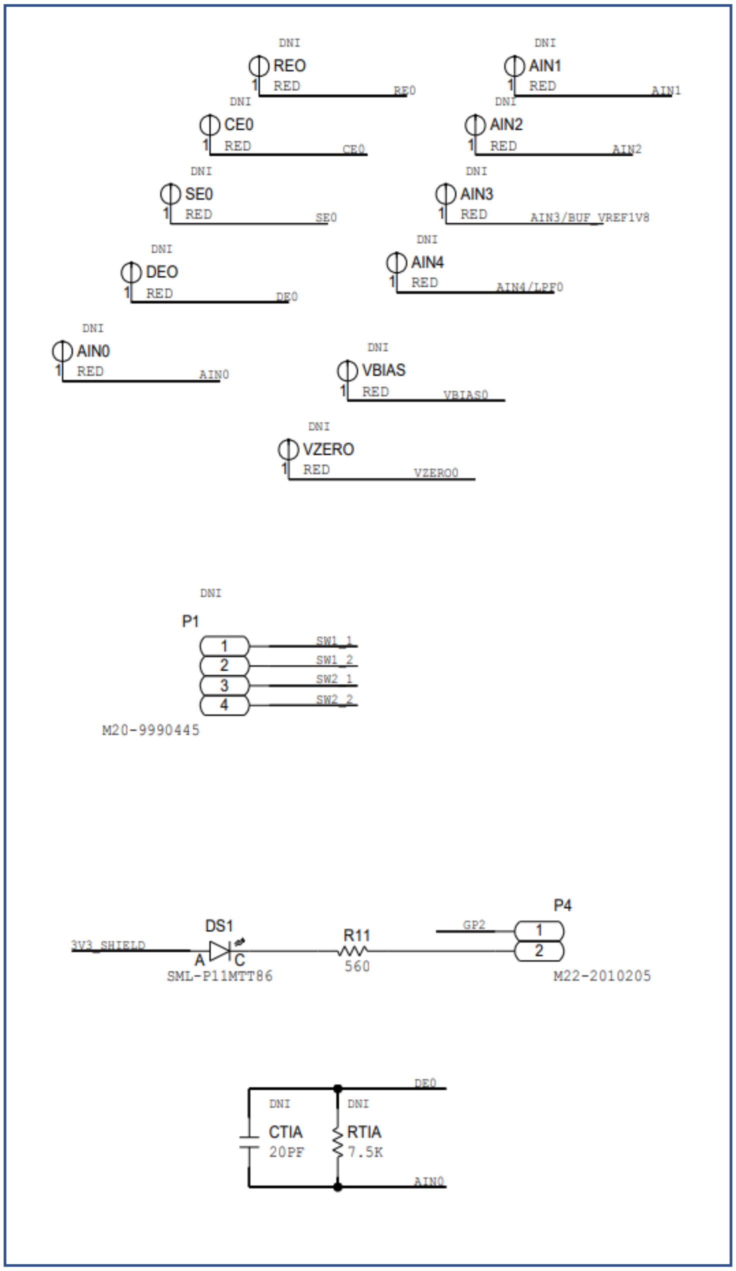

Figure 3: Test points

Amperometric Test Measurement

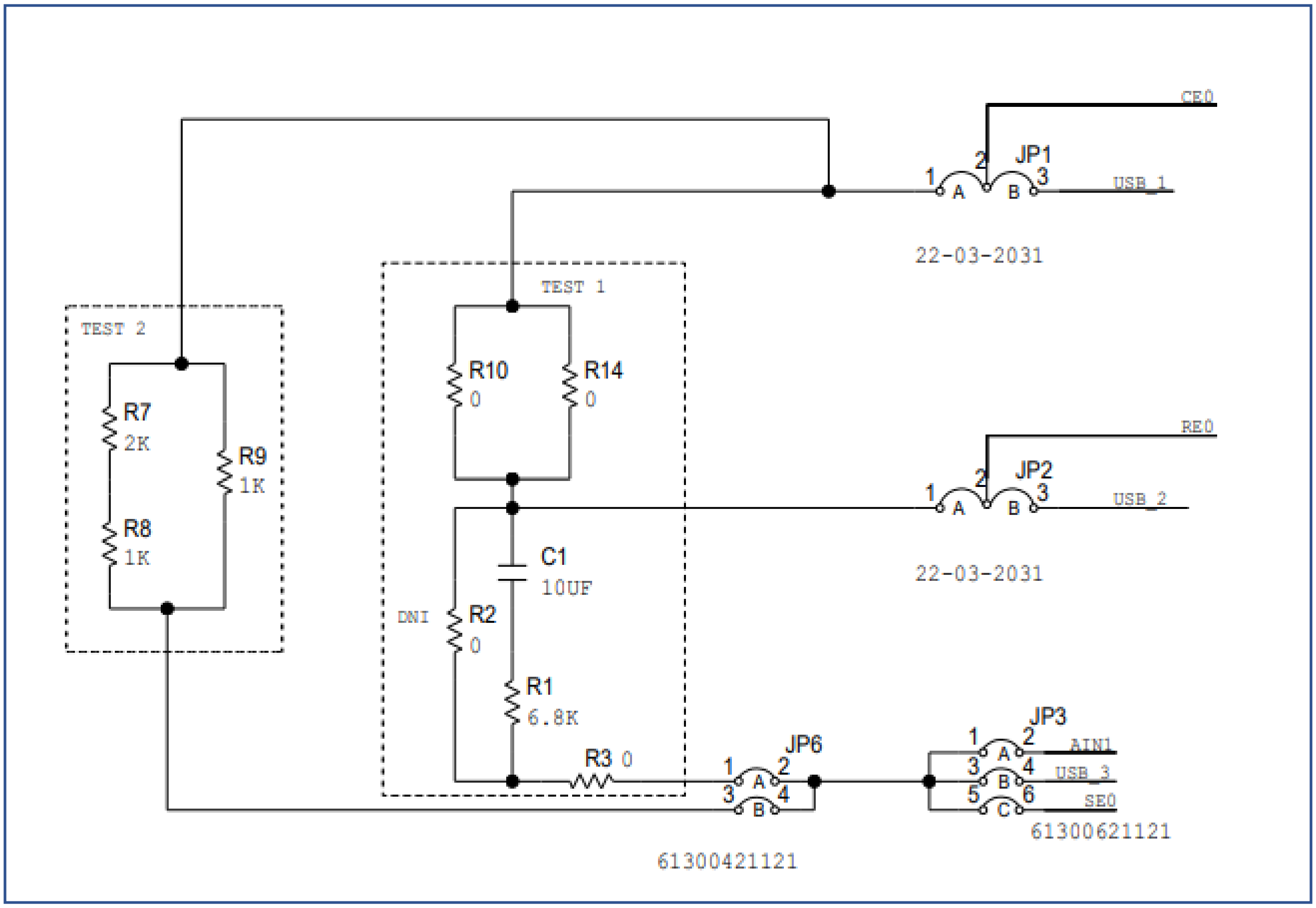

Figure 4: Amperometric Test Measurement

Resistors R7, R8 and R9 gives an equivalent of 750Ω as follows :

R7 in series with R8 = 2K+1K = 3K

3K in parallel with R9 $=1/(1/3+1)=1/1.33$

