Electrode Response Processing System for the Detection of Nitride Ions in Aqueous Solution.

A cost-effective method to determine nitrids concentration

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Introduction

- Identification and quantification of chemicals has a main role in environmental control.
- Particularly, nitrides are specially harmful for the environment.
- Current techniques to monitor the diverse concentrations of chemicals are still further from being economic and user-friendly.

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Introduction:
Impedance Spectroscopy

– Technique recently widespread to study electrode-electrolyte interface properties by means of the impedance response.
  - Ex. Conductivity measurements, cell behavior research.

– Data obtained can be interpreted using equivalent circuits

– Challenges: equivalent circuits might be ambiguous.

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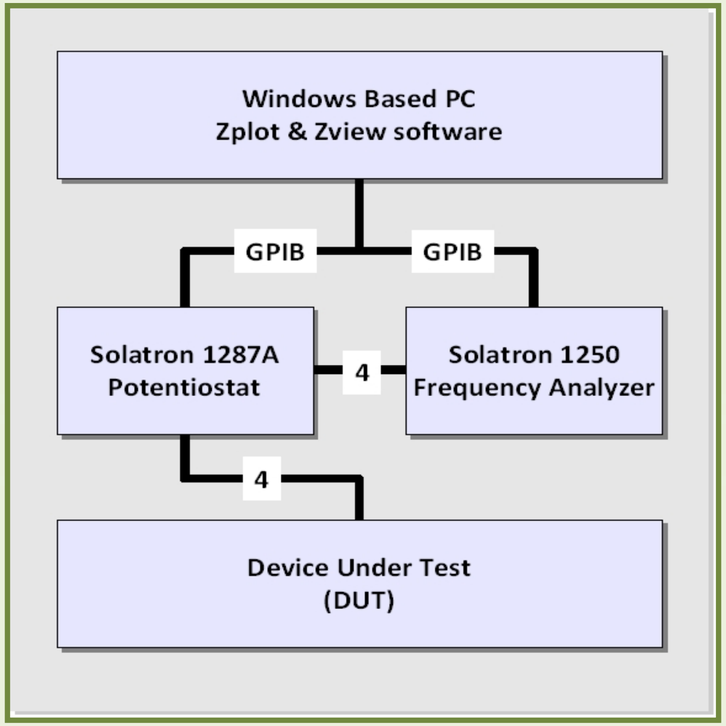
Introduction

- **Impedance spectoscopy (IS) : applications.**



- **Example:**

  Setup for conductivity (IS) measurements.

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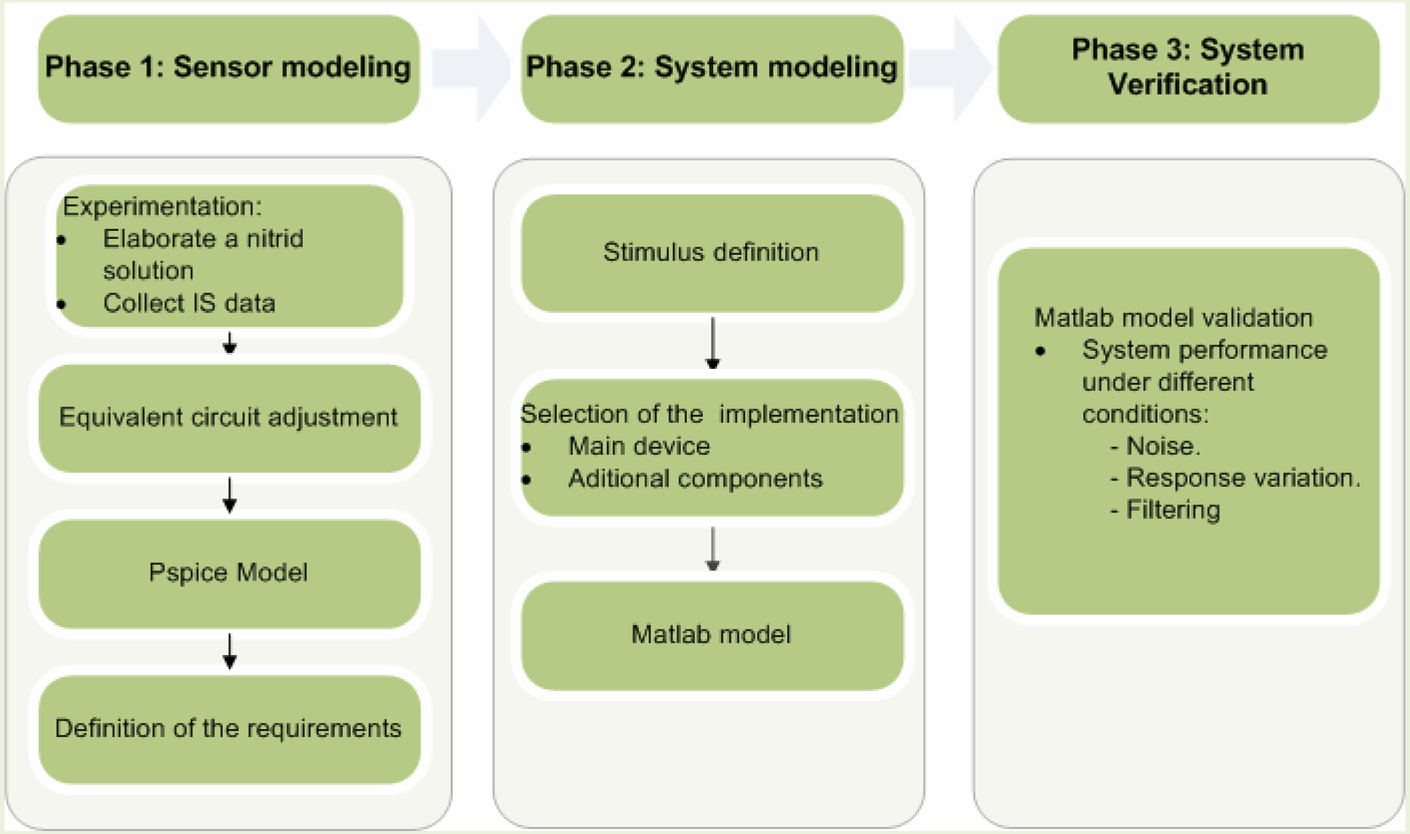
Goals

- Extend the applications of IS with the aim to improve the current technology that identifies nitrides.
- Development of a system:
  - Cost-effective.
  - Easy handling and portable.
  - Easily embedded in a more complex system

System development: Steps followed



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Phase 1: Sensor Modeling

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Phase 1: Experimentation

The electrode is made of Ag-AgCl polimer-paste.
Its dimensions are 12x20mm.
The solution from which the data was collected: NaNO3.

