5. EXPERIMENTAL PROCEDURE

5.1. ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

5.1.1. Equipment

The equipment employed to execute the electrochemical corrosion testing, comprises basically, one electrochemical cell, one potentiostat, and one computer to supervise and control the measurement process, and to save and evaluate the corrosion data acquired during these experiments.

The electrochemical cell consists of three electrodes, reference electrode, work or test electrode, and counter electrode, submerged the three of them in an electrolyte. In this case the electrodes and the electrolyte used were,

Reference electrode (RE)	$HgSO_4$ (637 mV)
Counter electrode (CE)	Pt
Test/Work electrode (WE)	Aluminum alloys under study
Electrolyte:	Na_2SO_4 0,1N

With the potentiostat, the potential of the test electrode was controlled (by measuring the amount of electrical current supplied by the potentiostat, the test electrode potential change can be determined). The model utilized was the EG&G model 283.

In order to minimize the noise that can occur when using current interrupt, the electrochemical test cell was enclosed during the measurements inside of a Faraday's cage.

Before running an experiment, the Open Circuit Potential was measured. A measurement would begin with a frequency of 100 kHz, and would finish at a frequency of 10 mHz, being 30 points collected in this frequency range (included the two extreme frequencies values). The AC amplitude used to acquire the impedance spectrum was 10 mV.

The test electrode area was 0,8 cm^2, and for the electrolyte, a volume of 0,4 l was used. Why were finally these values taken and not others will be discussed in the following sections.

4.1.2. Measurement Program

The measurement program, was not an standard method to follow, that means, that there was not such a laboratory manual, were the proceed to obtain the corrosion data were depicted, for example, it was not known, how long should be waited between two subsequent measurements, so the system were not perturbed. Thus the measurement program was during this research created.

Measuring the corrosion resistance at pH 7 constant: an iterative program consisting of a loop of X measurements (normally X between 7 and 15), with a delay time of 2 hours between every two consecutives measurements was used.

Measuring the corrosion resistance at higher pH values: Starting with the previous program, until the resistance reaches steady state or a constant value at pH7, then an iterative program consisting of a loop of Y measurements (being Y normally 2 or 3) with a delay time of half hour between every two consecutives measurements, was used.

Measuring the corrosion resistance, using the proper adhesives bounding dissolved: Starting directly at the pH value of the adhesive solutions, with pH values around 9, using an iterative program of 4 measurements with a delay time of half an hour between consecutives measurements. These solutions are actually being used to cleave the sheets that together build up a car.

Here can be viewed an schema and a photo of the impedance data acquisition system employed during this research. In the schema, *figure 5.1.1*, WE is referred to the Working Electrode, RE to the Reference Electrode, and CE to the Counter electrode.
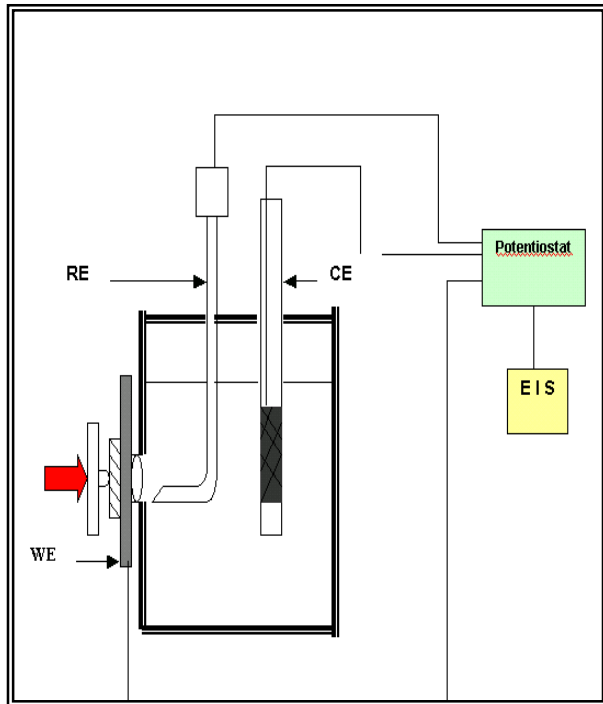
Fig.5.1.1. Electrochemical cell arrangement.   **Fig 5.1.2.** Electrochemical cell (3.28.2001).

5.1.3. Preliminary Experiments

The electrical resistance associated with the reference and work electrode separation, also called uncompensated solution resistance, can be described with the following mathematical expression:

$$R_{elec} = d * \rho_{elec} / A \qquad\qquad [C]$$

- d is the distance between electrodes (cm)
- ρ_{elec} is the solution resistivity in ohms*cm
- A is the work electrode area in cm^2

Before starting the measurements, object of this project, it was necessary to evaluate the influence of these parameters on the obtained corrosion data.

This previous essays were carried out using only samples from one of the alloys, concretely from alloy 6016 and for one of the electrolytes used during this research, the Na_2SO_4 solution

5.1.3.1. Work electrode and reference electrode arrangement.

Two different relatives position between the work electrode and the reference electrode were set, in order to study the influence of the distance between both electrodes on the corrosion data. The influence of the relative position between the electrodes, was studied for two different electrolyte concentration.

