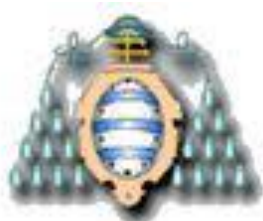


***DEVELOPMENT OF
ELECTROCHEMICAL
SENSOR FOR THE
DETECTION OF SILVER
NANOPARTICLES***

MASTER'S DEGREE IN ANALYTICAL CHEMISTRY
UNIVERSITY OF OVIEDO (SPAIN) AND UNIVERSITY OF
PAU ET DES PAYS DE L'ADOUR (FRANCE)

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1. INTRODUCTION

1.1 OBJECTIVE

The objective of this project is to develop a sensor for the detection of silver nanoparticles. This topic is within an international project (between France and Portugal), entitled “**In situ trace metal speciation monitoring**”. The aim of this international project is to develop an in-situ measurement probe based on the recent advances of electroanalytical techniques. Several analytical techniques were applied to the determination of metals in water and other samples: inductively coupled plasma mass spectrometry (ICP-MS), flame atomic absorption spectrometry (F-AAS), atomic emission spectrometry (AES), spectrophotometry, ion exchange chromatography (IEC) and laser excited atomic fluorescence spectrometry. These techniques, commonly used for trace measurement of silver (I) ion in the laboratory, are not suitable for the task of in situ testing and monitoring. Electrochemical methods are the most favourable techniques for the determination of metals because of its low cost, high sensitivity, easy operation, the ability to carry out speciation analysis and the possibility to do on field measurement.

In situ measurements avoid problems due to:

- 1 Contamination during sampling and storage.
- 2 Instability of metal species during transport and storage prior to measurement, through processes associated with aggregation, reequilibration of gaseous components and precipitation.
- 3 Metal absorption to container walls.

The difficulties connected with the development of these sensors arise first from the very low concentrations of the trace metals in natural waters (typically below 10^{-8} M), second from the need of bringing the equipment to the field (autonomy problems), third the problems related with the great variety of ligands existing in natural waters that are able to bind metals (speciation problems), and finally the fact that natural waters are generally subject to changing conditions and are practically never at chemical equilibrium (dynamic problems).

Due to their environmental relevance, silver, lead, cadmium, copper and zinc will be the main trace metals focused in this study.

In summary, the objectives of this international project are:

- Build and develop an in-situ measurement probe based in SSCP/AGNES/DMT (Scanned Stripping Chronopotentiometry, Absence of Gradients and Nernstian Equilibrium Stripping technique and Donnan Membrane Device).
- Perform laboratory studies in complex mixtures of polymers, nanoparticles and naturally occurring particles in order to understand the response of the techniques.
- Perform laboratory studies in complex mixtures of polymer coated nanoparticles (NP) and natural colloids in order to understand the role of NP as new vector of trace elements.
- Apply the in-situ probe to a pilot-scale study of a controlled microcosm and study the probe response as we add our successively more complex model systems.
- Validate the method of the in-situ probe in field samples taken in different seasons.

However, as far as I'm concerned, I focused my stage on the detection of silver, conception of the sensor, develop of the method and analysis of the metal. The techniques used in my study are Cyclic Voltammetry (CV) and Anodic Stripping Voltammetry (ASV). The electrodes used are Screen Printing carbon Electrodes (SPE).

1.2 CONTEXT

Industrial activity is responsible for the dissemination of toxic metallic elements, such as Ag, Pb, Cu, Cd and Zn, in rivers, oceans and soils in trace amounts. The determination of their impact on the environment relies on the precise monitoring of their concentration and speciation. In fact, metallic ions may be present as molecular species or as components of complex mineral solids. The first one has a much higher bioavailability than the second one, and, consequently, it has a higher toxicological impact on living organisms. Moreover, recent and rapid progresses in nanotechnology have led to the development of engineered nanoparticles (NPs). The high reactivity of engineered NPs has induced their incorporation in an increasing number of common products as well as to their use in many different industrial fields. However, this increasing development has a great impact in natural environments, due to their direct or indirect exposure to human beings and ecosystems. According to recent toxicological studies, NPs are able to cross physiological membranes, such as respiratory and digestive mucous tissues, and enter the blood system, resulting in their distribution throughout the whole organisms with a specific targeting of sensitive organs.

So NPs constitute a new class of micro-pollutants, and we have to be conscious of their impact on the environment systems.

Measurements of metal speciation in natural waters are challenging: methods must be both very **sensitive** for low concentrations and **specific** for distinction between chemical species.

1.3 THEORETICAL FUNDAMENT

The electrochemistry techniques used in the measurements are **Cyclic Voltammetry (CV)** and **Anodic Stripping Voltammetry (ASV)**.

- CYCLIC VOLTAMMETRY

In cyclic voltammetry, the electrode potential ramps linearly versus time. This ramping is known as the experiment's scan rate (V/s). The potential is applied between the reference electrode and the working electrode and the current is measured between the working electrode and the counter electrode. These data are then plotted as current (i) vs. potential (E). The forward scan produces a current peak for any analyte that can be reduced (or oxidized depending on the initial scan direction) through the range of the potential scanned. The current will increase as the potential reaches the reduction potential of the analyte, but then it falls off as the concentration of the analyte is depleted close to the electrode surface. If the redox couple is reversible then when the applied potential is reversed, it will reach the potential that will reoxidize the product formed in the first reduction reaction, and produce a current of reverse polarity from the forward scan. This oxidation peak will usually have a similar shape to the reduction peak. As a result, information about the redox potential and electrochemical reaction rates of the compounds are obtained.

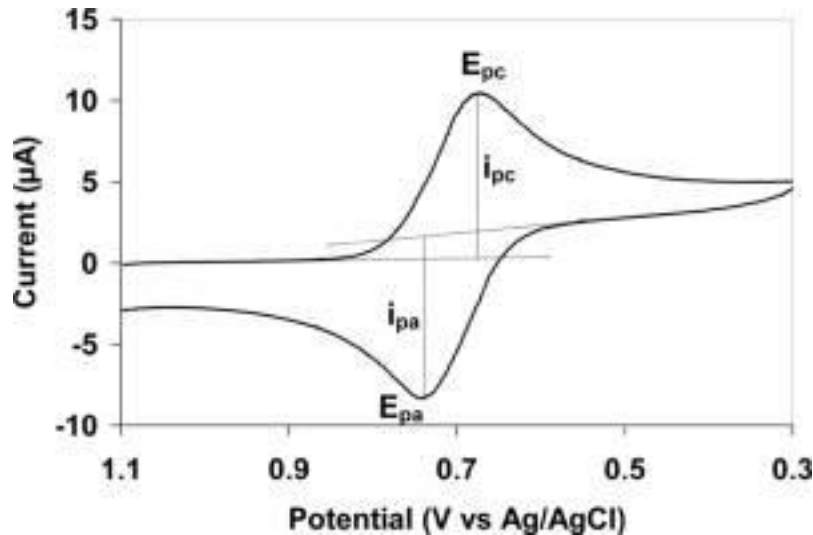


Figure 1. Cyclic voltammogram.

For instance if the electronic transfer at the surface is fast and the current is limited by the diffusion of species to the electrode surface, then the current peak will be proportional to the square root of the scan rate. This relationship is described by the **Cottrell equation**. The CV experiment then samples only a small portion of the solution, the material within the diffusion layer.

The Cottrell equation describes the change in electric current with respect to time in a controlled potential experiment. Specifically it describes the current response when the potential is a step function. For a simple redox event, the current measured depends on the rate at which the analyte diffuses to the electrode. That is, the current is said to be "**diffusion controlled**."

$$i = \frac{nFAc_j^0\sqrt{D_j}}{\sqrt{\pi t}}$$

i = current, in unit A

n = number of electrons (to reduce/oxidize one molecule of analyte j , for example)

F = Faraday constant, 96,485 C/mol

A = area of the (planar) electrode in cm^2

c_j^0 = initial concentration of the reducible analyte j in mol/cm^3 ;

D_j = diffusion coefficient for species j in cm^2/s

t = time in s.

Deviations from linearity in the plot of i vs $t^{-1/2}$ sometimes indicate that the redox event is associated with other processes, such as association/dissociation of a ligand or a change in geometry.

In practice, the Cottrell equation simplifies to $i = kt^{-1/2}$, where k is the collection of constants for a given system (n, F, A, c_j^0, D_j).

Furthermore, (scan rate) $^{1/2}$ is used in place of $t^{-1/2}$. Typical scan rates are in the range 20 to 2000 mV/s.

The ratio $i_p/(\text{scan rate})^{1/2}$, where i_p is the peak current, is sometimes referred to as the "current function."

- ANODIC STRIPPING VOLTAMMETRY

This method consists on electroplate the analyte on the working electrode during a deposition step, and oxidize it from the electrode during the stripping step. The current is measured during the stripping step. The oxidation of species is registered as a peak in the current signal at the potential at which the species begins to be oxidized. The stripping step can be either linear, staircase, square wave, or pulse. In our case, it is **square wave (SWASV)**.

Anodic stripping voltammetry usually incorporates 4 steps. The solution is stirred during the first two steps at a repeatable rate. The first step is a cleaning step (**conditioning/cleaning step**), in which the potential is held at a more oxidizing potential than the analyte of interest for a period of time in order to fully remove it from the electrode. In the second step (**electroplating step**), the potential is held at a lower potential (E_{dep}), low enough to **reduce the analyte and deposit it on the electrode**. After the second step, the stirring is stopped, and the electrode is kept at the lower potential. The purpose of this third step is to allow the deposited material to **distribute more evenly in the electrode (equilibration step)**. The last step (**stripping step**) involves raising the working electrode to a higher potential (anodic), and **stripping (oxidizing) the analyte**.

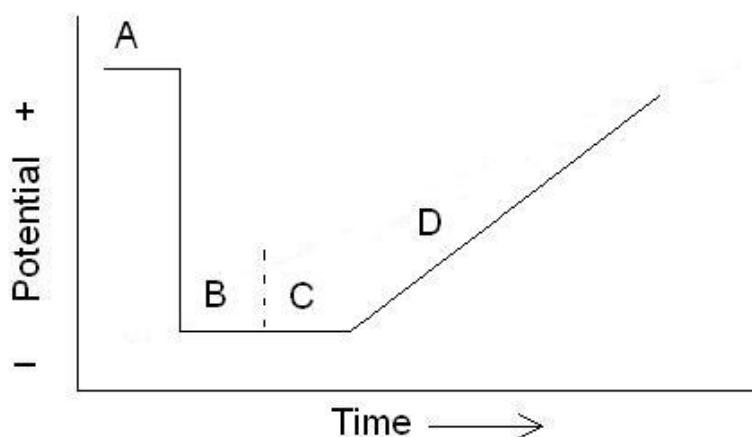


Figure 2. Steps in anodic stripping voltammetry. A) Cleaning step, B) Electroplating step, C) Equilibration step, D) Stripping step.