Setup

Electrode

Challenges: The electrode response seems to be unstable and unpredictable

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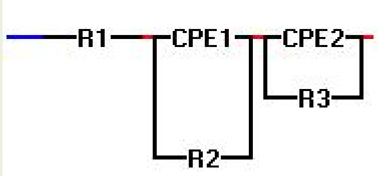
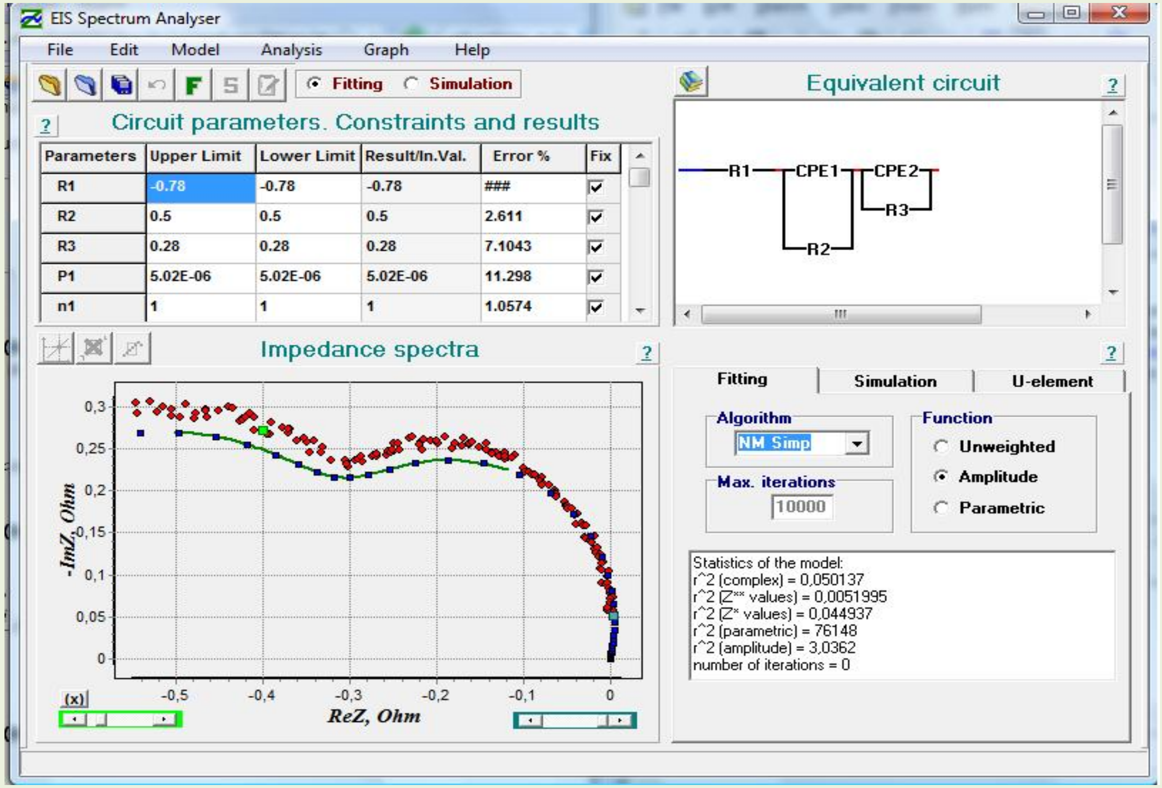
Phase 1: Equivalent Circuit adjustment

- Finding the EC:
  - EIS Spectrum Analyzer Sofware Tool
    - Complex Non-Linear Least square algorithm



- Final components:
  - 3 Resistors
    - One negative resistor that simulates the passivisation of the electrode.
  - 1 Capacitor
  - 1 CPE (Constant Phase Element)
    - Non-linear behaviour