How two different distances, between electrodes was made, is shown in the following schema, where "Position I" represent the minimum distance possible between electrodes (Angle = 0°), and "Position II" (Angle = 45°) an arbitrary bigger distance:
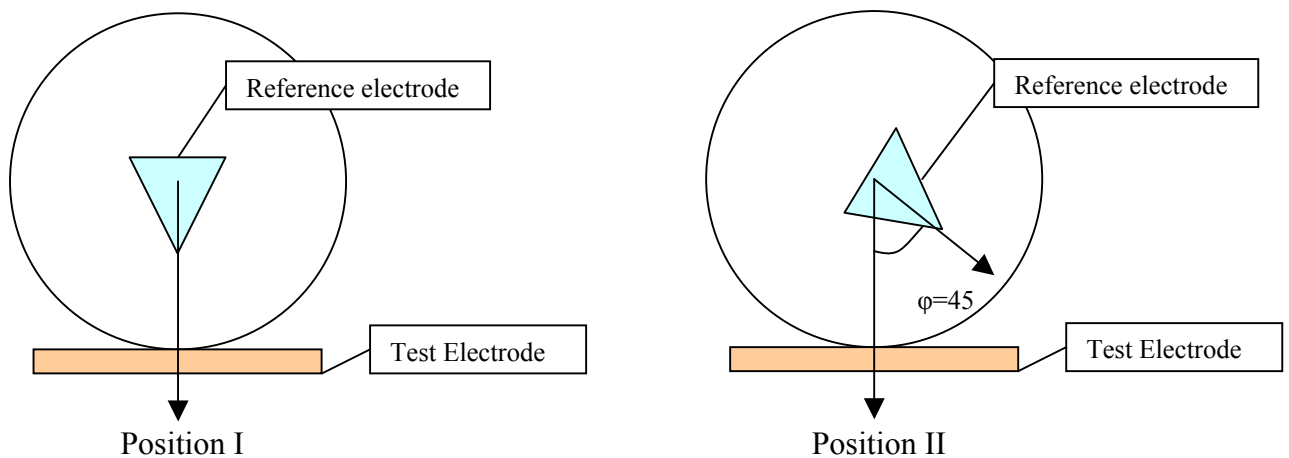

Fig. 5.1.3. Arrangement of the cell for two different positions of the reference electrode.

The results achieved are shown in the following graphics,

Alloy   6016
Electrolyte Na_2SO_4 0,2N pH7 (Position I ▮   Position II ▮)

                                Na_2SO_4 0,1N pH7 (Position I ▮   Position II ▮)

The graphics here shown, correspond with the first measurement done after the cell was assembled.
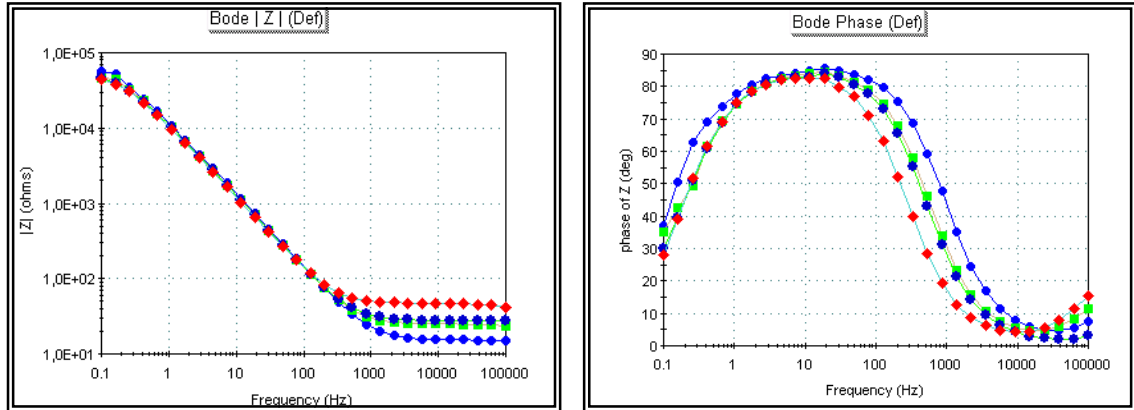
Fig. 5.1.4 Influence of the electrodes' arrangement on the electrolyte resistance.

In the high frequency zone (around 100kHz), R_{elec} can be evaluated. In this range of frequencies, an arbitrary value of f = 62 kHz has been taken to evaluate the value of this resistance. See *figure 5.1.5:*
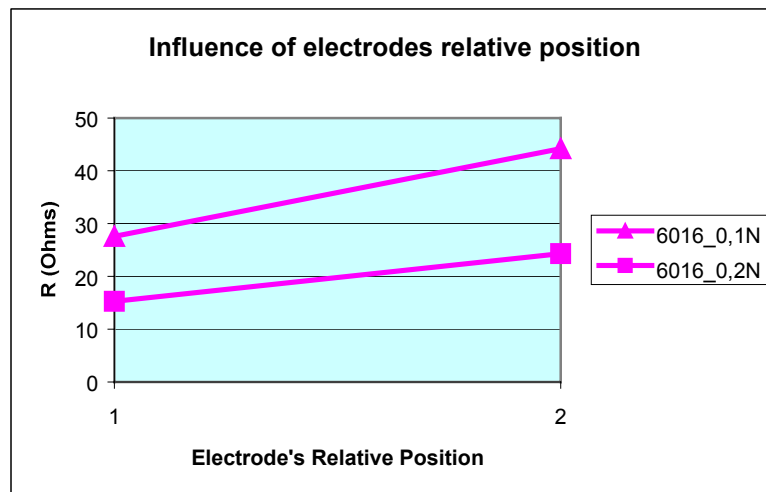

Fig. 5.1.5. Evaluation of R_{elec} at f = 62 kHz.