As it is said before, we used SWASV. This technique uses a square wave programme during the stripping step. The potential programme is a combination of a square wave modulation with a potential slope stair-shaped. The current is measured at the end of each semicycle (direct and inverse). Voltammograms obtained show an excellent sensibility and minimize the background currents.

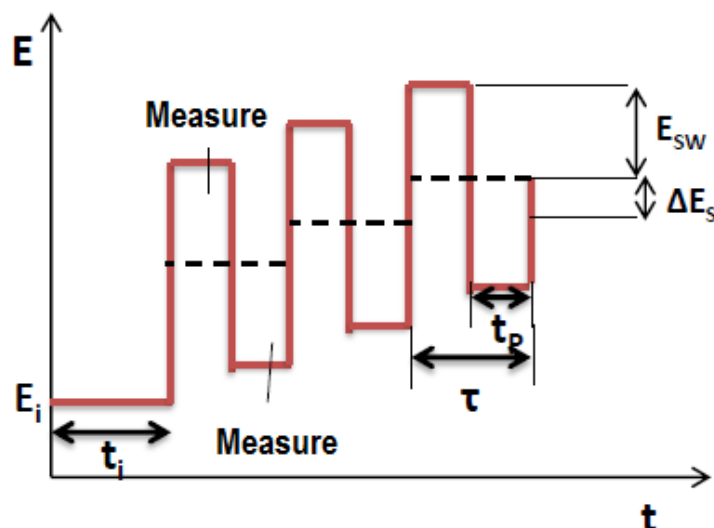


Figure 3. Squared wave programme.

In conclusion, stripping analysis is an analytical technique that involves (i) preconcentration of a metal phase onto a solid electrode surface at negative potentials and (ii) selective oxidation of each metal phase species during an anodic potential sweep.

2. BIBLIOGRAPHIC RESEARCH

Before starting the measurements, we should read some articles to update on the topic. There are very little publications on this field, which implies both an advantage and a drawback.

In many publications, the authors use **modified** carbon electrodes (glassy carbon and screen printing electrodes). The materials used as coatings are varied: organic compounds, multi wall carbon nanotubes (MWCNTs), magnetic nanoparticles, etc. In others, the electrodes used are boron-doped diamond.

In the most papers read, the species analysed were silver ions, but not silver nanoparticles. In this case the techniques used were electrochemical techniques, but when the species analysed were silver NPs, they usually use chromatography. So we had some difficulties to find out some references to start our work. In any case, before analysing silver NPs, we should start with the analysis of silver ions, so we could take advantage of these data.

The novelty of our work lies on the fact that we use directly screen printing carbon electrodes, without modify them. This fact has two advantages, since we avoid the step of coating the electrode (we save time) and it is not necessary to use any material as modifier (we save money and reagents).

Finally, after reading several articles and compare the different results, we decided to work with a buffer solution of acetate/ NH_4^+ , which gives a pH of 4,51.

3. EXPERIMENTAL

3.1. APPARATUS AND REAGENTS

All the electrochemical techniques were carried out on the potentiostat AUTOLAB. A traditional three-electrode system consisting of a Ag/AgCl/KCl reference electrode, and the counter and working electrode were SPE (the diameter of the counter electrode is bigger the working electrode).

All reagents were analytical grade and were used without further purification. The aqueous solutions were prepared using MilliQ water. We prepared solutions of different metals (Ag, Cu, Pb, Cd and Zn).

The electrodes were prepared with carbon ink.

We prepared an acetate buffer 0,2 M, pH = 4,51. The buffer is stored in the fridge.

3.2 ELECTRODES PREPARATION

The screen-printing fabrication technology is commonly used for large-scale production of extremely inexpensive and highly reproducible electrochemical sensors. In our case, we use **carbon ink**. Carbon inks are particularly attractive for sensing applications because they are relatively inexpensive and lead to **low background** currents and broad **potential windows**.

The basic steps in the process are screen-printing of carbon ink onto planar polystyrene substrate by forcing it through a patterned mask, followed by a proper thermal curing. This thermal curing consists on drying the electrodes for one hour at room temperature. After that, it is needed a second drying during one hour at 60°C. Finally, we isolate the electrodes, leaving a little portion of the electrode without isolating. For that, we screen-print the insolent by a patterned mask. The insolent consists on polystyrene dissolved in mesitylene. Once we have isolated the electrodes, we should wait around fifteen-twenty minutes to use them.

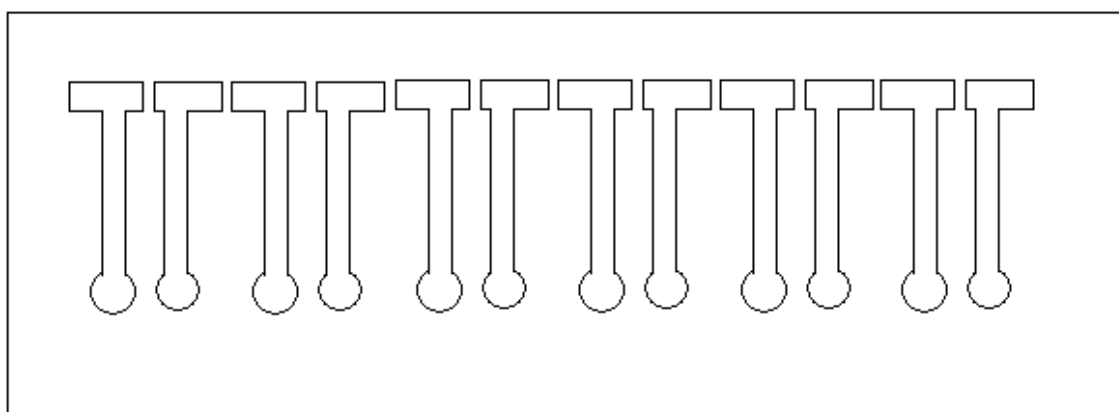


Figure 4. Patterned mask with the form of the electrodes we want to build.

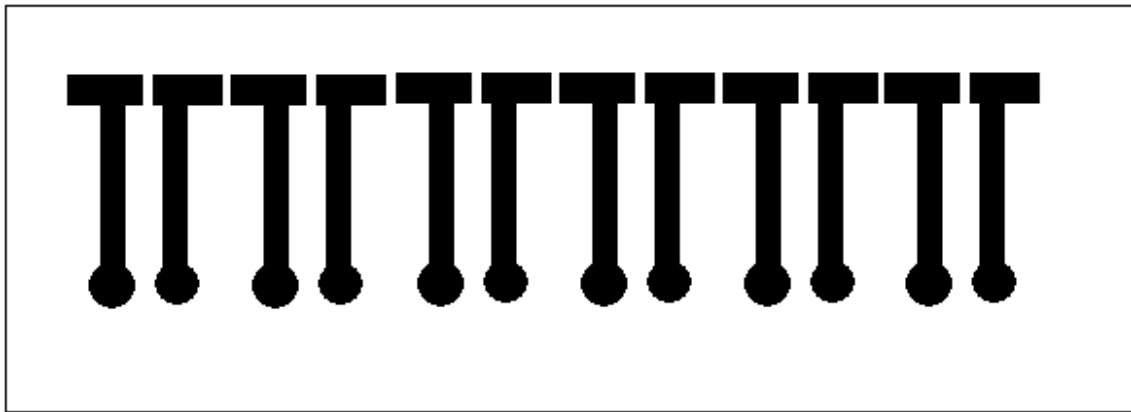


Figure 5. We put the carbon ink onto planar polystyrene substrate by forcing it through the patterned mask.

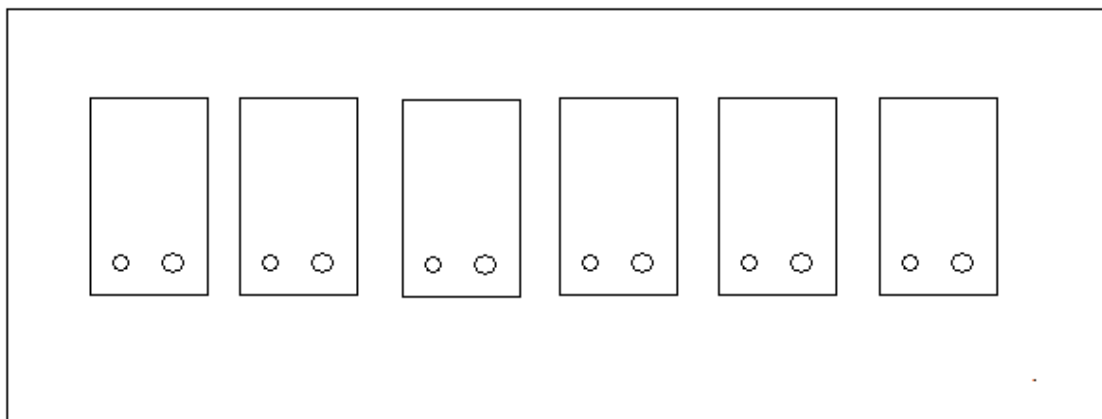


Figure 6. We isolate the electrodes with polystyrene dissolved in mesytilene by forcing it through an new patterned mask.

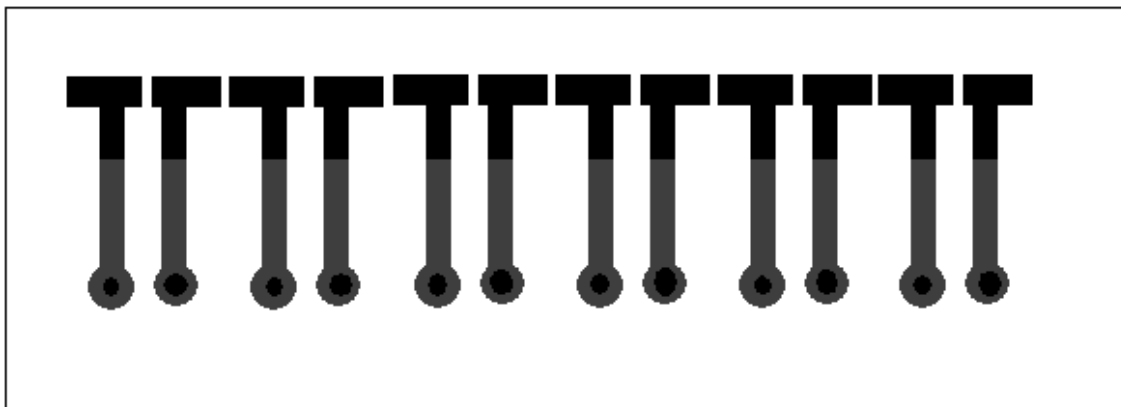


Figure 7. The final result is a serial of electrodes coated with an insolent, except for a little area, which supose the electrode surface.

3.3 ANALYTICAL PROCEDURE

The three electrodes are immersed in a 10 mL of buffer solution containing a known amount of Ag^+ ion and the solution is stirred. The stirring time is different depending on if we are using CV or ASV.

For all the manipulations we measured the area and the height, but in this report we only show the area because is more reproducible and linear.