Phase 1:
Equivalent Circuit adjustment



EIS Analyser Interface

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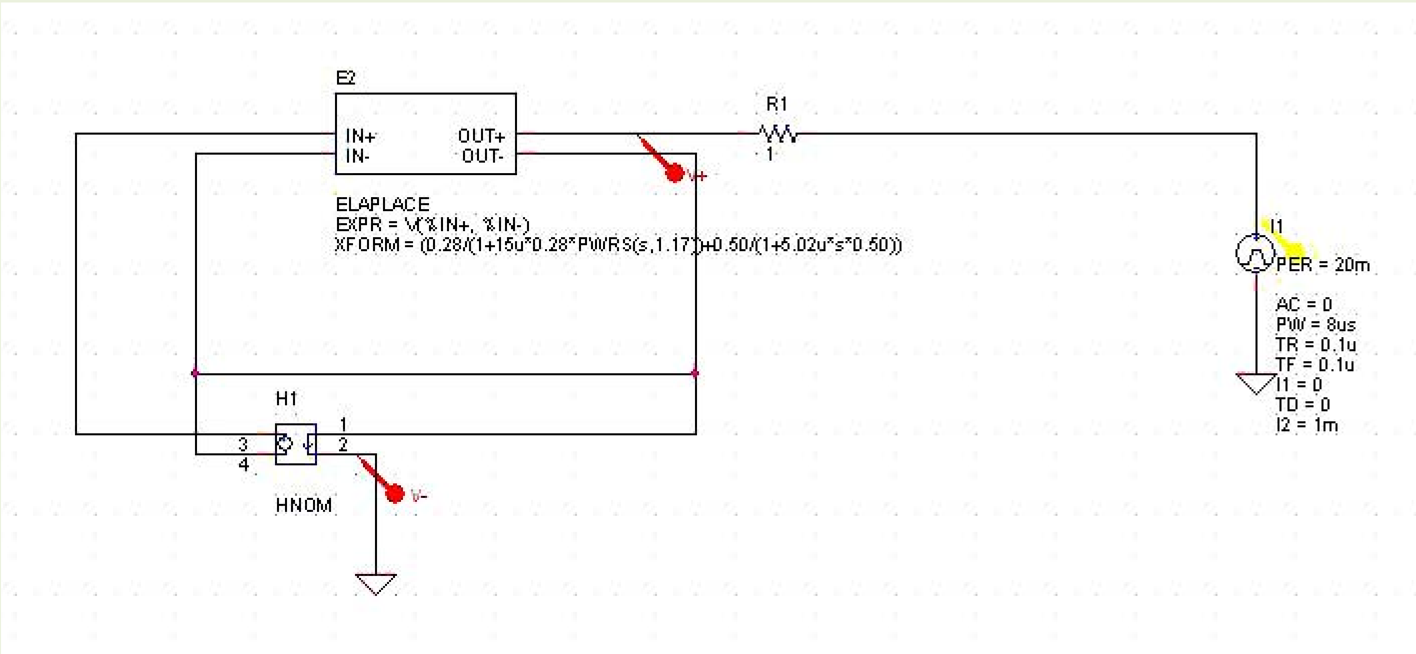
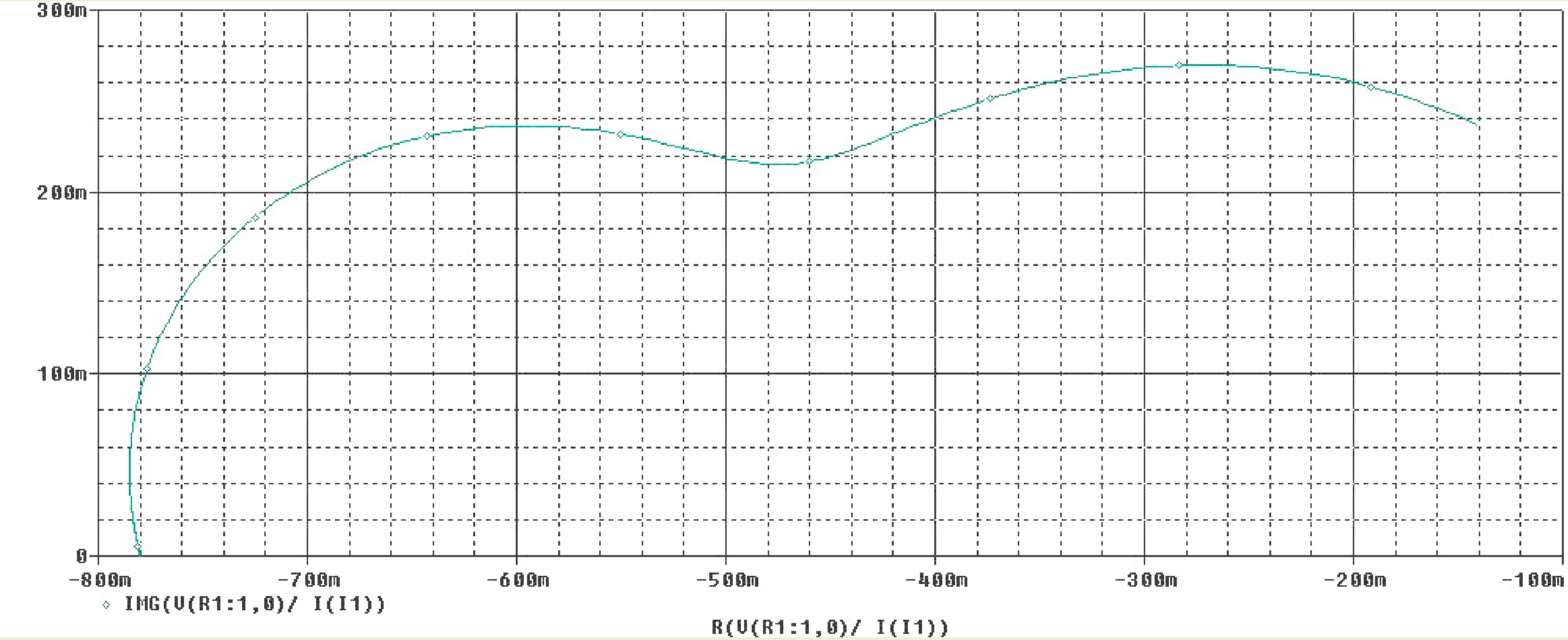
Phase 1: Pspice Model

- **Pspice model components.**
  - **AC or vpulse source depending on the analysis performed.**
  - **ELAPLACE element.**
  - **H (current dependent source).**