* As expected, R_{elec} is bigger when the distance between both electrodes is increased, and that occurs for both concentrations, it can be observed as well, that for a lower concentration of the electrolyte, the value of the resistance grows (decreasing the electrolyte's concentration is the same as increasing ρ_{elec})

* The corrosion resistance measured for this alloy at pH 7, at the lowest frequency available during this research, i.e., at f = 10 mHz, was about 1 Mohm (as already said, R_{corr} can be evaluated in the low frequency range of the spectrum), and the biggest R_{elec} measured was of around 50 Ohm, i.e. 5 order of magnitude smaller, therefore it can be supposed that it has almost no influence on the R_{corr} which one of these positions for each of these two concentration is chose.

It was decided to fix one position for all the measurements that would have to be done during this project. Position I was chosen and marked on the cell and electrodes, being all the results here described, obtained with this electrodes' arrangement.

* For everything here said, in what follows, the $R_{total} = R_{elec} + R_{corr}$, measured at the low frequency range, will be considered equal to R_{corr}.

5.1.3.2. Influence of the electrolyte concentration on the obtained corrosion data.

Since the solution resistivity grows when the electrolyte concentration decreases, by using different electrolyte concentrations, can be the influence of the solution higher or smaller resistivity on the corrosion data evaluated.

The data obtained for three different concentrations, i.e., three different values of the electrolyte resistivity for the alloy 6016, are shown in the following graphics,

Time	Na2SO4 0,05 N	Na2SO4 0,1N	Na2SO4 0,2N
0 hours	54	25,8	16,1
15 hours	55	26	16,4

(*) All the electrolytes were set with pH7
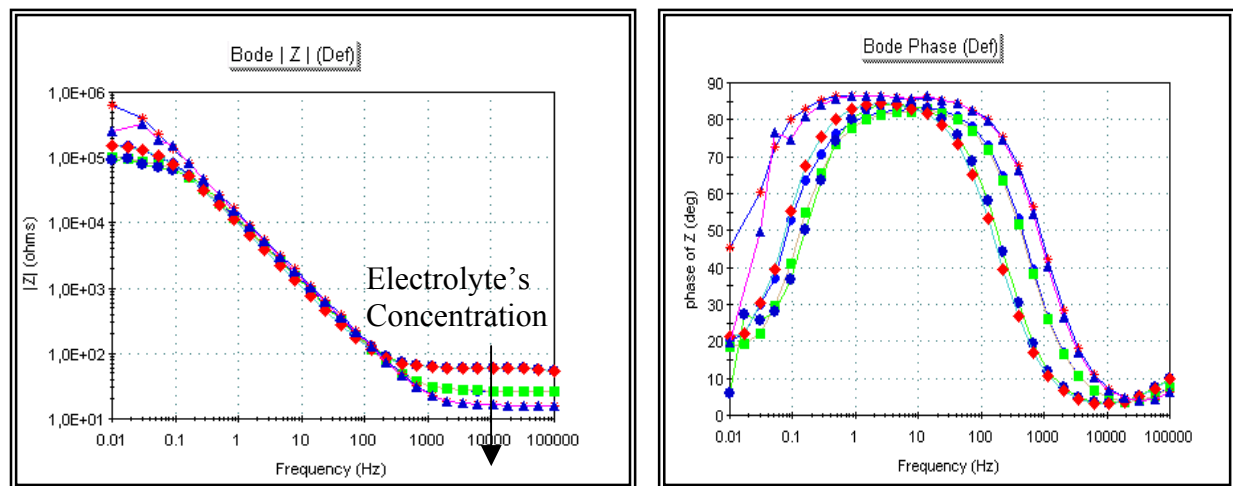**Table 5.1.1.** Values of R_{elec}(Ohm) for different concentrations and times.

Fig.5.1.6. Influence of the electrolyte's resistivity on the electrolyte resistance.