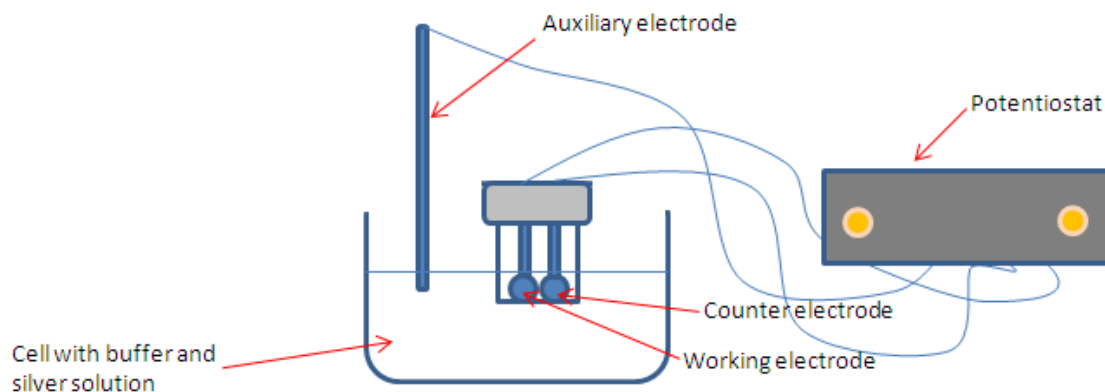


Figure 8. Scheme of the devices.

A) CYCLIC VOLTAMMETRY

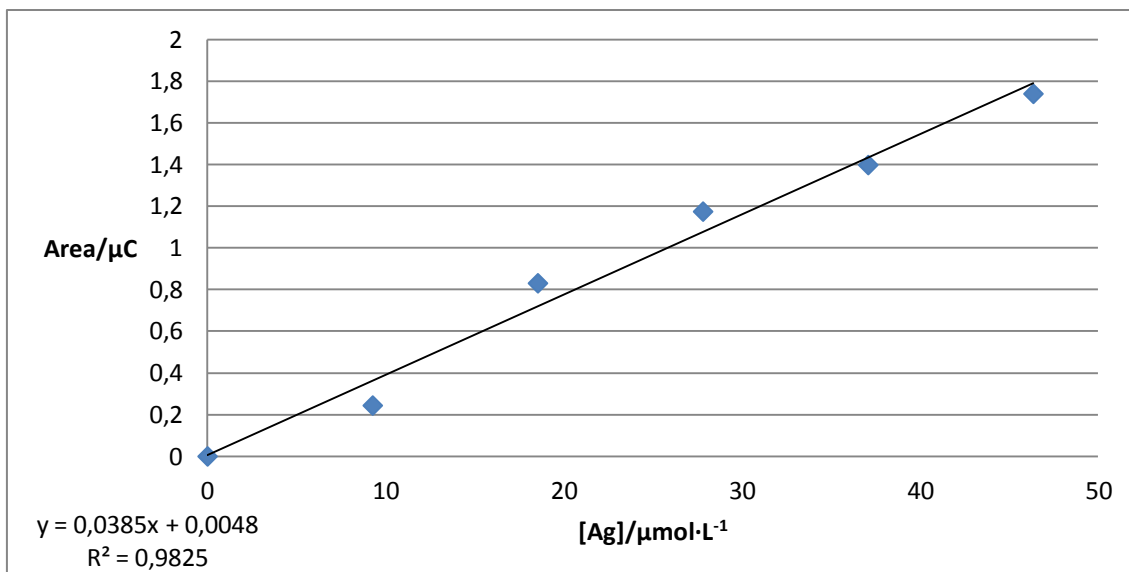
We first chose this technique because is easier and faster than ASV. But it is not very sensible.

- 1) We wanted to check if the response varies linearly with the **concentration**:

Parameters	Potential range/V	Scan rate/mV·s ⁻¹	t _{dep} /s
	from -0,75 to +1	100	30

		[Ag]/μmol·L ⁻¹				
		9,27	18,54	27,81	37,08	46,35
Area/μC	Replic 1	0,101	0,654	1,125	1,576	1,646
	Replic 2	0,284	0,864	1,167	1,088	1,751
	Replic 3	0,348	0,974	1,232	1,530	1,822
	Mean	0,244	0,831	1,175	1,398	1,740
	RSD	0,128	0,163	0,054	0,270	0,089
	%RSD	52,46	19,59	4,59	19,28	5,09
Height/μA	Replic 1	4,507	3,396	4,676	6,143	5,676
	Replic 2	1,743	3,943	5,723	4,307	6,279
	Replic 3	2,410	4,571	5,923	3,557	6,585
	Mean	2,887	3,970	5,441	4,669	6,180
	RSD	1,442	0,588	0,670	1,331	0,463
	%RSD	49,96	14,81	12,31	28,50	7,48

Table 1. Concentration study. Potential range: -0,75 V to 1 V; scan rate: 100 mV; deposition time: 30 s.



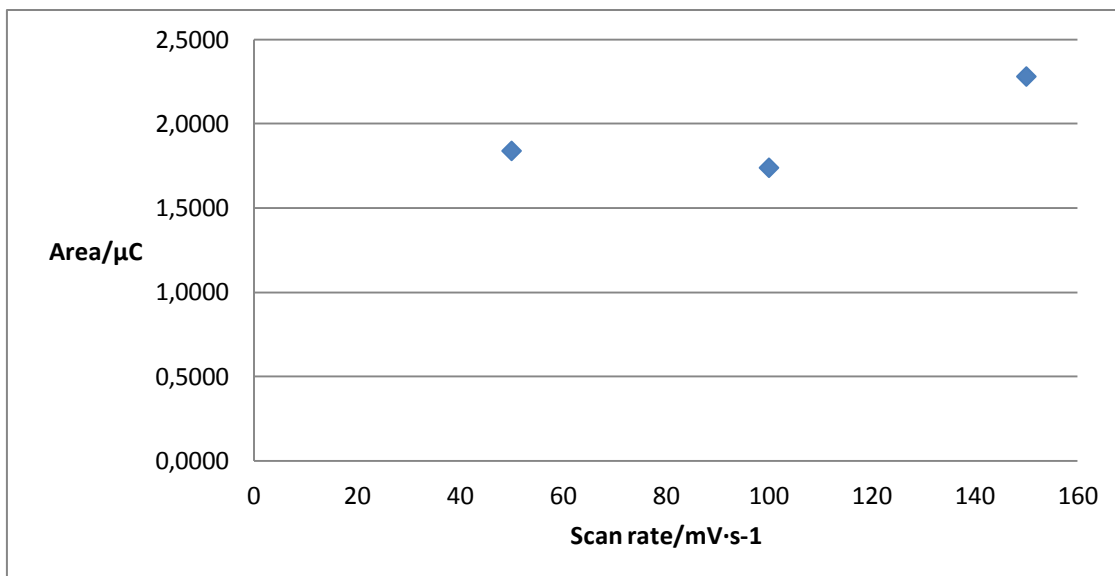
Graph 1. Area vs. Concentration.

As we can see, the response varies linearly. However, the difference between results of the same concentration has an important error. This error is not constant between different concentrations, but it seems to be bigger at lower concentrations.

- 2) In the next experiment, we fixed the concentration (46.35 $\mu\text{mol/L}$) and we changed the scan rate:

		Scan rate/ $\text{mV}\cdot\text{s}^{-1}$		
		50	100	150
Area/ μC	Replic 1	2,004	1,646	2,403
	Replic 2	1,780	1,751	2,263
	Replic 3	1,735	1,822	2,177
	Mean	1,840	1,740	2,281
	RSD	0,144	0,089	0,114
	%RSD	7,833	5,087	5,002
Height/ μA	Replic 1	4,089	5,676	10,670
	Replic 2	4,723	6,279	10,240
	Replic 3	4,970	6,585	10,120
	Mean	4,594	6,180	10,343
	RSD	0,454	0,463	0,289
	%RSD	9,891	7,484	2,796

Table 2. Study of the scan rate study.



Graph 2. Area vs. Scan rate.

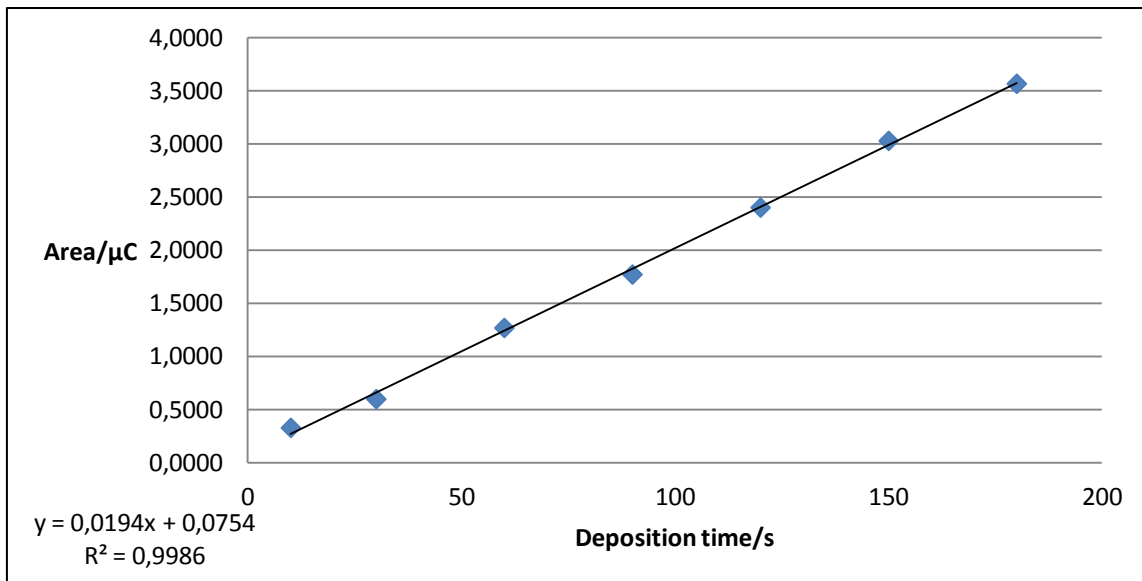
The response increases with the deposition potential. This tendency is logical because in voltammetry, the current depends on the square root of the scan rate, when the process is reversible.

3) Influence of the response with de **deposition time**:

Parameters	Potential range/V	Scan rate/mV·s ⁻¹
	from -0,75 to +1	100

		Deposition time/s						
		10	30	60	90	120	150	180
Area/μC	Replic 1	0,183	0,517	1,120	1,596	2,266	2,964	3,432
	Replic 2	0,334	0,585	1,281	1,787	2,341	2,964	3,554
	Replic 3	0,464	0,691	1,401	1,927	2,594	3,155	3,710
	Mean	0,327	0,598	1,267	1,770	2,400	3,028	3,565
	RSD	0,141	0,088	0,141	0,166	0,172	0,110	0,139
	%RSD	43,05	14,74	11,13	9,390	7,162	3,643	3,907
Height/μA	Replic 1	0,604	2,818	4,266	5,982	7,497	8,922	9,640
	Replic 2	1,563	3,213	4,782	6,370	7,973	9,320	10,140
	Replic 3	2,236	3,714	5,136	6,782	8,433	9,744	10,290
	Mean	1,468	3,248	4,728	6,378	7,968	9,329	10,023
	RSD	0,820	0,449	0,438	0,400	0,468	0,411	0,340
	%RSD	55,89	13,82	9,253	6,273	5,874	4,407	3,395

Table 3. Deposition time study.