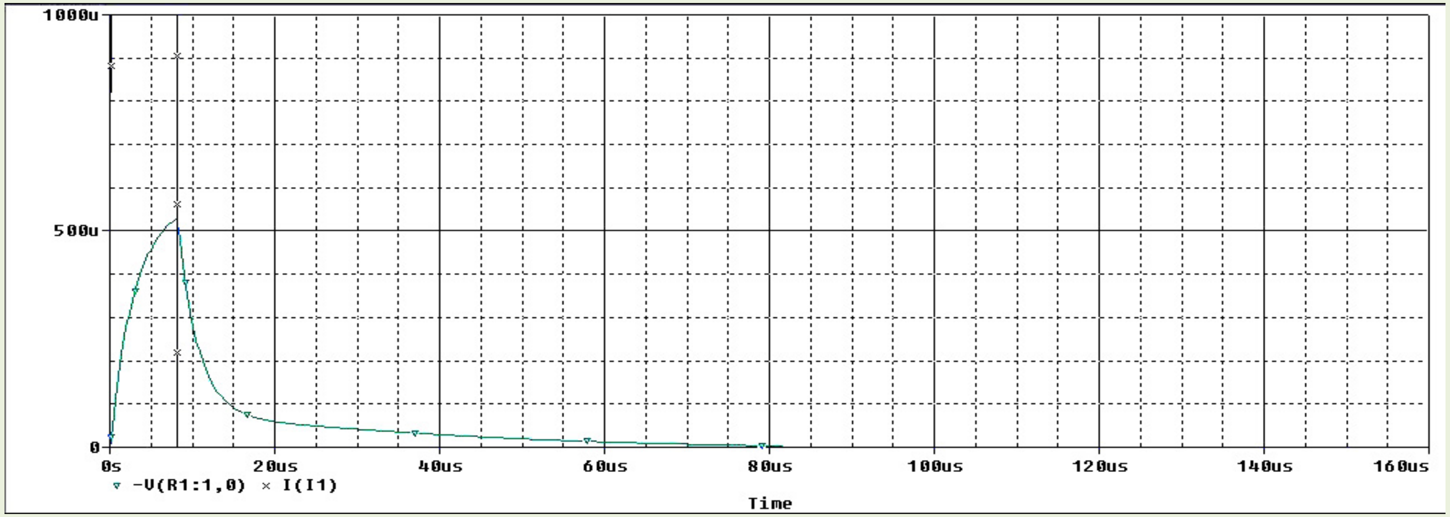
Phase 1: Pspice Model

- AC Analysis



Phase 1:PSPICE Model

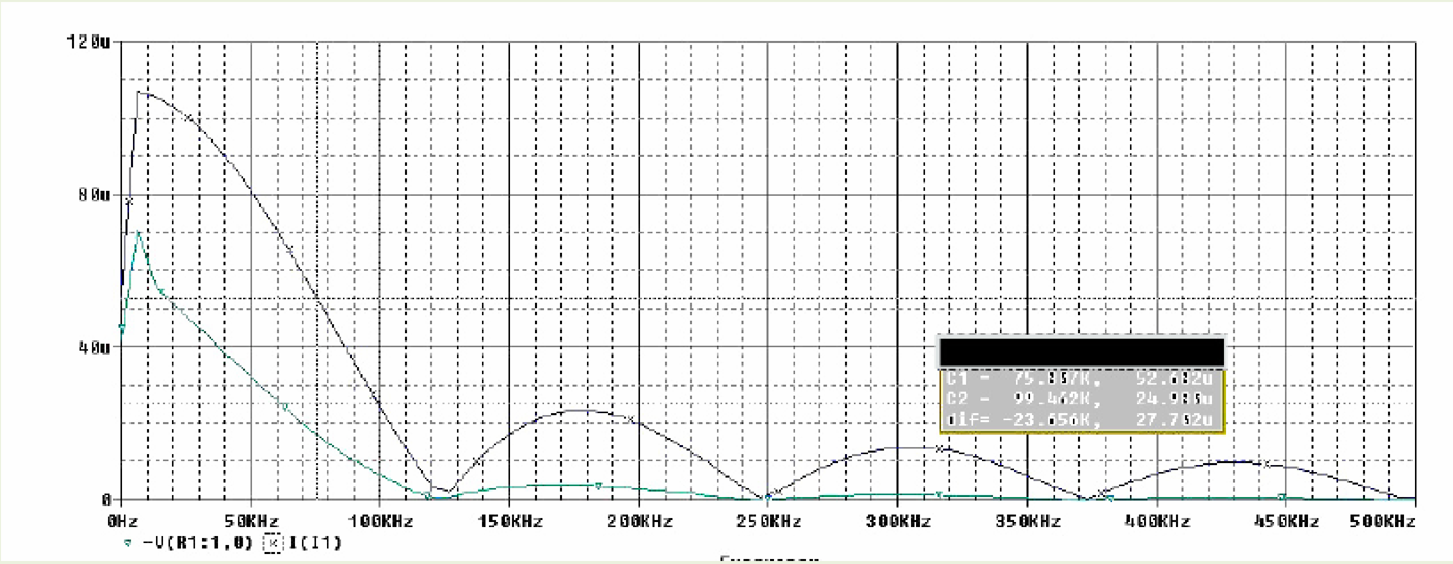
- **Transient analysis results.**
  - Meaningful bandwidth : < 65 KHz
  - Pulse stimulus : 1/(2 x 60 KHz) ≈ 8µs



Length of the impulse response ≈ 80µs

Phase 1:PSPICE Model

- **Frequency domain analysis results.**
  - **Aproximate Bandwidth: 100 KHz**
  - **Sampling Frequency : 100KHz x 2 = 200 Khz**



Length of the impulse response ≈ 80µs

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Phase 1: System requirement

- Relevant information inferred from the previous research:
  - Impulse response length = 80µs
  - Noisy environment.
  - Low-amplitude signals involve.
- Final requirements
  - Low-cost.
  - Small size (portable).
  - Good behavior in a noisy environment.
  - Low signal distortion.