In this case the highest frequency of the range, f = 100 kHz, was used to evaluate R_{elec} (see *figure 5.1.7*). For each concentration of the electrolyte, there is drawn two curves which are one behind the other in the Bode Magnitude diagram, and may be easier to identify in the Phase diagram.
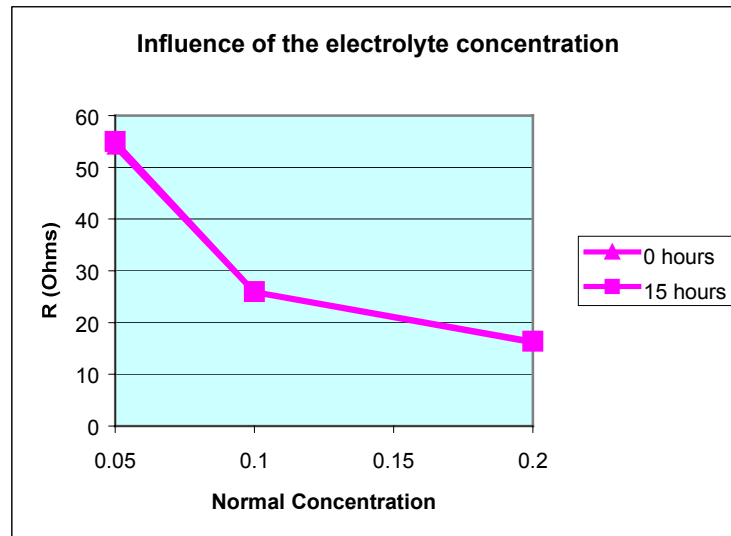
Fig. 5.1.7. Evaluation of R_{elec} at f = 100 kHz.

* As expected, the lower that the concentration of the solution (the higher the ρ_{elec}) is, the bigger that the R_{elec} goes, but the biggest value of the resistance encountered, R_{elec} = 60 Ohm, is so small (when compare to with R_{corr}), that the three concentrations can be considered valid, to realize further measurements.

It was arbitrary decided to take a solution of Na_2SO_4 0,1N as electrolyte for the impedance measurements done during this project.

* As here shown, the time has no influence over the R_{elec}, i.e. it remains constant. That will not occur with R_{corr}, that depends directly, from the changes that the oxide layer suffer when submerged in the electrolyte (*See next sections*)

5.1.3.3. Influence of the test electrode area on the corrosion data.

Two different areas were used during in this study:

Reference alloys	Area = 5,31 cm^2
New alloys	Area = 0,8 cm^2

Several specimens of each size have been measured in this part of the project, and the electrolyte used in both cases was Na_2SO_4 0,1N pH 7.

The graphics here shown, correspond with a first measurement after the cell was assembled, i.e. t = 0 hours,
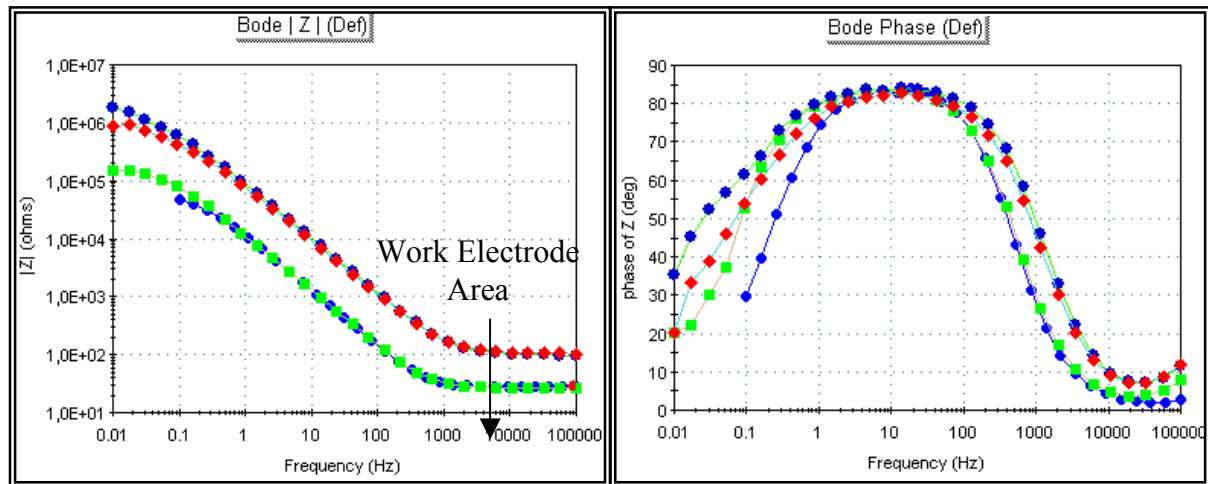
Fig. 5.1.8. Influence of the test electrode's area on the electrolyte resistance.

The last part from one of the curves is not shown, the reason of this missing was that the Potentiostat was overloaded at the frequency f = 34 mHz not being possible the data acquisition under this frequency. At all events, R_{elec} will be evaluated in the high frequency zone, where no perturbation of the results is observed.

* As already said, this essay was several times repeated so the reproducibility of the measurements could be checked too. The obtained results shown a very high reproducibility, being possible to represent each group of measurements (each area) with few experiments, in this case have been 2 of 10 measurements of each group, which have been used to evaluate the R_{elec}, and which are representative of all the measurements.

* As the theory guess, using the old specimens (bigger area) as test electrode, R_{elec} is smaller in both cases. See *table 5.1.2:*

	Area = 5,31 cm^2	Area = 0,8 cm^2
R_{elec} (Ohm)	27,5	26,4
$r = R_{elec0,8}/R_{elec5,31}$	3,9	4,0

Table 5.1.2. Values of R_{elec} for different test electrode's areas.