Graph 3. Area vs. Deposition time

When the deposition time increases, the response increases too. The longer the time, it exists more time for the substance to diffuse towards the electrode surface and accumulate on it.

4) Calibration curves

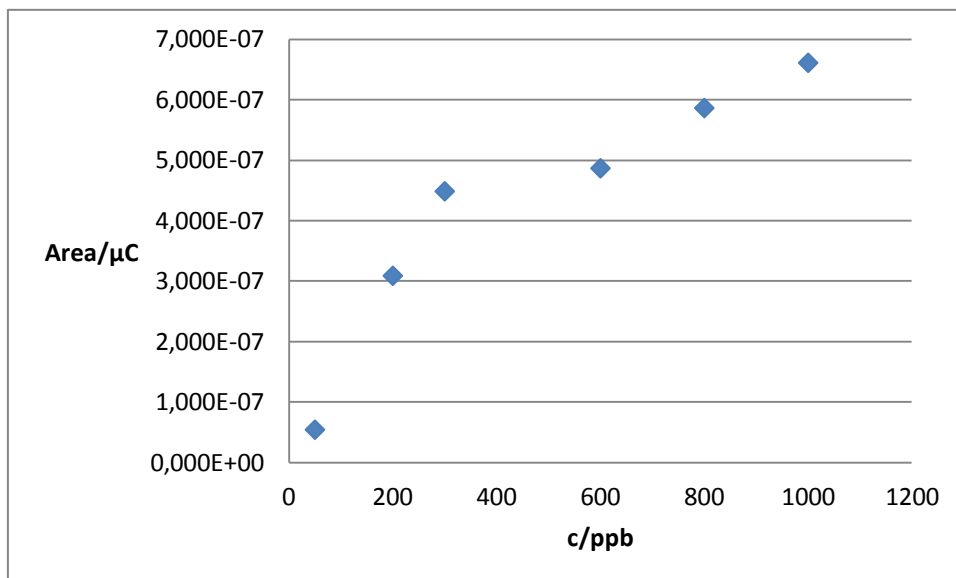
After seeing how the response varies with these variables, we can start to do some calibration curves.

For the beginning, we try with a concentration range between 50 ppb to 1000 ppb, fixing the following values for the parameters.

Parameters	E_{dep}/V	t_{dep}/s
	-0,2	60

c/ppb	Area/μC	Height/μA
50	5,446E-08	4,216E-07
200	3,090E-07	2,110E-06
300	4,488E-07	2,581E-06
600	4,869E-07	2,740E-06
800	5,865E-07	2,918E-06
1000	6,613E-07	3,144E-06

Table 4. Calibration curve from 50 ppb to 1000 ppb.



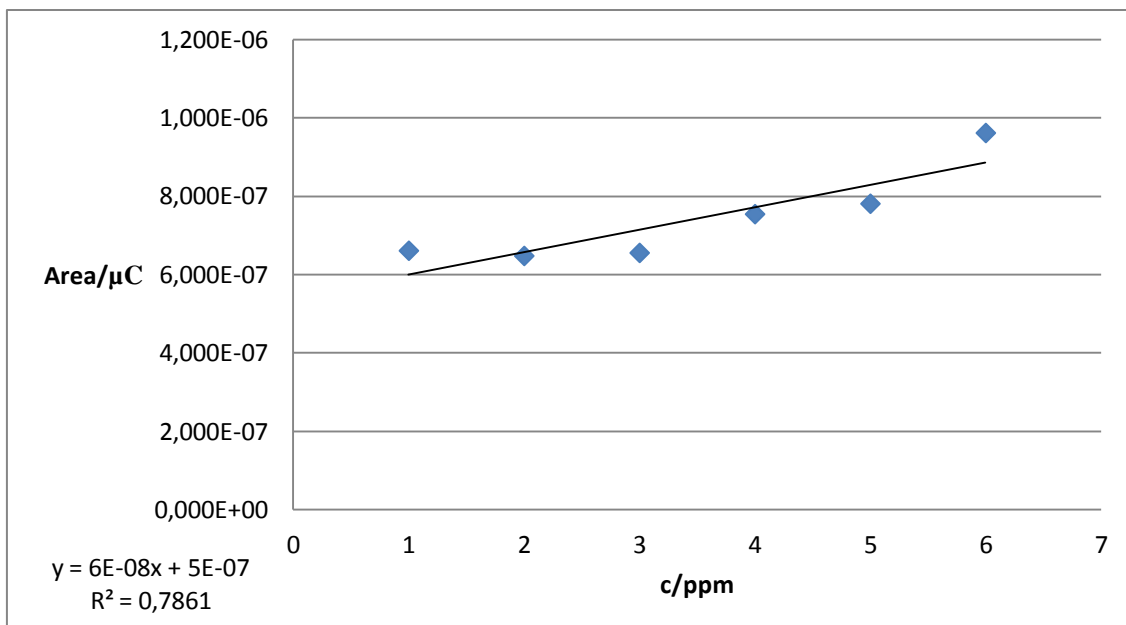
Graph 4. Calibration curve from 50 ppb to 1000 ppb. $E_{dep} = -0,2 \text{ V}$; $t_{dep} = 60 \text{ s}$.

In this case we do not obtain a linear curve. We can observe two different tendencies, one for low concentrations, and other one for higher concentrations.

Cyclic voltammetry is not a very sensible technique. This could be the reason why we do not obtain a good calibration curve. Therefore, the next step is trying to do a calibration with solutions of higher concentration: from 1 ppm to 6 ppm. The parameters are the same than before.

c/ppm	Area/μC	Height/μA
1	6,613E-07	3,144E-06
2	6,480E-07	2,517E-06
3	6,558E-07	2,750E-06
4	7,547E-07	3,043E-06
5	7,812E-07	3,259E-06
6	9,617E-07	3,675E-06

Table 5. Calibration curve from 1 ppm to 6 ppm.



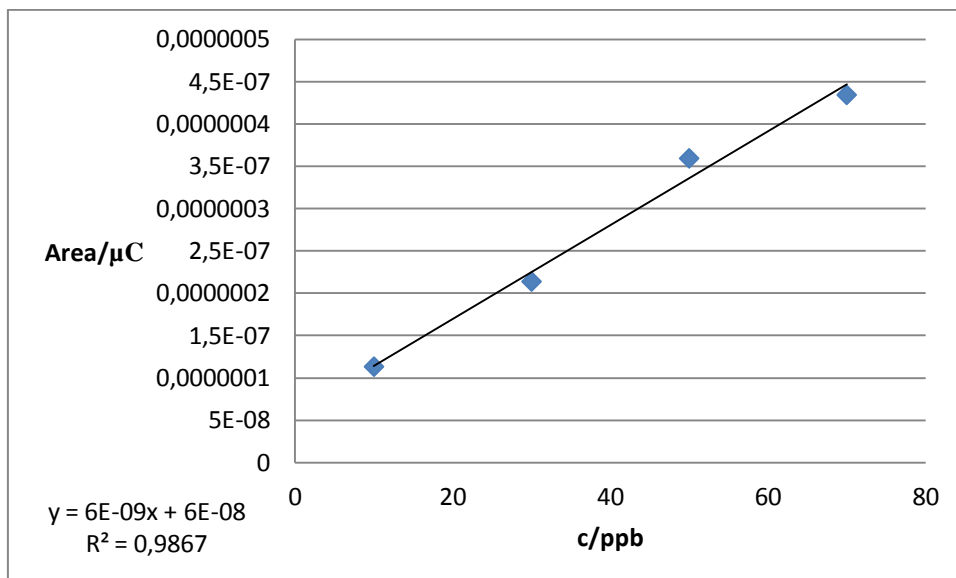
Graph 5. Calibration curve from 1ppm to 6 ppm. $E_{dep} = -0,2$ V; $t_{dep} = 60$ s.

The results of the calibration curve for high concentrations are not very satisfactory. Finally, we try to do a new calibration curve for slow concentrations by changing the deposition time. It has to be longer.

Parameters	E/V	t_{dep}/s	Replics
	-0,2	120	3

		Concentration/ppb				
		10	30	50	70	100
Area/μC	Rep 1	1,017E-07	1,577E-07	3,301E-07	4,039E-07	6,555E-07
	Rep 2	1,277E-07	2,217E-07	3,567E-07	4,335E-07	7,382E-07
	Rep 3	1,108E-07	2,625E-07	3,917E-07	4,660E-07	8,050E-07
	Media	1,134E-07	2,140E-07	3,595E-07	4,345E-07	7,329E-07
	RSD	1,319E-08	5,283E-08	3,090E-08	3,106E-08	7,489E-08
	%RSD	11,63	24,69	8,595	7,148	10,22
Height/μA	Rep 1	4,383E-07	1,113E-06	1,835E-06	2,700E-06	3,366E-06
	Rep 2	7,677E-07	1,594E-06	1,989E-06	2,822E-06	3,662E-06
	Rep 3	7,675E-07	1,923E-06	2,297E-06	3,000E-06	3,994E-06
	Media	6,578E-07	1,543E-06	2,040E-06	2,841E-06	3,674E-06
	RSD	1,901E-07	4,074E-07	2,352E-07	1,509E-07	3,142E-07
	%RSD	28,90	26,40	11,53	5,312	8,552

Table 6. Calibration curve from 10 ppb to 100 ppb.



Graph 6. Calibration curve from 10 ppb to 100 ppb. $E_{dep} = -0,2 \text{ V}$; $t_{dep} = 120 \text{ s}$.

- 5) Finally, we calculate the **repeatability** by analysing two solutions: one of 10 ppb and other of 50 ppb.

		[Ag]/ ppb	
		10	50
Area/ μC	Rep 1	1,39E-03	2,17E-01
	Rep 2	4,636E-03	2,997E-01
	Rep 3	8,063E-03	3,545E-01
	Rep 4	1,052E-01	4,023E-01
	Rep 5	1,198E-01	4,517E-01
	Rep 6	1,240E-01	4,295E-01
	Mean	6,052E-02	3,591E-01
	RSD	6,150E-02	8,850E-02
	%RSD	101,63	24,66
Heigh/ μA	Rep 1	1,384E-01	1,335E+00
	Rep 2	4,030E-01	1,647E+00
	Rep 3	6,352E-01	1,192E+00
	Rep 4	8,184E-01	2,267E+00
	Rep 5	9,346E-01	2,645E+00
	Rep 6	9,535E-01	2,751E+00
	Mean	6,472E-01	1,973E+00
	RSD	3,238E-01	6,733E-01
	%RSD	50,04	34,13

Table 7. Repeatability of the technique cyclic voltammetry.

By analyzing the results, we can observe that the error for the 10 ppb concentration is too high. However, this value is better at 50 ppb. So we can conclude that cyclic voltammetry is a technique suitable for high concentrations, but not for the low ones.