Phase 2: System Modeling

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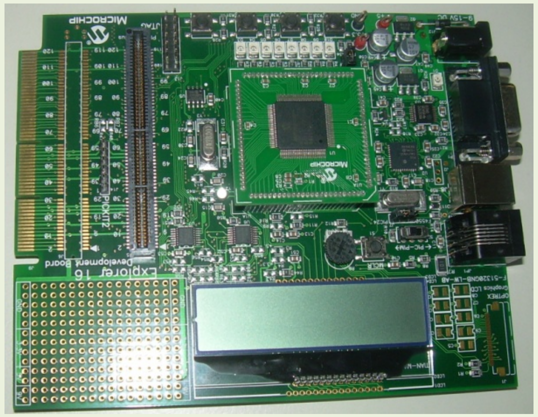
Phase 2: Stimulus definition

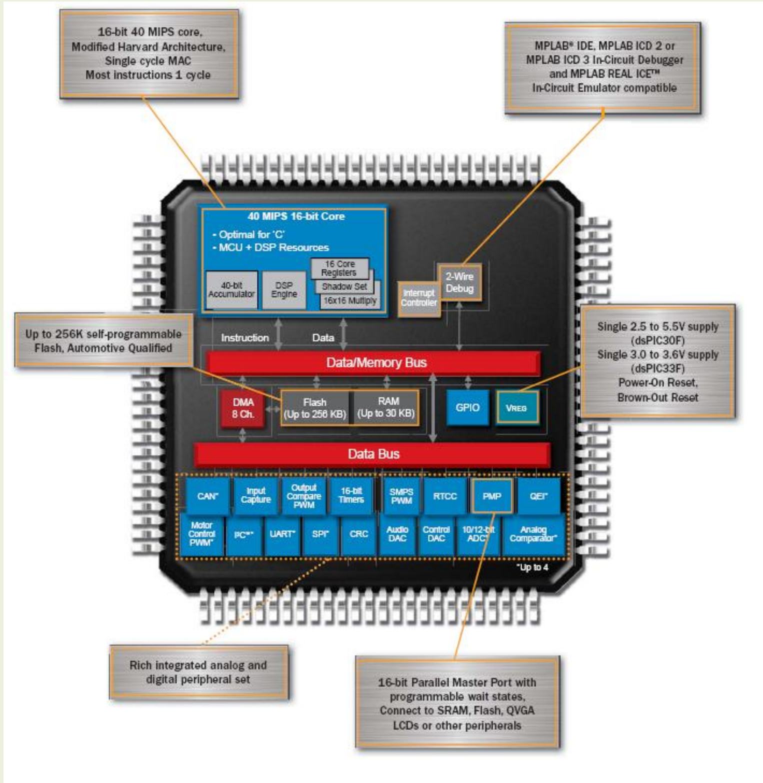
- An MLS (Maximum Length Sequence) signal was defined as the stimulus.
  - Main Characteristics:
    - Rejects the DC component.
    - High Signal-to-Noise ratio.
    - Easy Generation: shift register.
    - Effective processing procedure. (Fast Hadamard Transform)
    - Each sequence has its own distortion pattern. Changing the sequence eliminates the previous distortion.
  - Requirements:
    - The system must behave as a LTI System.
      - Linear.
      - Invariant.
    - The duration of the MLS signal must be longer than the impulse response of the system.

Phase 2: System definition

- The workload would be implemented by a microcontroller, particularly, the DSPIC30F3256GP710 provided by Microchip.
- Additional nets are necessary



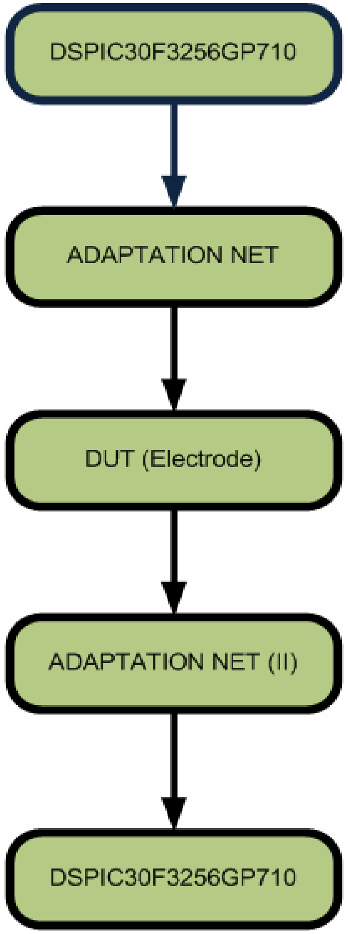
Micro plus Development Board



DSPIC30F3256GP710
Major characteristics

Phase 2: Stimulus definition

- **Schematic of the system**



MLS generation (length = 4095, duration = 20.4 ms)
Output voltage: 0-3.3V

The digital output of the microcontroller must be adapted to the potentiostad.

- MLS bipolar.
- Required amplitude: ±1.5V

An amplifier is needed in order to adapt the amplitude levels.

The electrode is represented by its equivalent circuit.
Transient analysis: it has determined the length of the system impulse response.
The potentiostat is connected to the electrode.

A second adaptation net is required. It interfaces between the potentiostat and the microcontroller input.
It will be made of:

- Amplifier (adapt amplitude levels)
- Filtro antialiasing (opcional)

The signal is processed in the microcontroller.