Thus $R_{equivalent}$ = 0.75KΩ (or) 750Ω

Micro USB

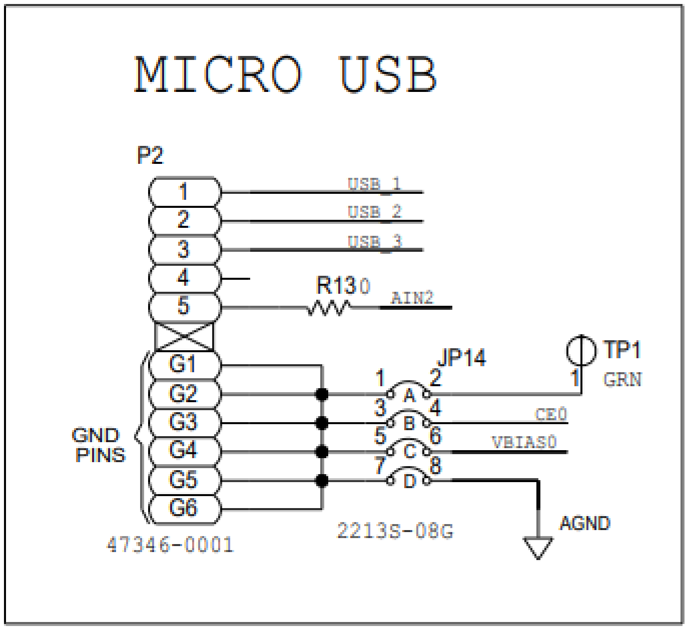

Figure 5: Micro USB schematics

I2C Memory

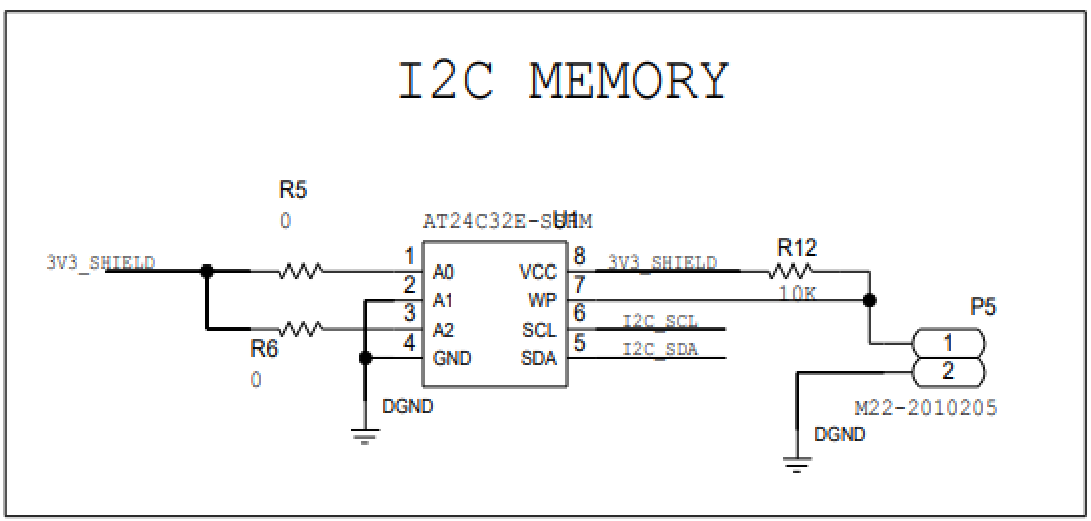

Figure 6: I2C Schematics

Sensor Board Connection

The following figures give us an idea of the sensor board connection and explains how the layout is made:

Analog Signals

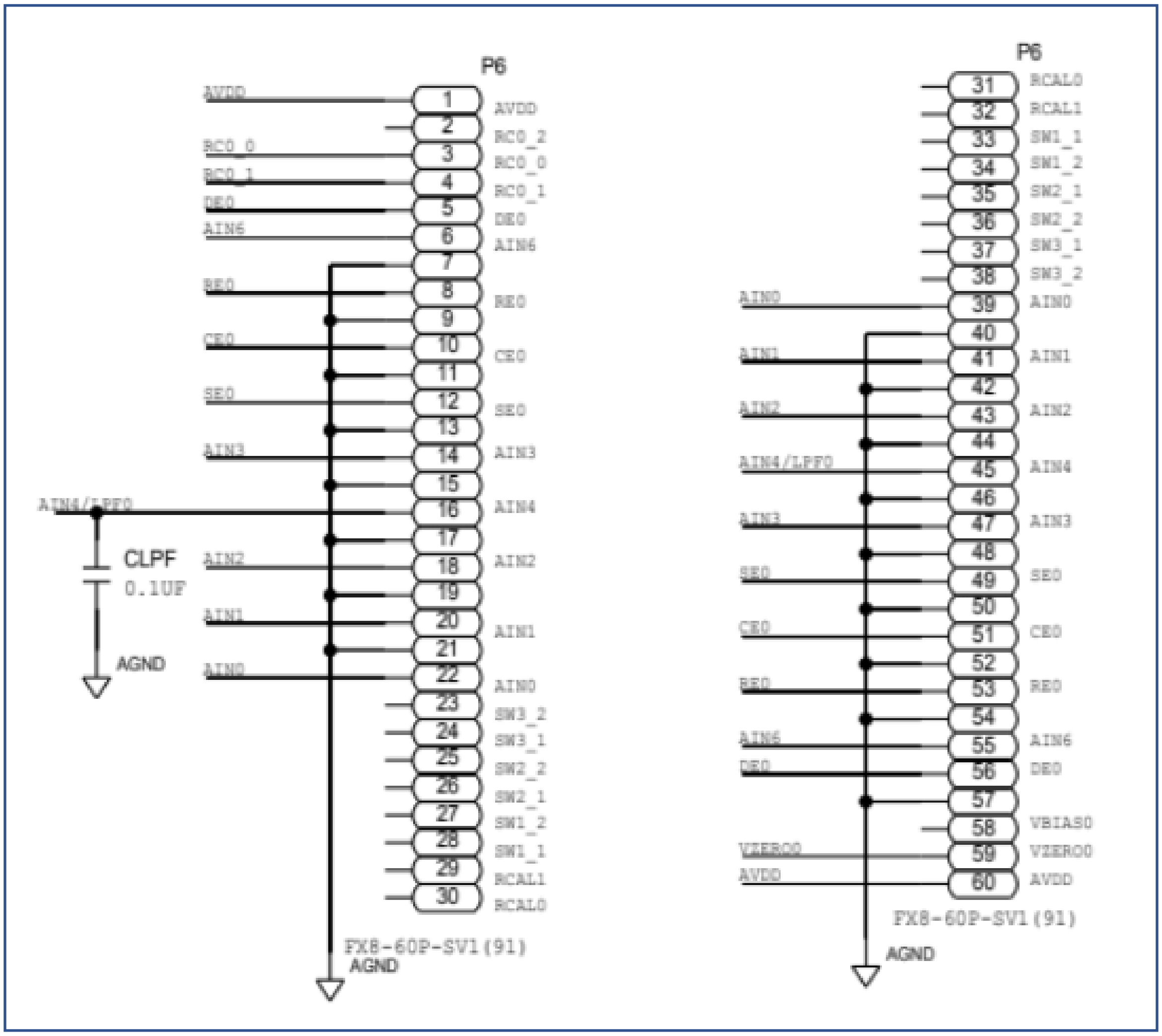

Figure 7 : Analog Signals

Digital Signals

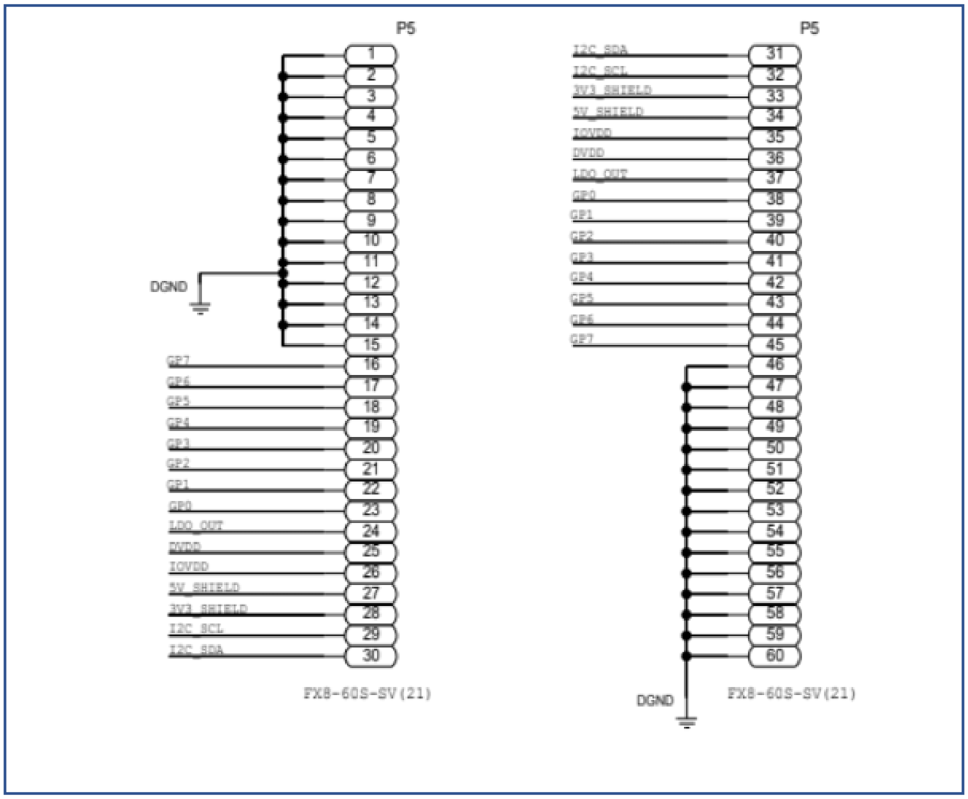

Figure 8 : Digital Signals

Standard Footprints

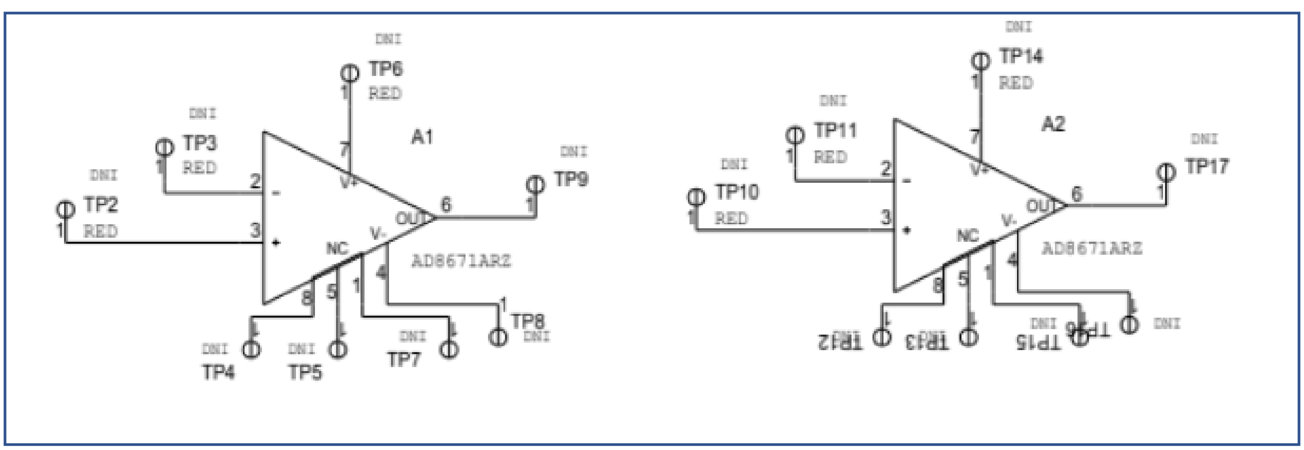

Figure 9: Standard footprints

CHAPTER 3. RELATED SOFTWARE

To run a specific measurement on the hardware, one of the following methods can be used:

- SensorPal graphical user interface tool
- IAR Embedded Workbench® firmware
- Realterm

For this creative component, we use IAR Embedded Workbench and RealTerm.

IAR Embedded Workbench

IAR Embedded Workbench Window View

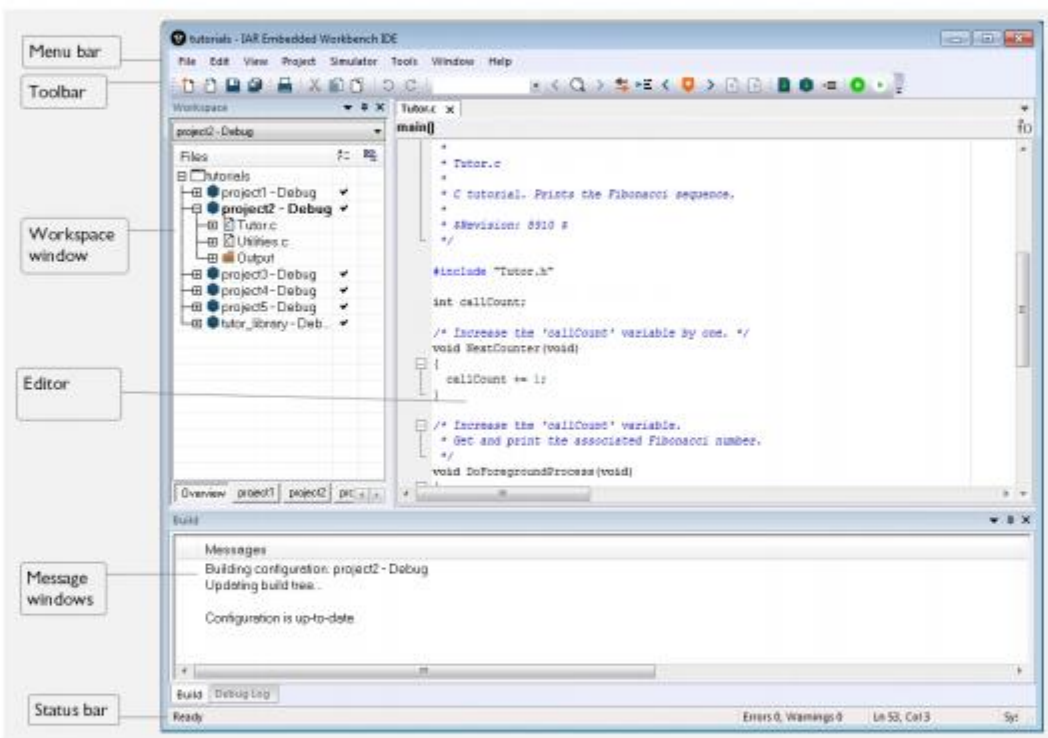

Figure 10 : IAR Embedded Workbench window

The menu bar contains:

- File: Commands for opening source and project files, saving and printing, and exiting from the IDE.
- Edit: Commands for editing and searching in editor windows and for enabling and disabling breakpoints in C-SPY.
- View: Commands for opening windows and controlling which toolbars to display.
- Project: Commands for adding files to a project, creating groups, and running the IAR Systems tools on the current project.
- Simulator Commands specific for the C-SPY simulator. This menu is only available when you have selected the simulator driver in the Options dialog box.
- C-SPY hardware driver Commands specific for the C-SPY hardware debugger driver you are using, in other words, the C-SPY driver that you have selected in the Options dialog box. For some IAR Embedded Workbench products, the name of the menu reflects the name of the C-SPY driver you are using and for others, the name of the menu is Emulator.
- Tools User-configurable menu to which you can add tools for use with the IDE.
- Window Commands for manipulating the IDE windows and changing their arrangement on the screen.
- Help Commands that provide help about the IDE.

Menu commands view

Figure 11 : Menu commands

The buttons on the IDE toolbar provide shortcuts for the most useful commands on the IDE menus, and a text box for typing a string to do a quick search. For a description of any button, point to it with the mouse pointer. When a command is not available, the corresponding toolbar button is dimmed, and you will not be able to click it. [4]

Status Bar

Figure 12 : Status bar

The status bar displays:

- Source browser progress information
- The number of errors and warnings generated during a build
- The position of the insertion point in the editor window.
- The character encoding
- The state of the modifier keys caps Lock, num lock, and overwrite

RealTerm

RealTerm is a terminal program specially designed for capturing, controlling and debugging binary and other difficult data streams. It is a tool for debugging commands and understanding the data that is being captured by the hardware.

Baud Rate and Ports

The baud rate can be set as per the hardware’s specifications. RealTerm can connect to both SERIAL ports (real uarts, as well as USB, and network virtual uarts) or TCP/Telnet ports.

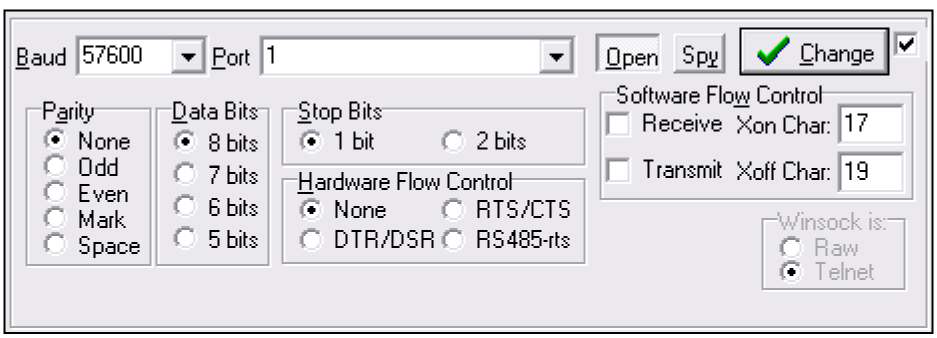

Figure 13 : Baud Rates and Ports

Pins and Status

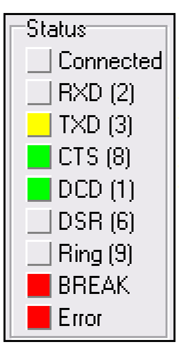

Figure 14: Example of pins and status

Capturing Data

Incoming data can be captured to file. The capture can automatically stop (and restart) after a certain time or number of characters. RealTerm can be hidden, and capture controlled from the tray icon. , popup menu, and automation interfaces.

This provides a very easy way to (say) collect serial data, and graph it live using Matlab.

It can either capture "direct" or via the terminal window. When DIRECT capture is used, the terminal window is turned off, and the echo port operation will cease.

The tray Icon and main icon changes to show a red dot (as shown below) when it is capturing. The dot rotates as data bytes are actually being received.[5]

Figure 15: Red dot appears when data is being captured

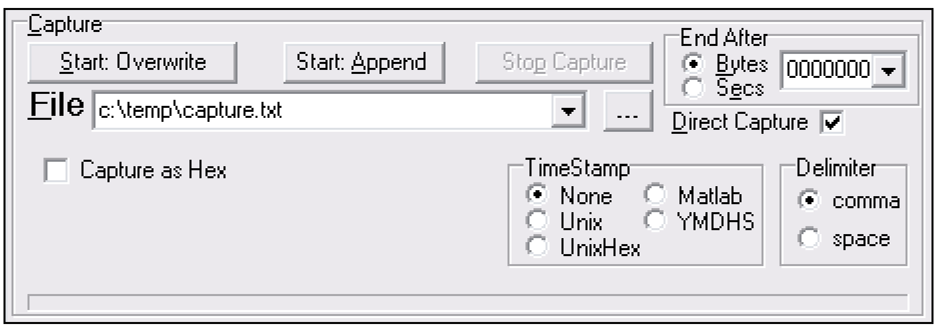

Figure 16: Capture window

CHAPTER 4. ASV MEASUREMENT

For performing ASV using the evaluation board, square wave voltammetry is implemented. Square-wave voltammetry is an electrochemical technique where the voltage between the reference and sense electrode is incremented in a square wave fashion as shown below :