B) ANODIC STRIPPING VOLTAMETRY

We are interested in the analysis of silver. This metal is in very low concentrations in water. Therefore, we need a technique more sensible than cyclic voltammetry. Anodic stripping voltammetry is the suitable technique for our purpose.

First of all, it is needed to optimize some parameters.

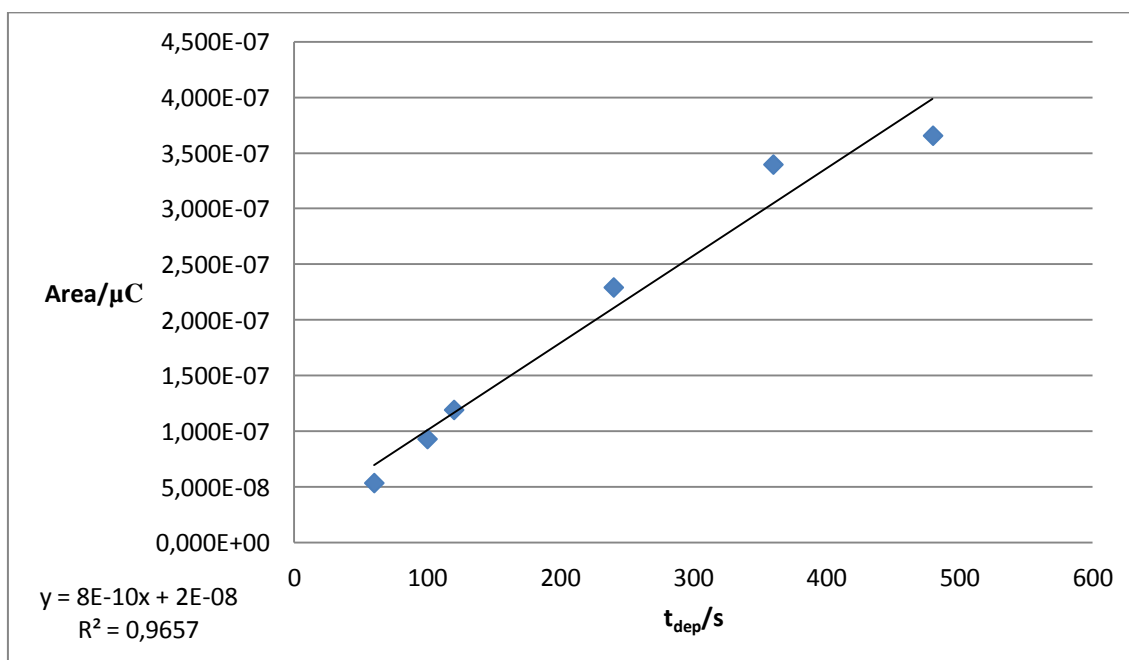
1 Optimization of the deposition time:

We held the value for the deposition potential.

Parameters	c/ppb	E/V	Replics
	30	-0,3	3

		Deposition time/s					
		60	100	120	240	360	480
Area/ μC	Rep1	4,074E-08	8,743E-08	1,131E-07	2,217E-07	3,331E-07	3,670E-07
	Rep2	6,002E-08	9,560E-08	1,207E-07	2,307E-07	3,346E-07	3,674E-07
	Rep3	6,021E-08	9,659E-08	1,243E-07	2,358E-07	3,518E-07	3,629E-07
	Media	5,366E-08	9,321E-08	1,194E-07	2,294E-07	3,398E-07	3,658E-07
	RSV	1,119E-08	5,027E-09	5,718E-09	7,139E-09	1,039E-08	2,491E-09
	%RSD	20,85	5,390	4,790	3,110	3,060	0,680
Height/ μA	Rep1	6,853E-07	2,129E-06	2,824E-06	5,930E-06	8,317E-06	1,026E-05
	Rep2	9,404E-07	2,129E-06	2,711E-06	5,737E-06	8,346E-06	1,048E-05
	Rep3	1,038E-06	2,244E-06	2,909E-06	5,895E-06	8,003E-06	1,021E-05
	Media	8,879E-07	2,167E-06	2,768E-06	5,854E-06	8,222E-06	1,032E-05
	RSV	1,821E-07	6,640E-08	7,990E-08	1,028E-07	1,902E-07	1,436E-07
	%RSD	20,51	3,060	2,890	1,760	2,310	1,390

Table 8. Responses at different deposition times.



The response is more or less linear from 60 s to 360 s. At 480 s the increase is not proportional. This can be due to the saturation of the electrode surface.

As in cyclic voltammetry, the longer the time, the substance has more time to be deposited on the electrode surface, therefore, the quantity of the deposited substance is higher and the response is higher too.

For choosing the best value for the deposition time, we need to take that which gives a good response, but it has to be not very long. The shorter the deposition time, the faster the analysis.

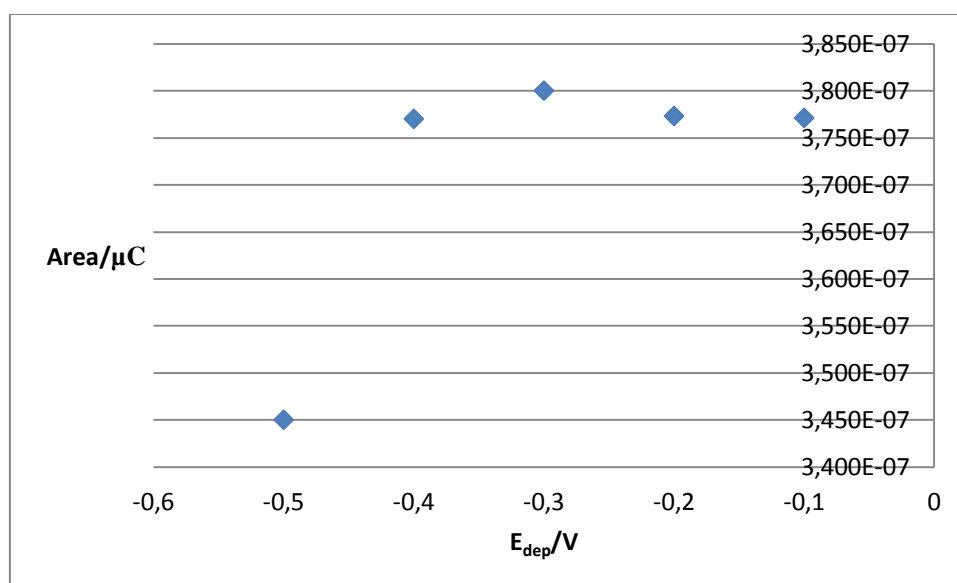
Following this argumentation, we finally chose two values for the deposition time: $t = 120\text{s}$ and $t = 240\text{s}$. The reason of taking two values is because we are going to do several calibration curves of different concentrations. We will take $t = 120\text{s}$ for calibration curves of high concentration and $t = 240\text{s}$ for calibration curves of low concentrations.

2 Optimization of the deposition potential:

Parameters	t_{dep}/s	c/ppb
	240	30

E/V	Area/ μC	Height/ μA
-0,5	3,450E-07	9,024E-06
-0,4	3,77E-07	8,778E-06
-0,3	3,800E-07	8,773E-06
-0,2	3,773E-07	8,688E-06
-0,1	3,771E-07	8,600E-06

Table 9. Responses at different deposition potential (E_{dep}).



Graph 8. Optimization of the deposition potential (E_{dep}). $C = 30\text{ ppb}$; $t_{\text{dep}} = 240\text{ s}$.

The deposition potential which gives a better response is $-0,3\text{ V}$. So this is the potential we are going to use from now on.

3 Calibration curves

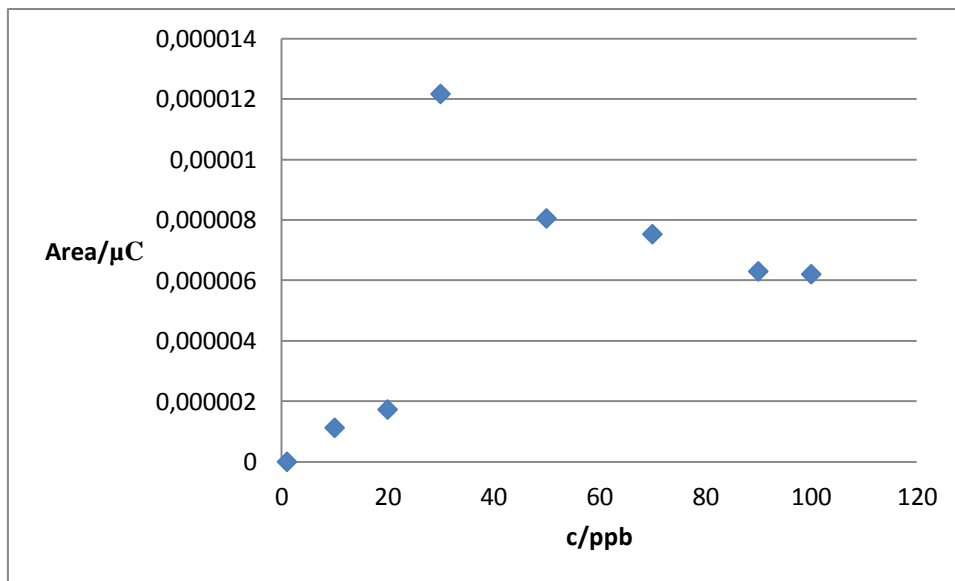
Once we optimized the variables (deposition time and deposition potential) we can start to do the calibration curves. We show in this report several calibration curves of different concentration ranges (from high to low).

3.1 Calibration curve from 10 ppb to 100 ppb:

Parameters	E_{dep}/V	t_{dep}/s
	-0,3	120

c/ppb	Area/ μC	Height/ μA
10	1,126E-06	2,591E-05
20	1,730E-06	3,877E-05
30	1,217E-05	1,321E-04
50	8,052E-06	1,070E-04
70	7,531E-06	9,536E-05
90	6,301E-06	8,714E-05
100	6,207E-06	8,065E-05

Table 10. Calibration curve from 10 to 100 ppb.



Graph 9. Calibration curve from 10 ppb to 100 ppb. $E_{\text{dep}} = -0,3 \text{ V}$; $t_{\text{dep}} = 120 \text{ s}$.

We can observe that there is an increase of the values until 30 ppb, being the increase of this last value very marked. Then, the values begin to decrease. We can think that this method is so sensible that at high concentrations the electrode surface gets saturated and then, the response decreases.