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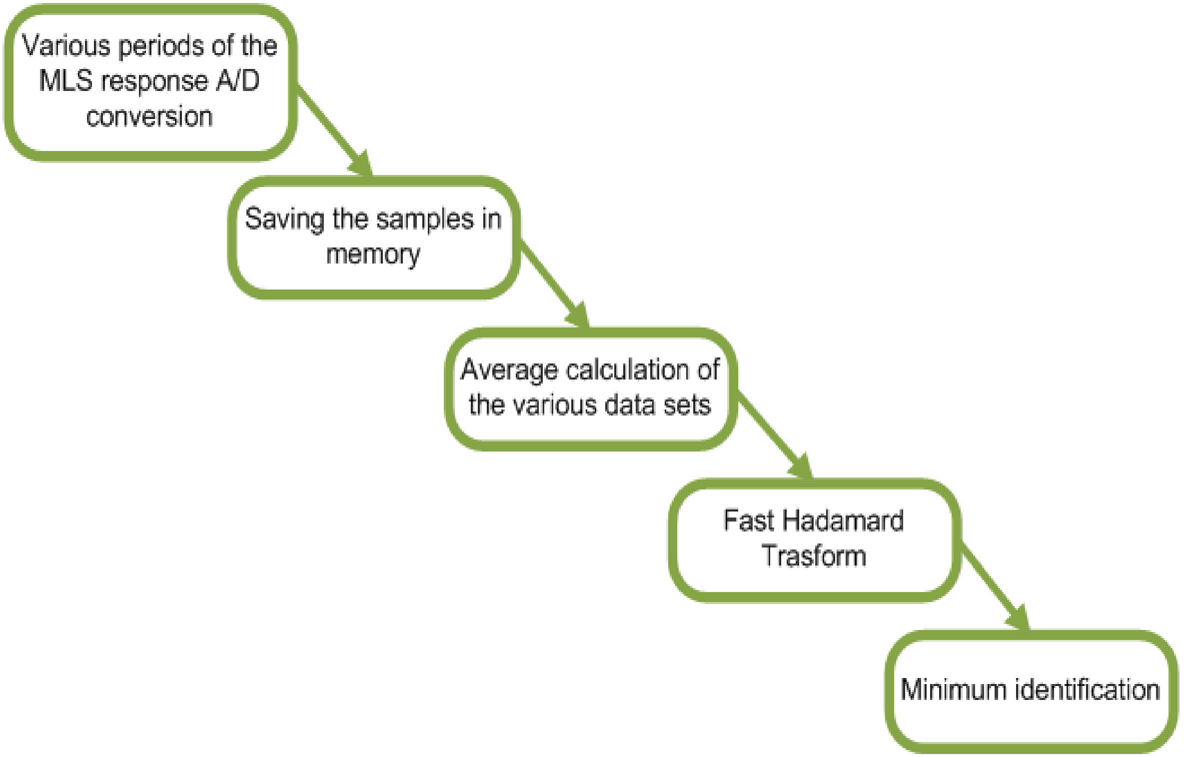
Phase 2: System definition

- **Processing Schematic**

Minimum identification



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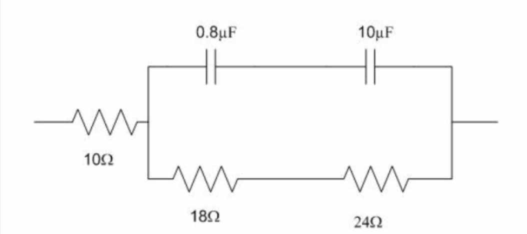
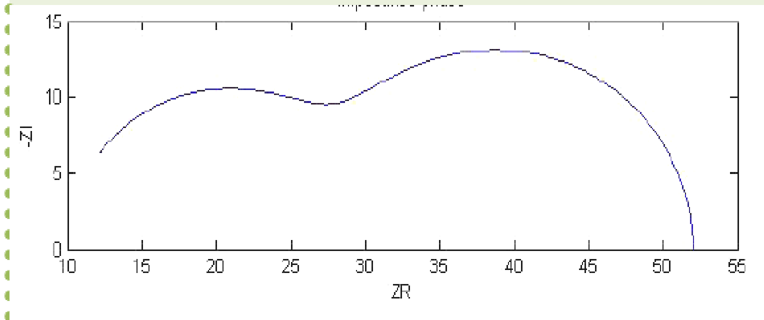
Phase 2: Matlab Model

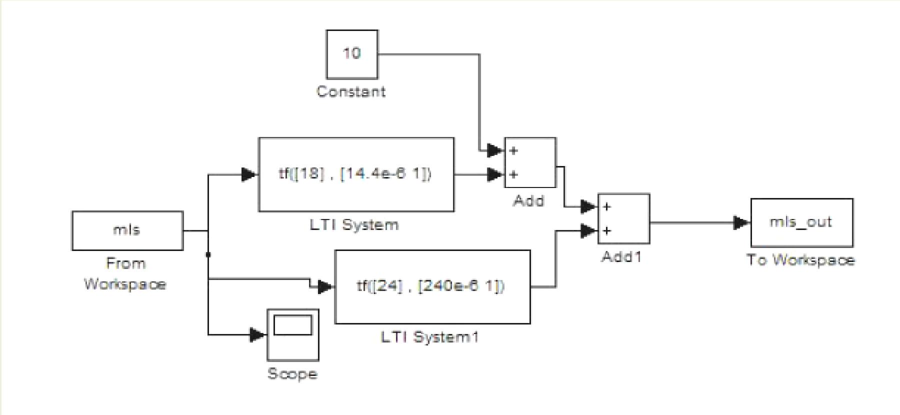
- **Net equivalent to the CE model.**
  - **Characteristics.**
    - **Similar impulse response.**
    - **Existence of the Laplace transform.**
      - **(CPE non-linear)**
    - **LTI behavior.**



RC system under test

Impedance response obtained using Matlab





Simulink Model of the net

Phase 2: Matlab Model

- Main steps of the processing algorithm.
  1. Generate the matrix M from one period of the m-sequence. M is formed by shifted versions of the original MLS stimulus.
  2. Factor [M] into [R] and [C].
  3. Obtain the row tags of [R] and the column tags of [C] according to the integer equivalence of their m-binary digits.
  4. Reorder the elements of the system MLS response by using the column tags of [C] and add a zero element to obtained the permuted column matrix [Y0] to form [Y00].
  5. Apply the Fast Hadamard transform to [Y00] to give [H00].
  6. Omit the rst element of [H00] and reorder the elements of the resulting matrix, H0, by using the row tags of [R] to give the impulse response [h]. The reordering process will be reversed.