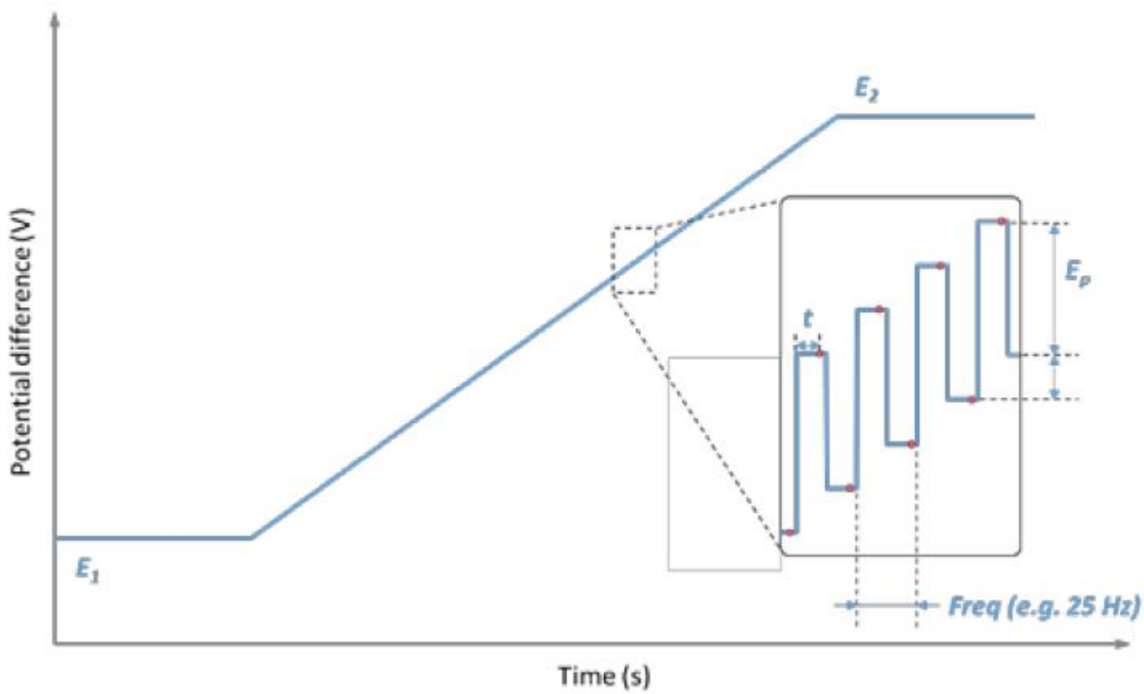

Figure 17: Square Wave Voltammetry

Hardware Configuration

To set up the hardware, connect the EVAL-AD5940ARDZ evaluation board into the connectors on the EVAL-ADICUP3029.

Plug The AD5940Sens2 daughter card is plugged into the EVAL-AD5940ARDZ evaluation board.

On the AD5940Sens2 board, the following jumper connections are made:

- JP1 – Jumper on PIN1 and PIN2
- JP2 – Jumper on PIN1 and PIN2
- JP3 – Jumper on PIN5 and PIN6
- JP6 – Jumper on PIN3 and PIN4

The EVAL-ADICUP3029 is connected to the computer via the micro USB cable.

The electrodes are connected to a pogo pin and using wires, connected to the evaluation board as shown in the following figures:

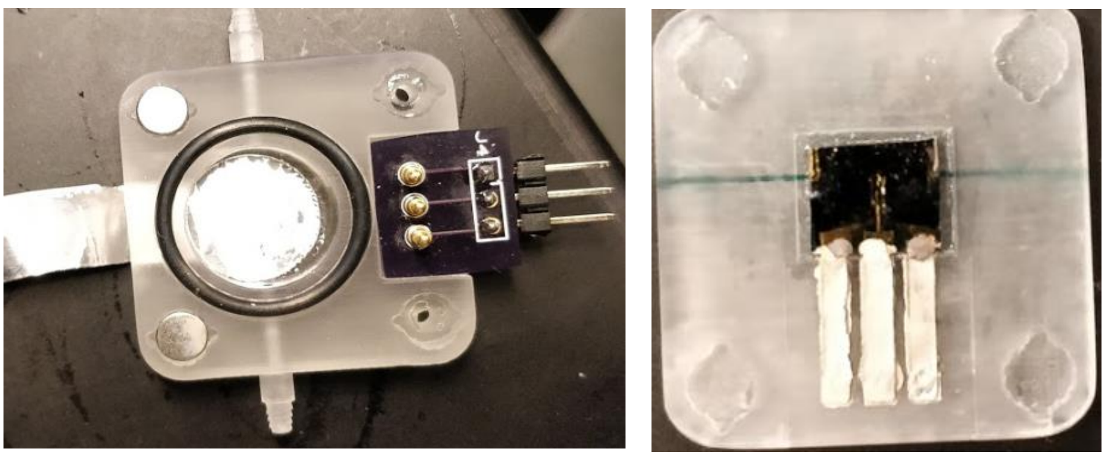

Figure 18: Electrodes connected to a pogo pin

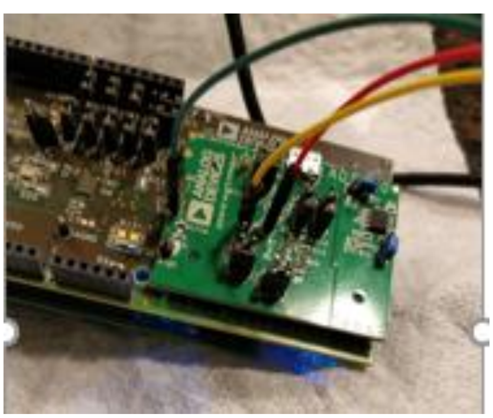

Figure 19: Wires from the pogo pin connected to the board

Setting up

For the scope of this creative component, IAR Embedded Workbench firmware example is used. This software has built in examples and codes and for our purpose, we use ‘AD5940_SqrWaveVoltammetry’ project. This project has files built in as shown :