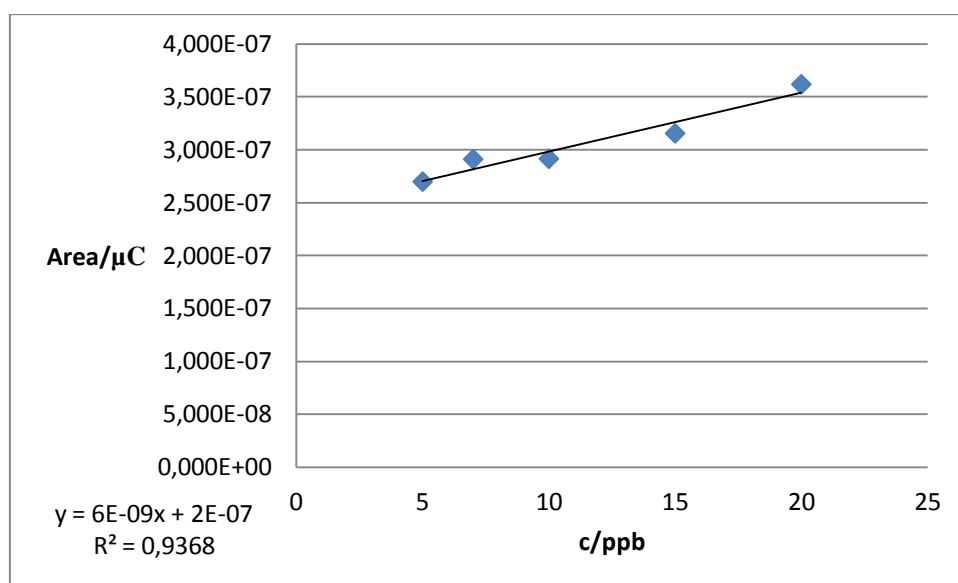
Now we are trying to do some calibration curves at lower concentrations, with a higher deposition time.

3.2 Calibration from 1 ppb to 5 ppb

Parameters	E/V	t _{dep} /s
	-0,3	240

	Concentration/ppb				
	5	7	10	15	20
Area/μC	2,697E-07	2,909E-07	2,913E-07	3,153E-07	3,617E-07
Height/μA	7,585E-06	7,371E-06	7,392E-06	8,499E-06	9,656E-06

Table 11. Calibration curve from 5 ppb to 20 ppb.



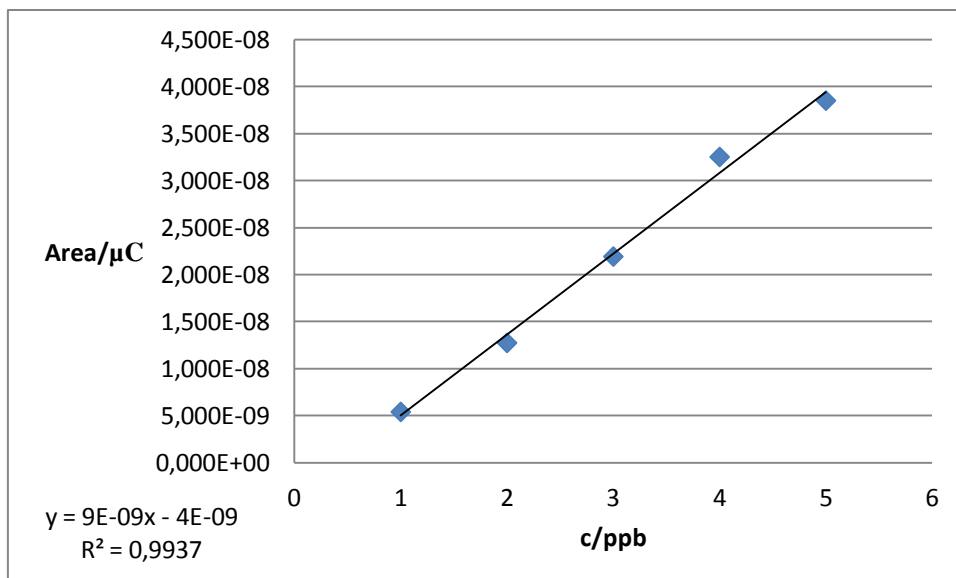
Graph 10. Calibration curve from 5 ppb to 20 ppb. $E_{dep} = -0,3 \text{ V}$; $t_{dep} = 240 \text{ s}$.

3.3 Calibration from 1 ppb to 5 ppb:

Parameters	E/V	t _{dep} /s
	-0,3	240

	Concentration/ppb				
	1	2	3	4	5
Area/μC	5,414E-09	1,275E-08	2,193E-08	3,252E-08	3,851E-08
Height/μA	8,993E-08	3,699E-07	6,767E-07	1,086E-06	1,288E-06

Table 12. Calibration curve from 1 ppb to 5 ppb.



We can observe that the responses follow a linear tendency.

If we analyse the last two curves we can observe that the response at 5 ppm is not the same in both calibrations curves. If we pay attention to the area, the value for the high concentration calibration is one order of magnitude higher than for the low concentration calibration.

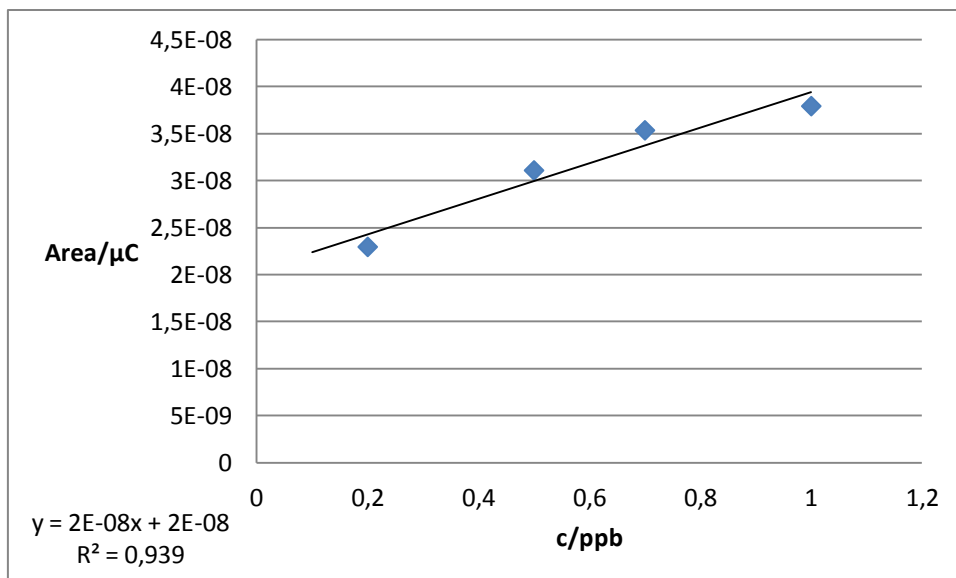
3.4 Calibration from 0.2 ppb to 1 ppb:

We tried with 0,1 ppb but we did not obtain any response.

Parameters	E/V	t_{dep}/s	Replics
	-0,3	240	3

		Concentration/ppb			
		0,2	0,5	0,7	1
Area/ μC	Rep1	2,317E-08	3,213E-08	3,529E-08	3,953E-08
	Rep2	2,194E-08	3,051E-08	3,566E-08	3,786E-08
	Rep3	2,376E-08	3,063E-08	3,511E-08	3,639E-08
	Media	2,296E-08	3,109E-08	3,535E-08	3,793E-08
	RSD	9,286E-10	9,027E-10	2,804E-10	1,571E-09
	%RSD	4,044	2,904	0,793	4,142
Height/ μA	Rep1	6,766E-07	8,192E-07	1,029E-06	1,121E-06
	Rep2	6,062E-07	8,185E-07	1,027E-06	1,094E-06
	Rep3	6,388E-07	8,493E-07	1,011E-06	1,076E-06
	Media	6,405E-07	8,290E-07	1,022E-06	1,097E-06
	RSD	3,523E-08	1,758E-08	9,866E-09	2,265E-08
	%RSD	5,500	2,121	0,965	2,065

Table 13. Calibration curve from 0,2 ppb to 1 ppb.



Graph 12. Calibration curve from 0,2 ppb to 1 ppb. $E_{dep} = -0,3 \text{ V}$; $t_{dep} = 240 \text{ s}$.

We did not obtain any signal at 0,1 ppb. So we can assume that the detection limit of the technique is 0,2 ppb.

4 Repeatability of the method

We use one couple of electrodes and we measure ten times a 10 ppb solution.

Replics	Area/ μC	Height/ μA
1	4,382E-08	1,373E-06
2	4,288E-08	1,286E-06
3	4,411E-08	1,239E-06
4	4,149E-08	1,168E-06
5	4,133E-08	1,152E-06
6	4,268E-08	1,146E-06
7	4,246E-08	1,141E-06
8	4,129E-08	1,122E-06
9	4,071E-08	1,101E-06
10	4,265E-08	1,094E-06
Media	4,234E-08	1,182E-06
RSD	1,123E-09	8,977E-08
%RSD	2,651	7,593

Table 14. Repeatability of the method.

We can observe that the error between different measurements is not too high.

5 Reproducibility of the method

To determinate the reproducibility of the method we measured a 10 ppb solution of Ag. We used 10 couples of electrodes, and we measured three times with each one. These are the results obtained:

	Electrode	1	2	3	4	5
Area/ μC	Rep1	6,733E-08	1,067E-07	1,006E-07	1,469E-07	1,855E-07
	Rep2	1,128E-07	1,181E-07	1,151E-07	1,663E-07	2,194E-07
	Rep3	1,561E-07	1,235E-07	1,116E-07	1,769E-07	2,323E-07
	Media	1,121E-07	1,161E-07	1,900E-07	1,634E-07	2,124E-07
	RSD	4,439E-08	8,577E-09	1,425E-07	1,521E-08	2,417E-08
	%RSD	39,61	7,390	39,61	9,310	11,38
Height/ μA	Rep1	1,592E-06	3,568E-06	3,789E-06	5,295E-06	6,324E-06
	Rep2	2,261E-06	3,805E-06	3,538E-06	4,954E-06	6,253E-06
	Rep3	2,608E-06	3,620E-06	3,543E-06	5,045E-06	6,288E-06
	Media	2,154E-06	3,664E-06	3,623E-06	5,098E-06	6,288E-06
	RSD	5,164E-07	1,246E-07	1,435E-07	1,766E-07	3,550E-08
	%RSD	23,98	3,399	3,960	3,464	0,565

Table 15. Reproducibility of the method (electrodes from 1 to 5).

	Electrode	6	7	8	9	10
Area/ μC	Rep1	1,129E-07	1,994E-07	2,011E-07	2,203E-07	1,637E-07
	Rep2	1,279E-07	2,503E-07	2,550E-07	2,739E-07	2,132E-07
	Rep3	1,434E-07	2,653E-07	2,695E-07	2,853E-07	2,457E-07
	Media	1,281E-07	2,383E-07	2,419E-07	2,598E-07	2,075E-07
	RSD	1,525E-08	3,454E-08	3,604E-08	3,471E-08	4,129E-08
	%RSD	11,91	14,49	14,90	13,36	19,90
Height/ μA	Rep1	4,100E-06	6,905E-06	6,785E-06	7,881E-06	5,847E-06
	Rep2	3,925E-06	7,798E-06	7,704E-06	8,490E-06	6,362E-06
	Rep3	4,108E-06	7,830E-06	7,704E-06	8,306E-06	7,062E-06
	Media	4,044E-06	7,511E-06	7,398E-06	8,226E-06	6,424E-06
	RSD	1,034E-07	5,251E-07	5,306E-07	3,123E-07	6,098E-07
	%RSD	2,557	6,990	7,172	3,797	9,494

Table 16. Reproducibility of the method (electrodes from 6 to 10).