$$M_7 = \begin{bmatrix} 1 & 1 & 1 & 0 & 1 & 0 & 0 \\ 0 & 1 & 1 & 1 & 0 & 1 & 0 \\ 0 & 0 & 1 & 1 & 1 & 0 & 1 \\ 1 & 0 & 0 & 1 & 1 & 1 & 0 \\ 0 & 1 & 0 & 0 & 1 & 1 & 1 \\ 1 & 0 & 1 & 0 & 0 & 1 & 1 \\ 1 & 1 & 0 & 1 & 0 & 0 & 1 \end{bmatrix} = \underbrace{\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 1 & 0 \\ 0 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 0 & 1 \end{bmatrix}}_{[R]} \begin{matrix} 4 \\ 2 \\ 1 \\ 6 \\ 3 \\ 7 \\ 5 \end{matrix} \quad \underbrace{\begin{bmatrix} 1 & 1 & 1 & 0 & 1 & 0 & 0 \\ 0 & 1 & 1 & 1 & 0 & 1 & 0 \\ 0 & 0 & 1 & 1 & 1 & 0 & 1 \end{bmatrix}}_{[C]}$$

$$\begin{matrix} 4 & 6 & 7 & 3 & 5 & 2 & 1 \end{matrix}$$

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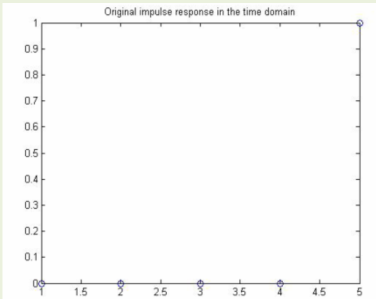
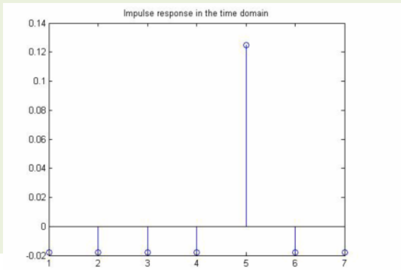
Phase 2: Matlab Model

- **Algorithm Implementation**
  - **Results:**
    - **Before the processing**



    - **After the processing (a DC component -0.02 can be seen)**




```
%The input vector are some periods of the data output, synchronized with the mls impulse used
%Output of this functions are: the y axis of the minimum and x axis of the minimum encounter,
%the ZR and ZI before using the polyfit function and the ZY and ZR adjusted (y_fit,x)
function[minimo_ejey, minimo_ejex, ZR, ZI, y_fit,x] = procesado_senal(data)
N=2^12 − 1;%Length of the mls sequence
M=12;%Order of the mls sequence
[mls, mls_ceros, temp] = generar_mls(1);%One period mls generation
input= data;
matriz_output = ordenar_periodos(input,N);
media = mean(matriz_output,1);%Mean colum calculation
media=media./max(abs(media));%Normalization
Noise = crear_noise_matrix(mls_ceros,N,M);%Generation of the noise Hadamard Matrix
%C,R and their respective tags generation
C = generar_C(Noise,M,N);
R = generar_R(Noise,N,M);
tagR = generar_Row_tags(R,M,N);
tagC = generar_Column_tags(C,M,N);
sout = reordenar_senal(input,N,tagC);%Input preparation before applying the FHT
h_inter=fhtnat(sout);%Fast Hadamard Transform
H= reordenar_hinter(h_inter(2:end),N,tagR);%System impulse response
%figure(1); stem(H(1:150));figure(2);w =[0:1/255:1];
H=fft(H,256);
% subplot(121);plot(w,abs(H));title('Magnitud respuesta en frecuencia del sistema')
%subplot(122); plot(w,phase(H));title('Fase respuesta en frecuencia del sistema')
%figure(3); plot(real(H),imag(H))
ZI = imag(H);
ZR = real(H);
%figure(3); plot(real(H),imag(H))
%figure(4);plot(ZR,ZI)
indices_ZI =find(ZI>0);%ZI elements values under 0 are dropped
ZI_n = ZI(indices_ZI);
ZR_n = ZR(indices_ZI);
[indices_ZR] = find(ZR_n<0);%ZR elements values over 0 are dropped
ZR = ZR_n(indices_ZR); %The important information is condensed in ZR negative values
ZI = ZI_n(indices_ZR);
%figure(5);plot(ZR_n,ZI_n)
ZI=ZI/max(abs(ZI));%Normalization before applying polyfit
ZR=ZR/max(abs(ZR));
[P, S] = polyfit(ZR,ZI,5);%Order 5 polyfit: x axis vector is ZR, y axis vector is ZI
x= ZR;
y_fit=aplicar_funcion(P,x);%Calculation of the adjusted ZI
%figure(7);plot(x,y_fit); title('Ajuste de la funcion de impedancia aplicando polyfit de grado 5');
P_dev=derivar(P);
Y_dev=aplicar_funcion(P_dev,x);
%figure(8); plot(x,Y_dev);title('Calculo de la derivada de la señal')
[maximo, minimo]=hallar_minimo(P_dev);%Desired minimum is the fist element of the output minimo
```