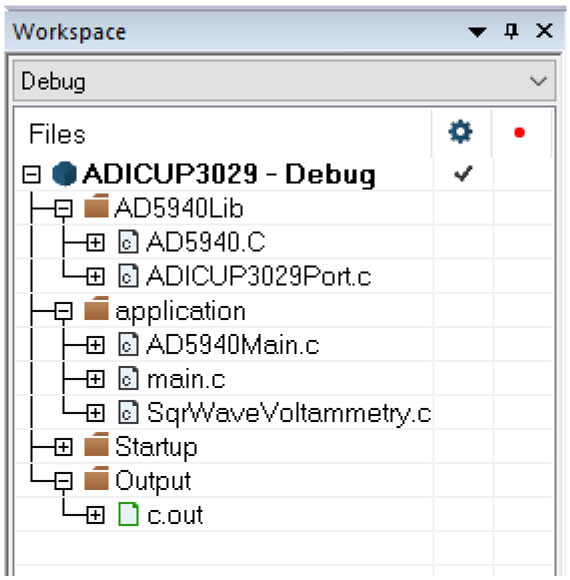

Figure 20: AD5940 Files

The ‘AD5940Main.c’ file contains an initialization function which is used to configure the ASV measurement parameters (AD5940SWVStructInit())

```c
void AD5940RampStructInit(void)
{
  AppSWVCfg_Type *pRampCfg;

  AppSWVGetCfg(&pRampCfg);
  /* Step1: configure general parmaters */
  pRampCfg->SeqStartAddr = 0x10;
  pRampCfg->MaxSeqLen = 1024-0x10;
  pRampCfg->RcalVal = 10000.0;
  pRampCfg->ADCRefVolt = 1820.0f;
  pRampCfg->FifoThresh = 480;
  pRampCfg->SysClkFreq = 16000000.0f;
  pRampCfg->LFOSCClkFreq = LFOSCFreq;

        /* Step 2:Configure square wave signa
  pRampCfg->RampStartVolt = 1000.0f;
  pRampCfg->RampPeakVolt = 400.0f;
  pRampCfg->VzeroStart = 1300.0f;
  pRampCfg->VzeroPeak = 1300.0f;
  pRampCfg->Frequency = 25;
  pRampCfg->SqrWvAmplitude = 25;
  pRampCfg->SqrWvRampIncrement = 8;
  pRampCfg->SampleDelay = 10.0f;
  pRampCfg->LPTIARtiaSel = LPTIARTIA_200R;
}
```

Figure 21: Function for initializing parameters for ASV measurement

This function is used to configure parameters such as the ramp voltages, frequency, delay time, etc.

The variables shown in Figure 14 can be correlated to the following table:

Variable in the figure	**Variable in the program**
E1	RampStartVolt
E2	RampPeakVolt
Freg	Frequency
Ep	SqrWvAmplitude
Estep	SqrWvRampIncrement

Table 1 : Correlation of variables from Figure 14 and variables in the program

Running ASV

To download the code to the microcontroller and begin a debug session, the green play icon is clicked.

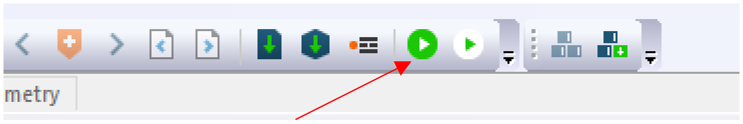

Figure 22 : Running the debugger

To view the measured data, a terminal program such as RealTerm is used.

The baudrate is set to 230400 and the corresponding communication port is selected.