We can observe that the results are more or less the same with the same electrode, but these results vary slightly between different electrodes.

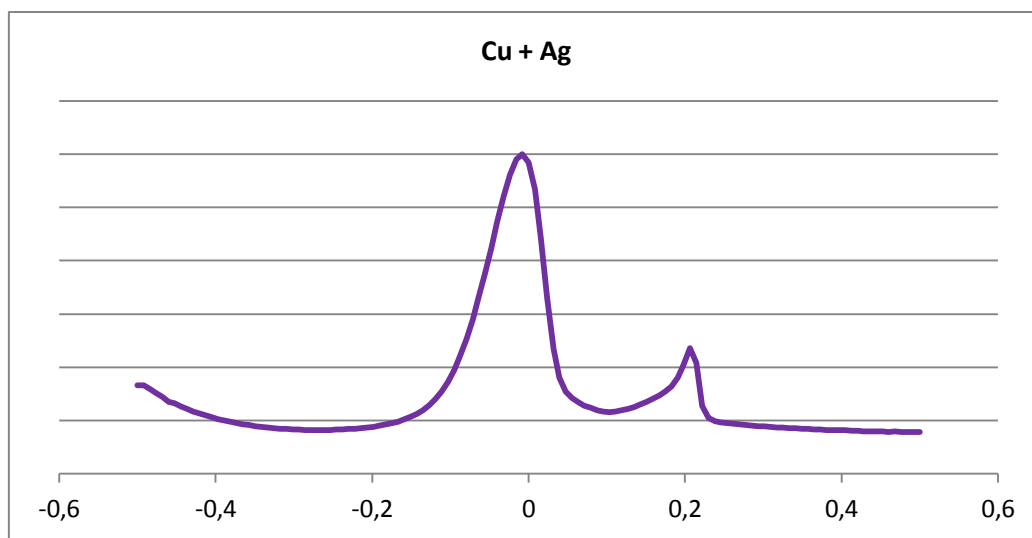
To improve the reproducibility we changed some parameters. At the beginning of each electrode, we did a conditioning step with the following parameters: $E=1\text{V}$; $t = 60\text{s}$. Then, between measurements, the conditions are the same as always: $E = 0,5\text{ V}$; $t = 90\text{ s}$. If we analyse the results, the %RSD varies a lot between different electrodes, so we could not enhance the reproducibility with this change in the conditioning step.

Finally, we apply these last conditions at the beginning and between measurements. But, unfortunately, it did not work either. These are the results:

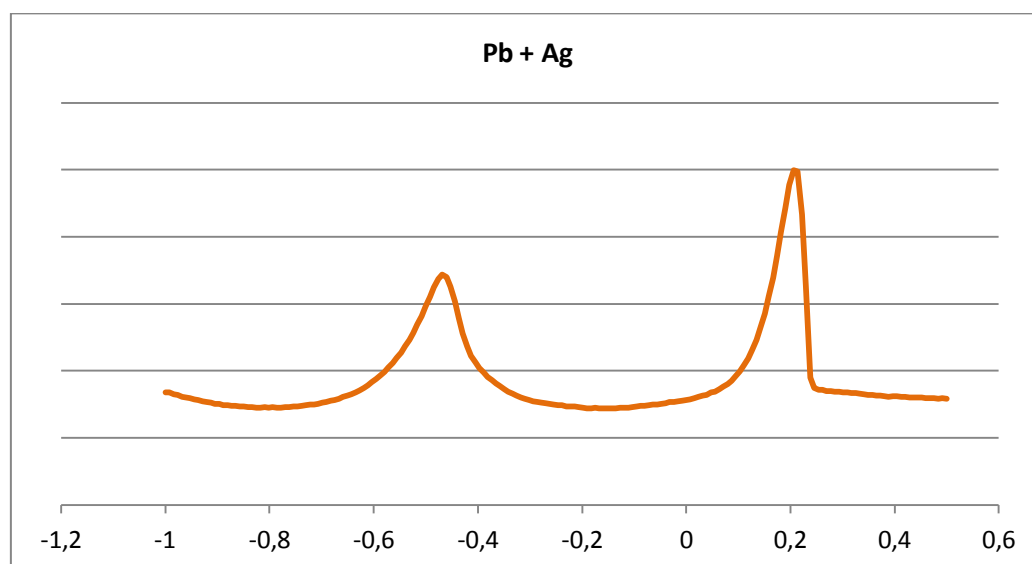
So, we can conclude that the repeatability is good but not the reproducibility. It is necessary to do the calibration and the measurements with the same couple of electrodes. This fact is one of the limits of this method.

6 Study of interferences

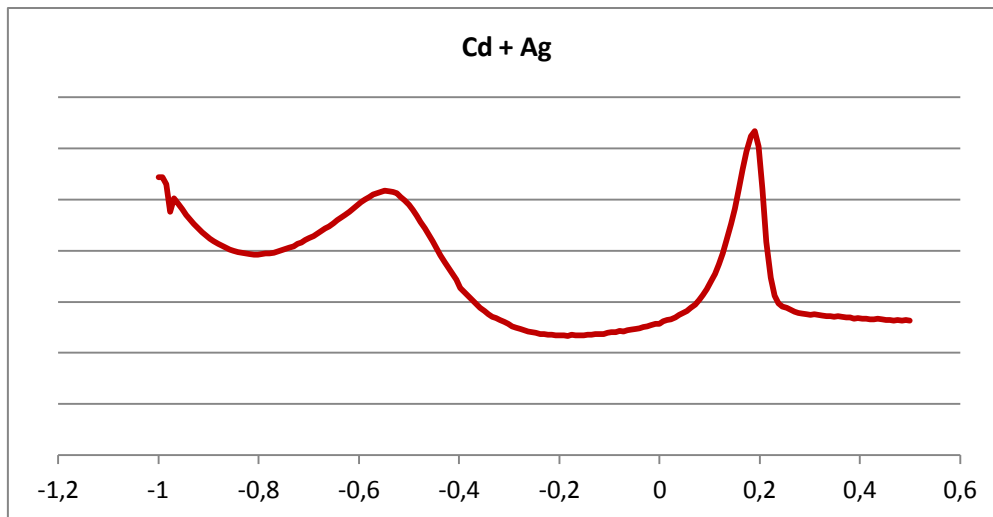
To check the possible interferences in the determination of silver, we tried with these metals: Cu, Pb, Cd and Zn. First of all, we measure each metal combined with silver, to check its oxidation peak.



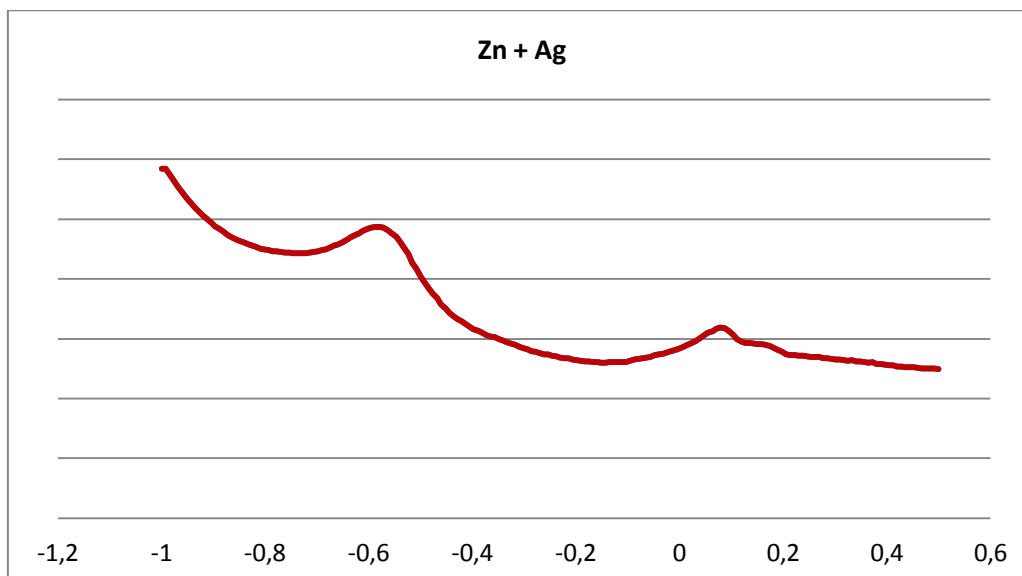
Graph 13. Oxidation peak of copper ($E = 0 \text{ V}$) and silver ($E = 0,2 \text{ V}$).



Graph 14. Oxidation peak of lead ($E = -0,5 \text{ V}$) and silver ($E = 0,2 \text{ V}$).



Graph 15. Oxidation peak ($E = -0,6$ V) of cadmium and silver ($E = 0,2$ V).



Graph 16. Oxidation peak of zinc ($E = -0,6$ V) and silver ($E = 0,2$ V) .

For Pb, Cd and Zn the oxidation peaks are far from the oxidation peak of silver. So it is not probable that these metals influence silver determination. On the contrary, the oxidation peak of the copper is near to the oxidation peak of the silver, and we may take it into account in silver determination.

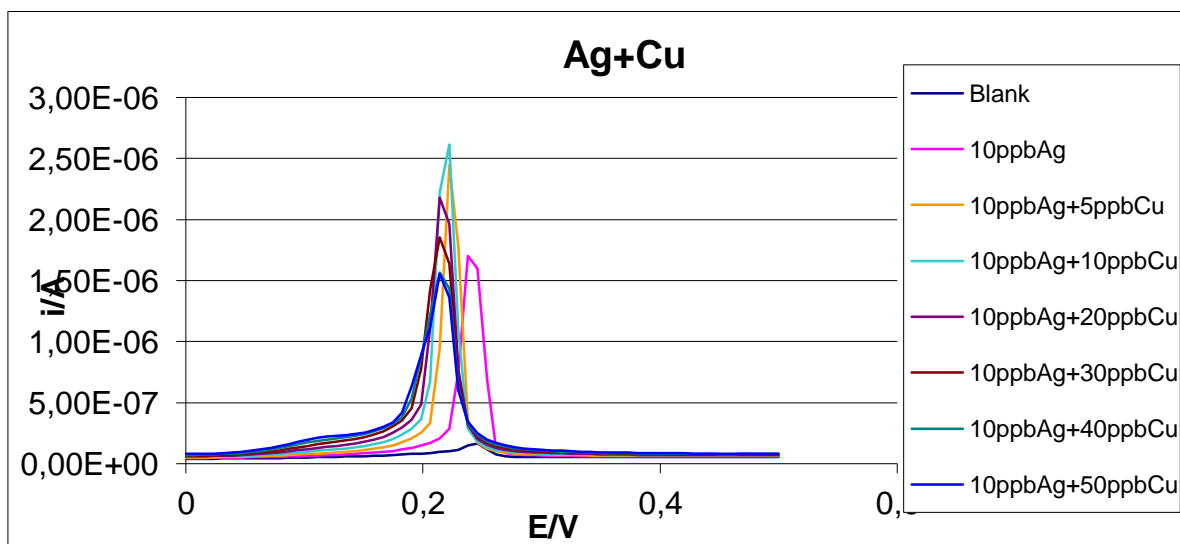
Once we know the position of each peak, we measure different concentrations of each metal with a different couple of electrodes.