The resistance ratio *r* should be the same as the area ratio (the inverse of). This area ratio, has a value of *a* = 5,31/0,8 = 6,6, being in all cases bigger as *r*. It has to be taken into account that the surface pretreatments of the "reference alloys and "new alloys were not the same, and that it has been also supposed that the electrolyte, resistivity and distance between electrodes have remained constant, but little variations while preparing the solution or mounting the cell could happened.

* When the test electrode area is very small, some problems during the measure could occur, e.g. an air bubble deposited upon the surface, can interfere in the experiment and would give false results. This influence would be much bigger whenever the surface is smaller. To avoid this kind of troubles, it would be better to work with an area of 5,31 cm^2 as electrode area.

The size of the sheets delivered was 8cm X 15cm, but as they were here received, by mistake, were cut into smaller pieces of about 1,5cm X 8cm and it was not possible to carry out the experiments with the desired area of the test electrode.

5.1.4 Parameters affecting the impedance measurements

* *pH stability of the solution*: since this work was carried out in aerated solutions, due to the presence of CO_2 in the atmosphere, the pH value was not constant, otherwise, it was decreasing within the time. This effect of the CO_2 can be observed by measuring the pH value of the solution, when the electrochemical cell is mounted, and after a certain time (see *table 5.2.1* referred to alloy AA6016, and *table 5.2.3* referred to alloy AA5182, which contain the electrolyte's pH values at the beginning and at the end of each series measurements).

When working at pH 7, it can be observed that the pH value goes in 24 hours, approximately from pH 7 to pH 6,5. A difference of pH from commence to end of 0,5 points has been considered not such a big variation, being likely to assume pH 7 constant in this interval, and therefore allowing in this range to study the alloy's behavior considering pH 7 constant.

To maintain the pH value, at higher pH values than pH 7, became a real problem. While maintaining the electrolyte pH, around pH 7, was possible during one or more days (between pH 6,5 and pH 7 it has been considered the same as pH 7 constant), maintaining pH 8, pH 9, and pH 10,it has been impossible for such a period of time. It would take only approximately half an hour, until the electrolyte's pH value would have dropped more than 0,5 points, being a drop of 0,5 points, the maximal drop allowed when working at a certain pH value.

Some consequences are derivate from this instability:

> *Few measures and short delay time:* It was not possible to carry out measures series, like already done at pH7, during one day or for longer periods. As a result of this instability, only four measures at each pH value different from seven, and with a short delay time between them, could have been used.

> *Experiment continuous watching:* It was required the presence of someone checking the electrolyte's pH value, every half an hour, to compensate the pH drop already mentioned by adding NaOH when it was necessary. This was the biggest inconvenience.

* *Temperature effect*: to run a loop of, for example, 10 successive measurements with a long delay time, e.g. 2 hours, between two consecutives measurements, it was required to run part of these measurements during the night. All through the night, the temperatures can suffer a big drop, affecting the impedance results. The electrochemical cell was not isolated, due to the high difficulty in it implied.

To find out whether or not, this possible temperature drop, affected the system, a temperature recorder was included as a part of the measurement system. The temperature recorder used, was the Testotor 175 Mini-logger, supplied by Daimler-Benz Company.

At the beginning, all the measurements were carried out without temperature control, the first one, in which the temperature (and the relative humidity) was registered during all the time, was the sample 8.5.3.b (for the alloy 6016) and which results are here shown:
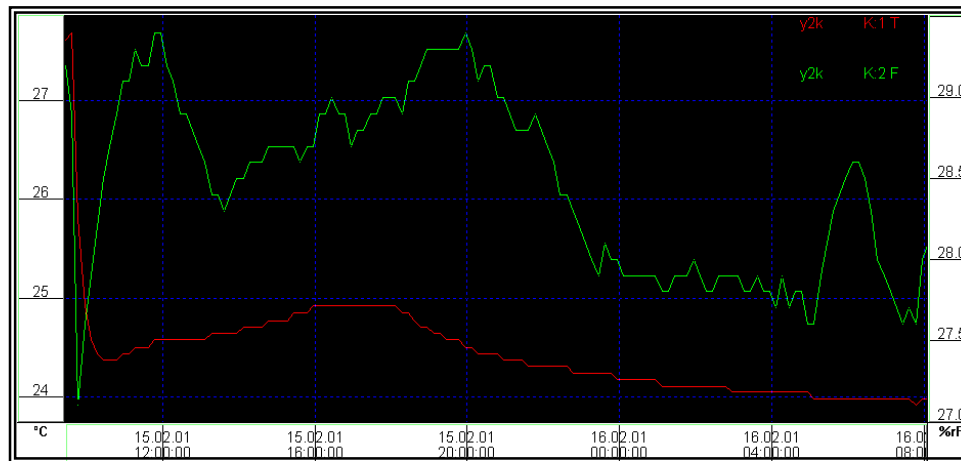

Fig. 5.1.9. Temperature (red) and relative humidity (green) measured during one of the impedance measurements of the alloy 6016.