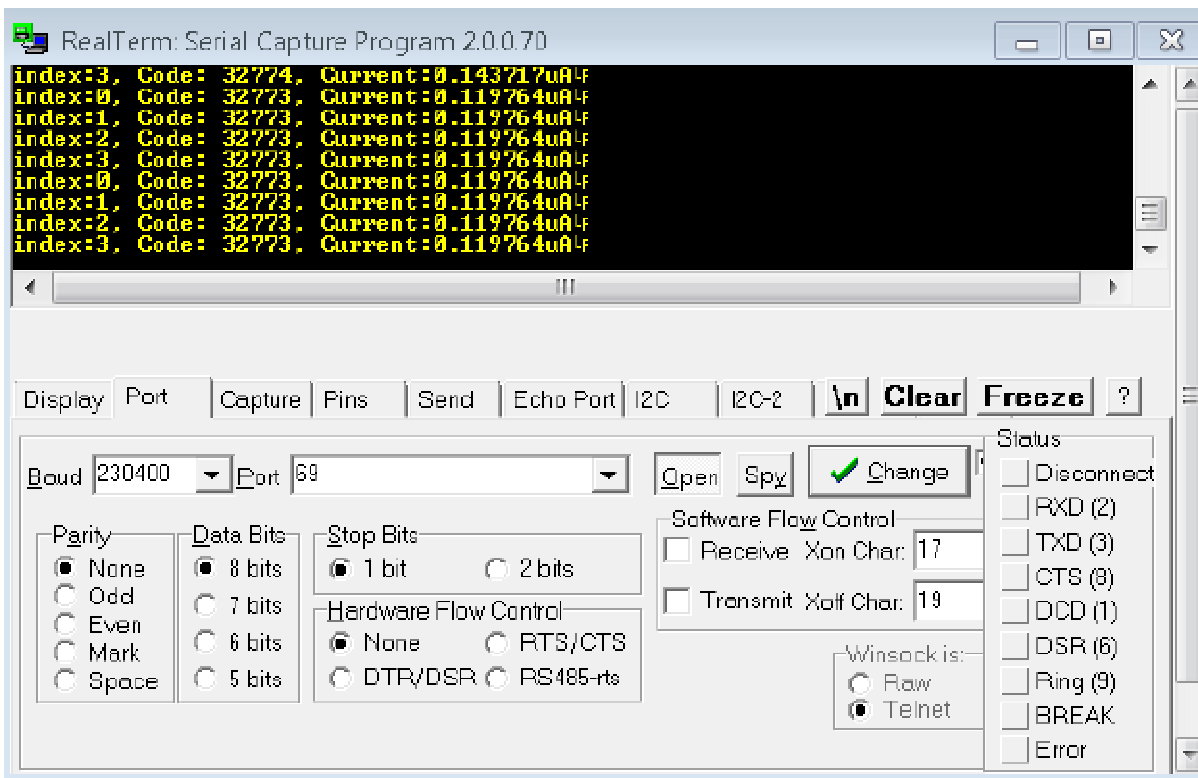

Figure 23 : RealTerm

To save the data, a valid file destination with a .csv extension is entered to view the results in Microsoft Excel.[2]

CHAPTER 5.   RESULTS AND FUTURE SCOPE

Results

The following figures show the current response after the required connections are made, program is modified as needed and debugged to the microcontroller and data is collected using RealTerm :

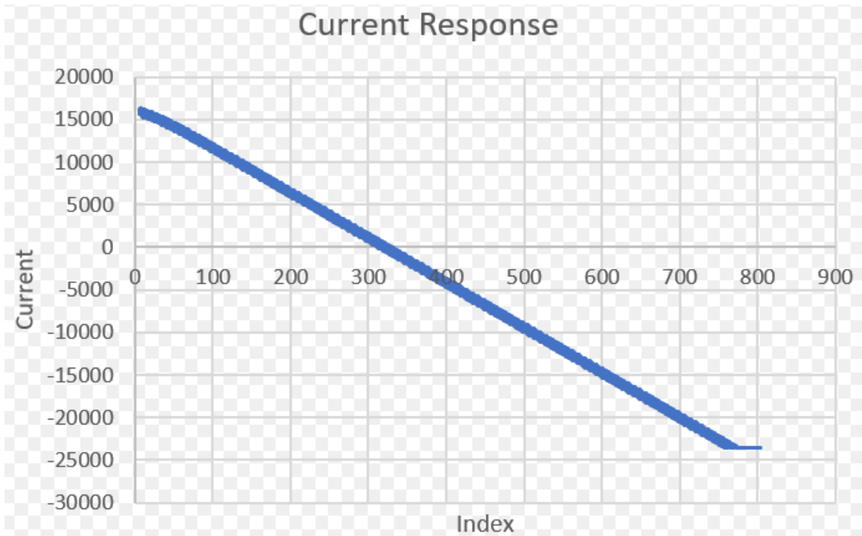

Figure 24:Current Response

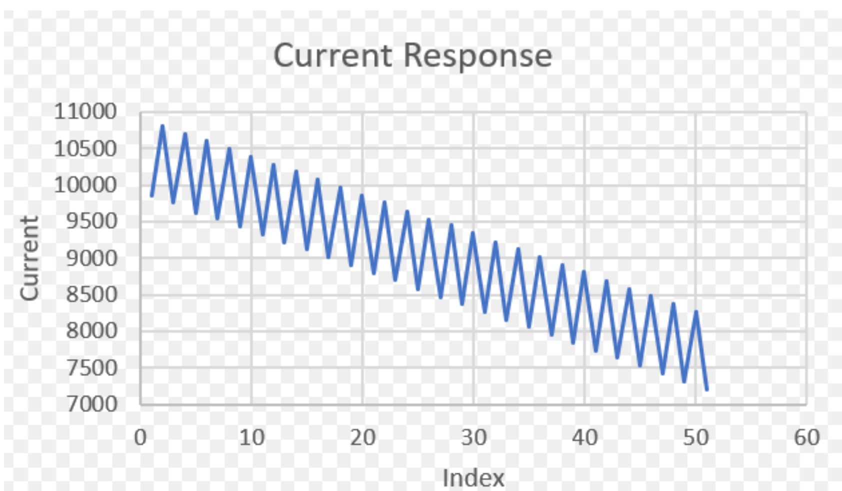

Figure 25: Current Response zoomed in

From the observations, it was found that the evaluation kit was performing as it should as is capable of performing ASV. The parameters of the square wave was configured as needed and the results were plotted.

Future Work

From the results, we find that the current is plotted against index. ASV can be better understood if current is plotted against voltage.

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5. https://realterm.sourceforge.io/#Display_Formats