- Electrode 1: 10 ppb Ag + Cu
- Electrode 2: 10 ppb Ag + Pb
- Electrode 3: 10 ppb Ag + Cd
- Electrode 4: 10 ppb Ag + Zn
- Electrode 5: 10 ppb Ag + mix of metals (Cu, Pb, Cd and Zn). In this mix, all the metals are in the same concentration.

We keep the parameters of the determination of silver.

Parameters	E_{dep}/V	t_{dep}/s
	-0,3	240

Copper

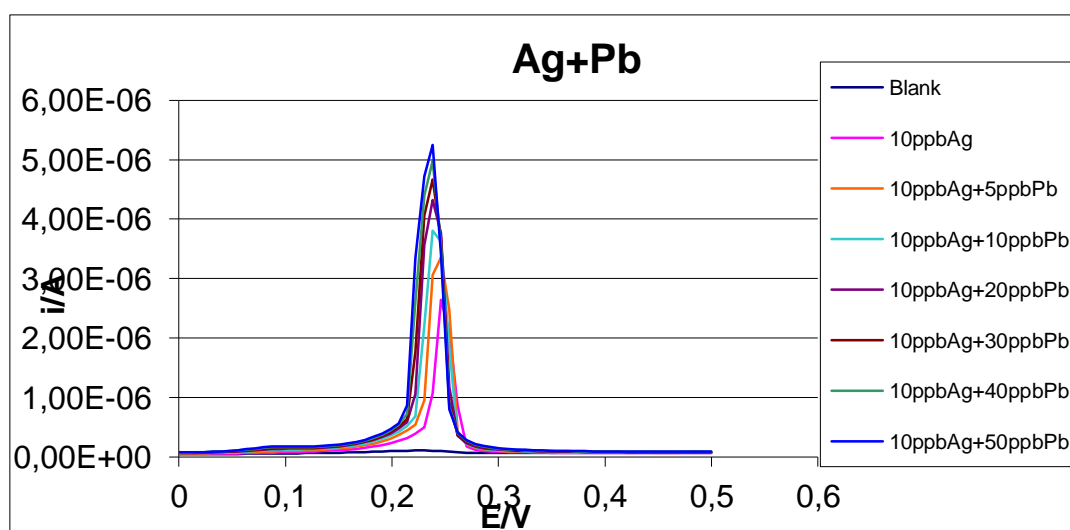


Graph 17. Study of the influence of copper in silver determination when the concentration of the interference increases.

We can observe an increase of the intensity. To discuss this result we have two possibilities:

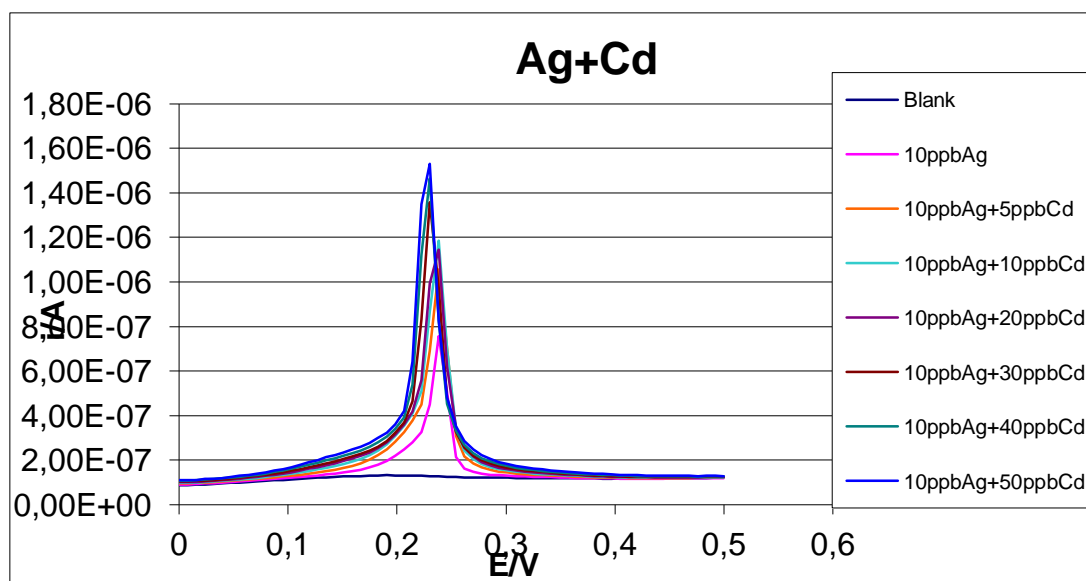
- 1- Copper appears at a potential near to that one for silver. Therefore, the peaks appear at the same potential, and the intensity is the sum of the two peaks.
- 2- Copper enhances the oxidation of silver. The higher the concentration of copper, more silver is oxidized.

Lead



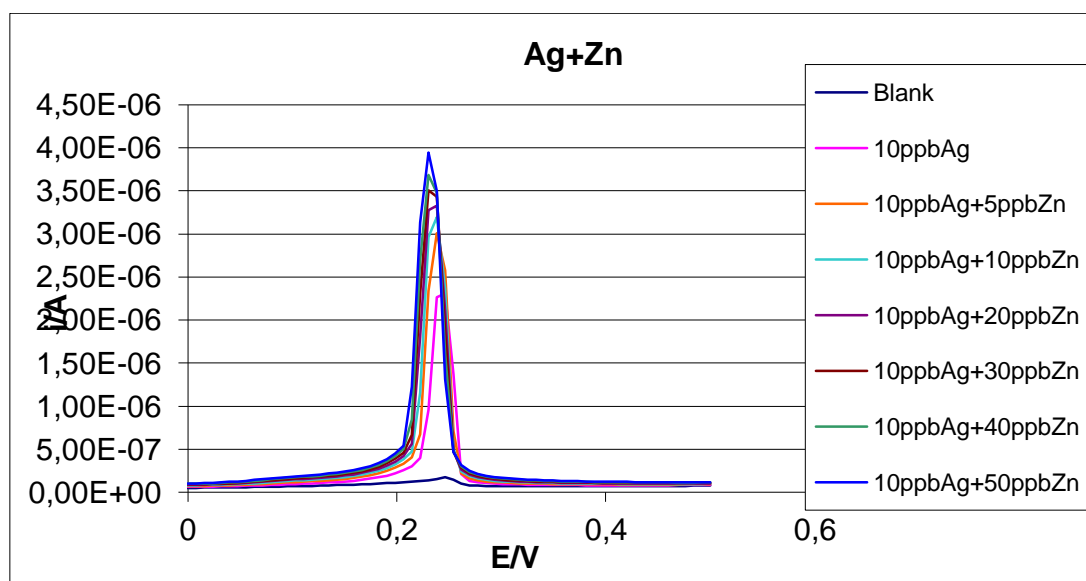
Graph 18. Study of the influence of lead in silver determination when the concentration of the interference increases.

Cadmium



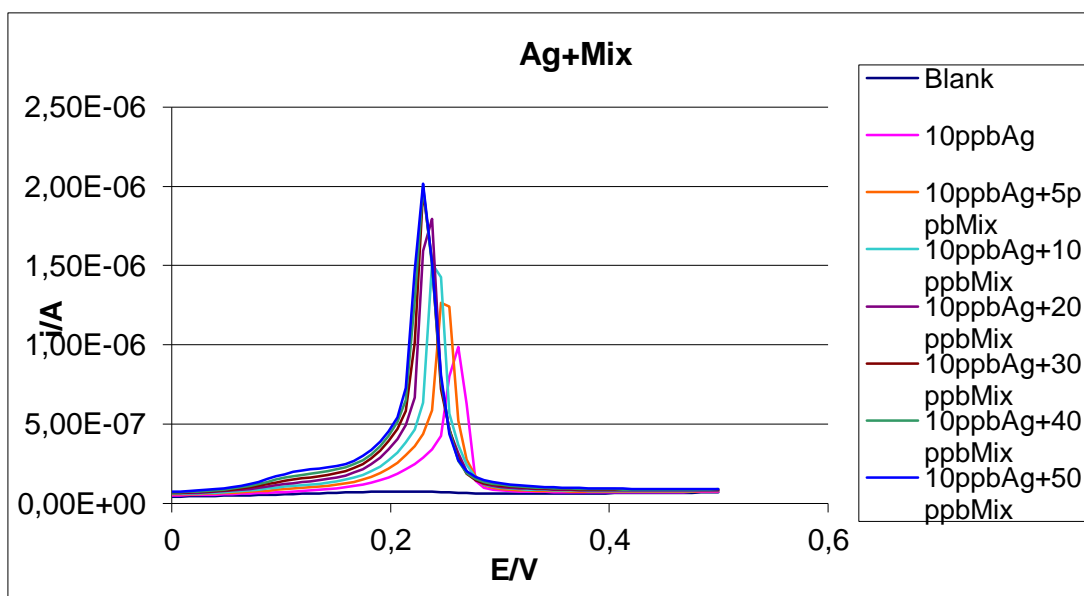
Graph 19. Study of the influence of cadmium in silver determination when the concentration of the interference increases.

Zinc



Graph 20. Study of the influence of zinc in silver determination when the concentration of the interference increases.

Mix of metals (Cu+Pb+Cd+Zn)



Graph 21. Study of the influence of a mix of metals (copper, lead, cadmium and zinc) in silver determination when the concentration of the interferences increases.

As conclusion, we can say that the concentration assayed do not interfere in the determination of silver. In all the cases we can observe a slightly increase of the signal when the concentration of the interference increases. We can suppose (except of copper) that this increase is due to the accumulation of silver in the electrode surface between measurements.

4. CONCLUSION

By the moment, we have been able to develop a **cheap, fast and easy** method for silver determination in aqueous solution. The electrodes used are inexpensive and easy building. By the contrary of the publications read, we do not use any coating on the electrode surface, so we save time, reagents and money.

We have achieved a detection limit of 0,2 ppb, which led to determine silver in trace amounts. Besides, the determination of silver is not influenced by the presence of other metals.

Despite of these advantages, the method has some drawbacks. First of all, we need to improve the reproducibility. Until now, if we want to analyze a sample, we need to do the calibration curve and the analysis with the same couple of electrodes, due to the variability between values obtained with different couples of electrodes. This fact is a limit of the method.

Moreover, we have tried with silver ions, but no with silver nanoparticles, so it is probable that the method works in a different way when we try these species.

Finally, due to the short period of time of my stage, we did not have enough time to analyze real samples, and, therefore, we do not know yet if a pretreatment of the sample is required.

To conclude, during this stage I worked in a new area for me. It was the first time I worked with electrochemical techniques, which allowed me to learn a bit more about this field.

5. REFERENCES

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