As shown, the highest temperature observed was 24,92°C (note that the highest peak at the start of the measurement,27,68°C, corresponds with the temperature of the person who placed the Testotor 175 in the faraday jail) and the lowest one, 23,92°C, i.e., not a significant decrease of
the temperature took place. This trend of the temperature to remain constant, was observed for the other samples too, as well as for alloy AA5182.

All the experiments were carried out during February, March, and April, being the temperatures in the same rank, without suffering big variations. It can be supposed that the temperature was constant during the experiments and therefore the study its influence on the results can be omitted.

* *Influence of the delay time:* It has been observed a big influence of this parameter on the obtained results.

It can be supposed, that the system need a certain time to reach its stability after one measurement. Since it is not under the scope of this project, to study all the possible perturbation of the system that can affect the corrosion data, it would be convenient, in order to avoid its influence on the results, a minimum delay time of two hours between measurements.

This effect of scatter growth of the impedance caused by a short delay time between two consecutives measurements, has been reported for both alloys .

In the graphic shown, see *figure. 5.1.10* and *figure. 5.1.11,* when the delay time between two consecutives measurements was 1 hour, the resultant curve oscillates towards its final value, while for a delay time of two hours (or bigger) these oscillations of the curve disappear (See *figure 6.2.1.*referred to alloy AA6016 and *figure 6.2.3* referred to alloy AA5182).

It is easier to visualize the perturbation produced to the system, when a short time is waited between measurements, through the Nyquist diagram,

Time	00:00	03:02	05:55	09:09	12:10	14:51
$Z_{10\,mHz}$	1044	1559	1844	2021	2202	2497

Table 5.1.3: Evolution of Z_{10mHz} (kOhms) within the time, with long delay time between measurements.

Time	00:00	01:25	03:04	04:35	06:03	07:40	09:16	10:56	12:31
$Z_{10\,mHz}$	1290	1892	1806	2156	2057	2034	2072	2160	2110

Table 5.1.4: Evolution of Z_{10mHz} (kOhms) within the time, with short delay time between measurements.
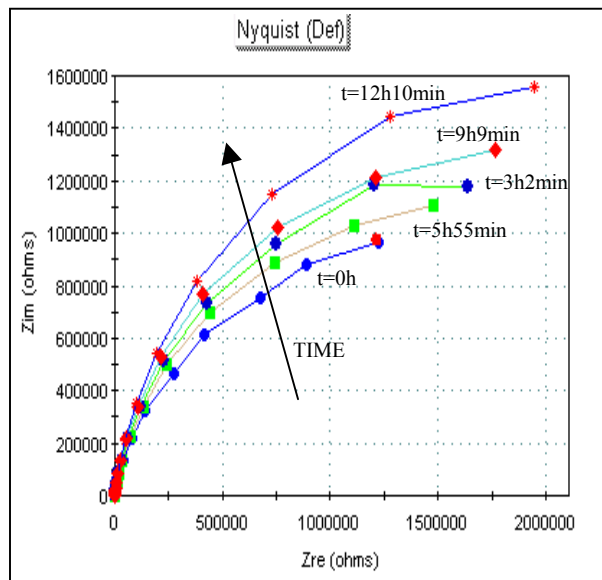

Fig. 5.1.10. Sample 8.7.5.a with a delay time between consecutives measurements of two hours.
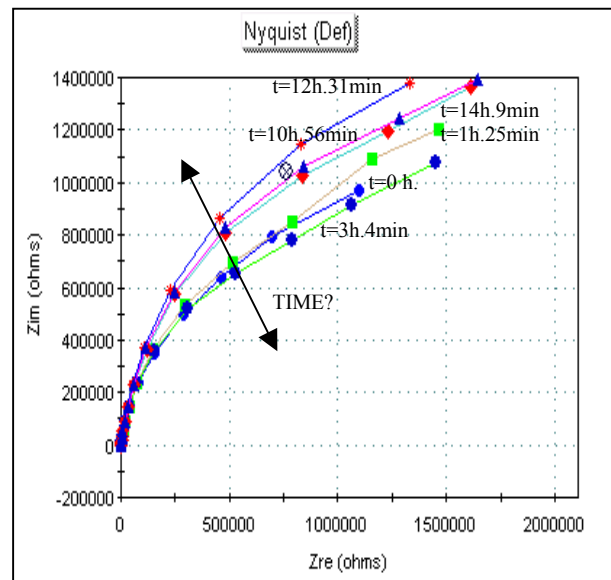
Fig. 5.1.11. Sample 8.5.1.a with a delay time between measurements of one hour.

This scatter growth of the curves within the time, it has been reported too, for shorter delay times between two consecutives measurements like half an hour and five minutes between measurements.

This was the reason, why a two hours time between measurements was established to study the alloy's behavior at pH 7.

When the pH value of the electrolyte was higher than pH 7, the measurements were performed with only half an hour of delay time between consecutives measurements due to the possible instability of the oxide layer (See *section 3.3.4*). It has to be mention, that no problems related to oscillating results, due to short delay time between measurements have been noticed.

* Electrolyte's contamination: The solution was prepared in 5 liter's bottles, using 7,1 gr of Na_2SO_4 solid pro liter of water. Normally the pH value of the solution was smaller than the desired pH value of 7. To adjust the pH value of the electrolyte, drops of NaOH 0,1N and NaOH 1N were added to the solution. The bottle with the electrolyte, was closed all the time and only opened to refill the necessary 400 ml, used in each experiment.