Phase 3: System Verification

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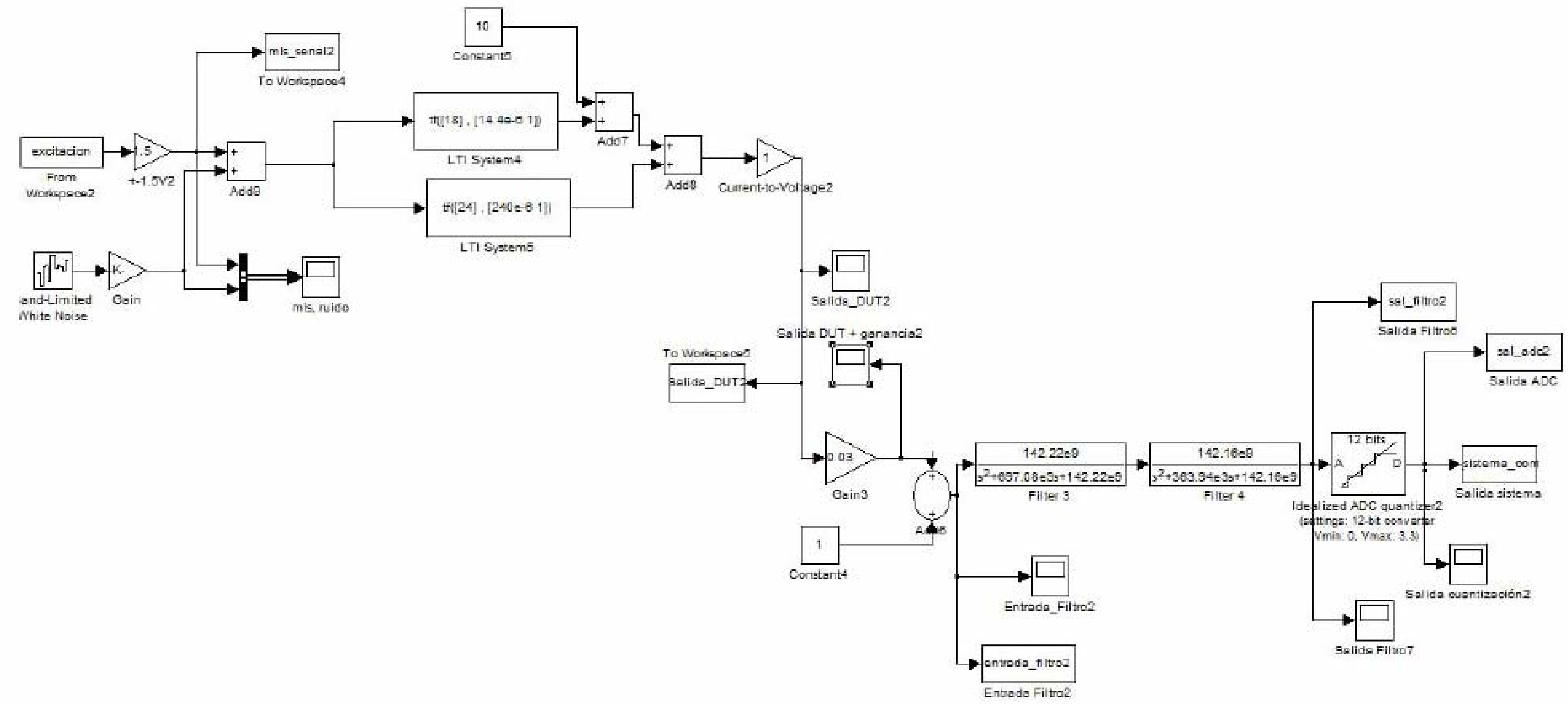
Phase 3: System Verification

- **Global system Simulink model.**



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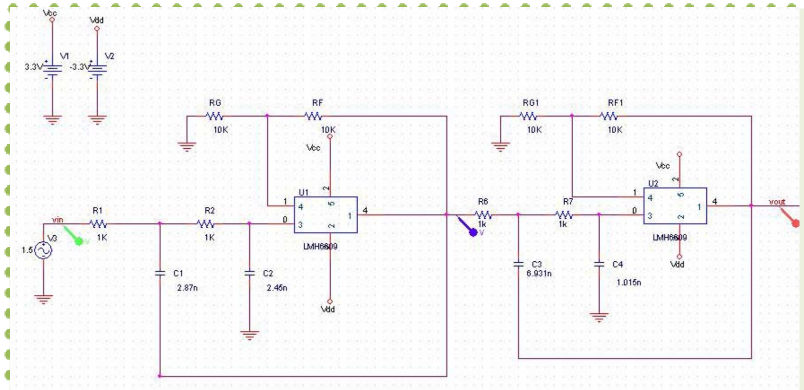
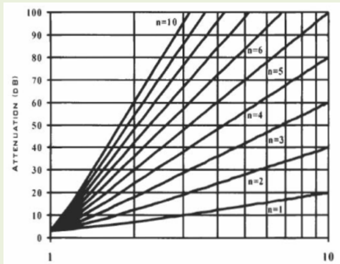
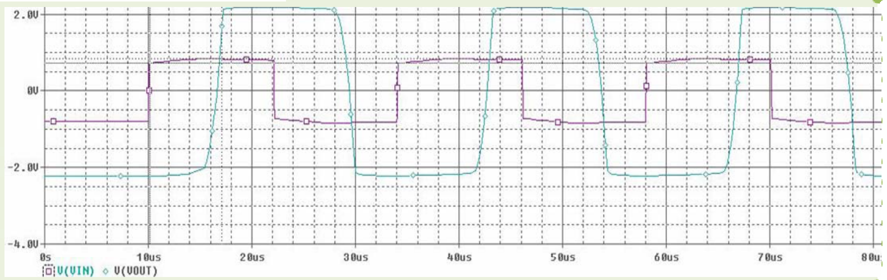


Antialiasing filter spice model

Butterworth Order



Transient response



- **Antialiasing filter**
  - **Butterworth filter, order 4.**
  - **Sallen-Key filter design.**
  - **Cut-o frequency for lter is 60 Khz (The main information of the spectrum is concentrated in the range from 10Khz till 30kHZ)**
  - **Filter attenuates the signal to > 20dB at 120 Khz.**

Phase 3: System Verification

- **Results:**
  - The original signal is recovered in a extremely noisy environment.
  - The analog Butterworth filter delays the reponse 2 samples. Its implementation and must be checked in the real application.
  - Averaging different data sets improves significantly the signal-to-noise ratio.
  - Savitzky-Golay smoothing techniques can keep the original minimun position in noisy environments. Althougth, its computational workload must be considered.

Conclusions

This technique can be an advance in enviromental control and monitoring

↓ **but**

It is necessary that the electrode system behaves as a LTI system.

↓

Further study of the electrode behavior is encouraged to be performed.

-Dynamics of the response (predictabiliity)

-Combination with other theories (Chaos)

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