For three measurements done with samples of alloy 6016 and two of alloy 5182, an electrolyte contamination has been detected. These results will not be considered in the discussion neither in the analysis of the results.

5.2. X-RAY PHOTOELECTRON SPECTROMETRY

5.2.1. Equipment

The equipment here in EADS used to perform ESCA analysis was provided by the American company, Physical Electronics, Inc. The exact model used is the PHI Quantum 2000 Scanning ESCA Microprobe.

The sample chamber, comprises the measurements setup and all the components required for an XPS. Both semi-spheres shown in the picture are isolated from the atmosphere, being these chambers joined trough sealing gaskets.

The ultrahigh vacuum chamber is communicated to the atmosphere trough the so called introchamber. In the antechamber, the pressure will drop from atmospheric pressure, value of the pressure required when entering the probes in the equipment, to vacuum values, required to place the probes in the ultrahigh vacuum chamber, where the measurements will take place. Thanks to the existence of a control-valve, these two chambers will be communicated, only when vacuum is present in both of them.

Ultrahigh vacuum is necessary, because otherwise scattering will distort the outcome of the experiment, therefore a minimum vacuum of 10^{-8} mbar is required [9].

The principal elements, which compose the XPS system depicted in *figure 5.2.1*, are:

1. Electron gun
2. Monochromator
3. Energy analyzer
4. Multi channel detector
5. Ar+ Ion gun

The "open excitation source" comprises the electron gun (LaB_6 filament), anode of aluminum, and an elliptic monochromator. This gun send an electron beam to the anode, at the anode, the the X-ray beam is emitted to the monochromator where it is reflected, and finally impinge upon the material surface under research.

When this low energy beam impacts the surface, electrons of the surface atoms are emitted. These emitted particles will be analyzed in the detector system. The system consist of an hemispherical energy analyzer and a 16-channels detector.

The Argon gun, integrated within the electron gun, is necessary, in order to neutralize the surface when required. While performing ESCA, the surface will be positive charged, due to the electrons emission of the surface. When working with *metals*, this neutralization is not necessary, thanks to the high conductivity of this kind of material, new electrons will come from inside to outside of the material to full the vacancies created when electrons are gone. When working with *semiconductors or polymers*, which do not have this good property (high conductivity), permanent neutralization of the probe during the experiment is necessary.

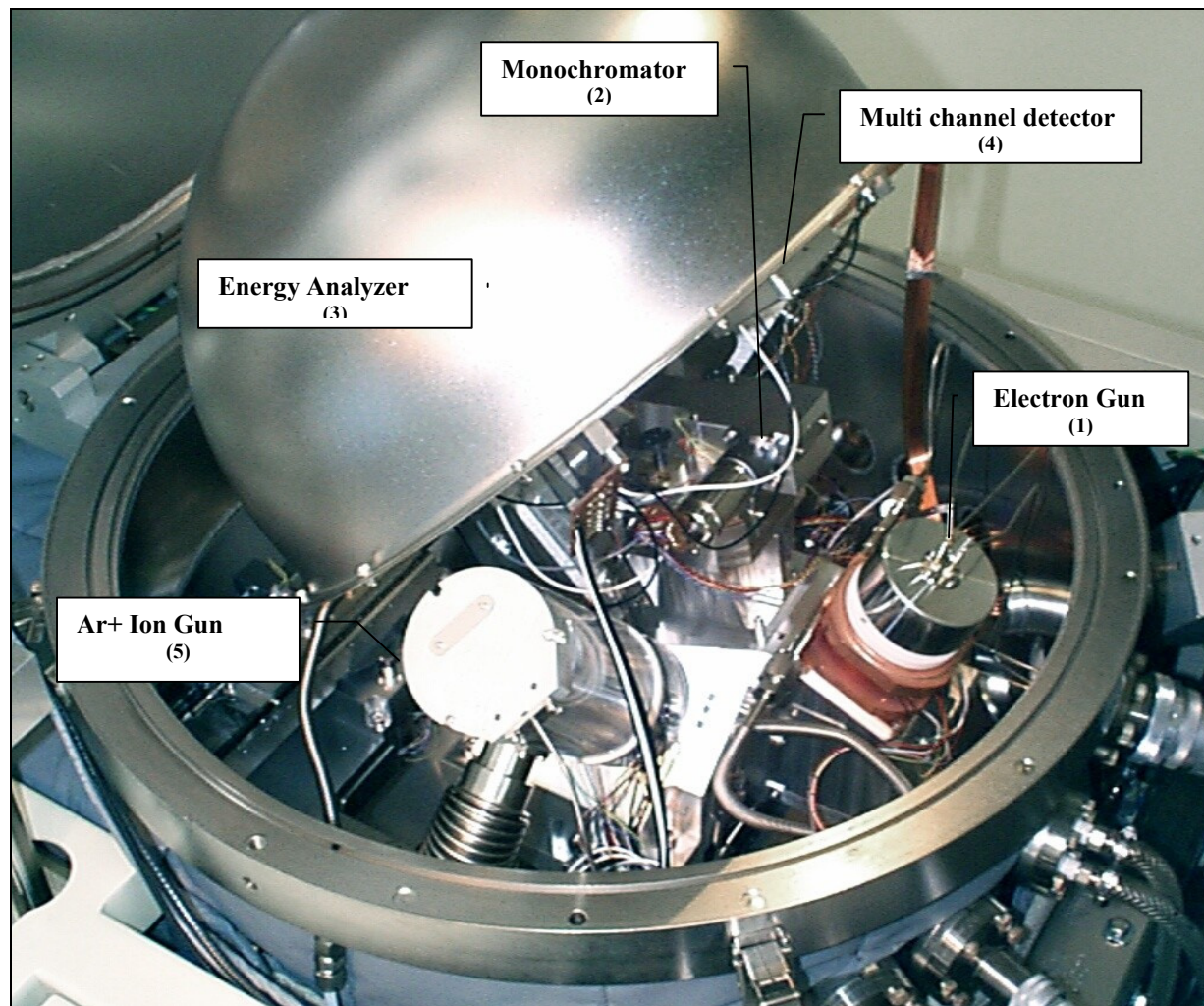The following picture depicts the equipment arrangement:

Fig. 5.2.1. XPS system.   [11]

In any case, when neutralizing the probe, the signal-noise ratio increases, that means, that the results (spectra obtained of the target material) will have higher quality as if no neutralization during the measurement was done.

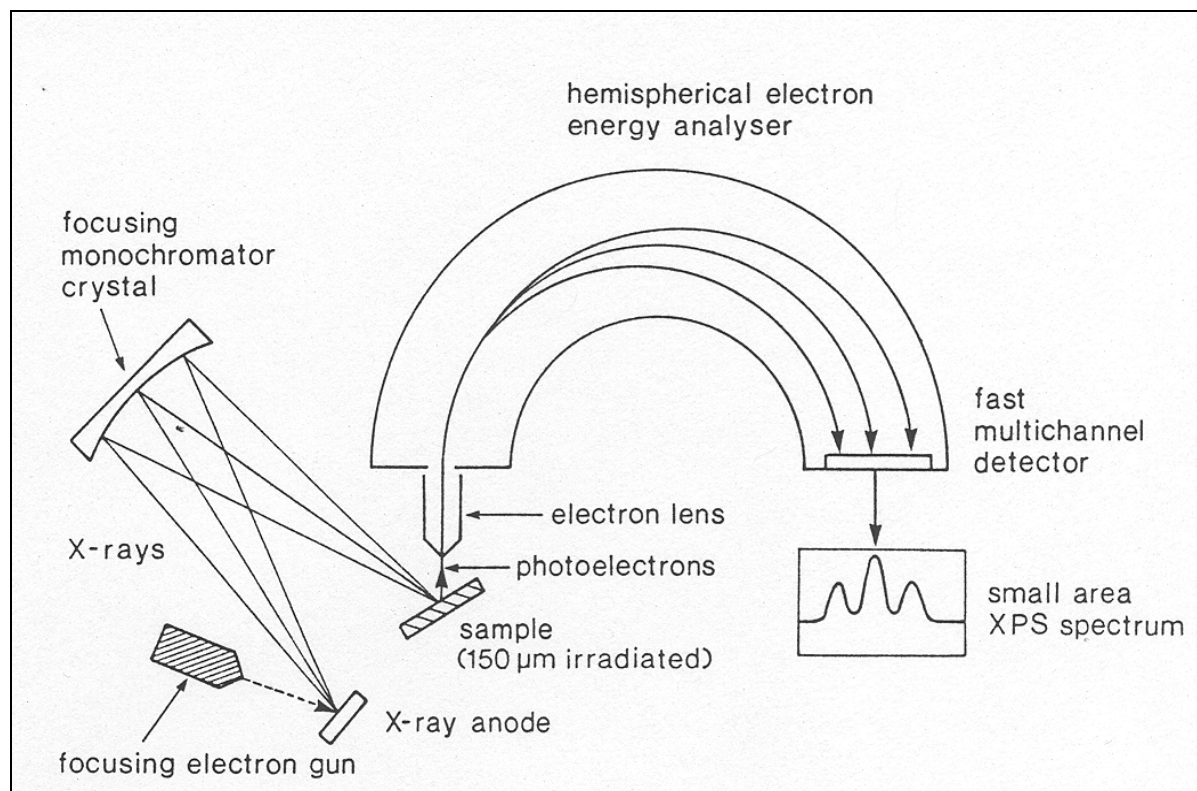The principles of how this XPS system works, is characterized by the following schema:

Fig.5.2.2. Principles of the XPS system.   [11]

The angle between the incident beam and the analyzer's shutter measured from the symmetric axe existing between the beam that goes from the X-ray anode to the monochromator, and the beam that is there reflected, has a value of $\varphi = 45°$.

As mentioned at the beginning, the system's components are "opened" inside of the recipient. Thus, all the integral parts of this device, can be contaminated with the pollution abounding in the container. The bigger disadvantage from this open construction, is the absorption of gas atoms in the electron and ion gun filaments. Hence a shorter service life of these components, has been reported [11].