Abstract

In recent years the legal framework concerning the amount of heavy metals allowed in the water discharges is constantly being redefined. Therefore, it is necessary to investigate the development of effective ecological and economical systems in anticipation of future needs. Among these systems, biosorption has proven to be one of the most attractive alternatives since it involves the upgrading of plant waste that otherwise would be incinerated.

Mercury was used as an electrode material for a long time due to their wide cathodic range in different voltammetric techniques. Nevertheless, due to the potentially toxicity of mercury vapors and mercury compounds and wastes, the research of alternative materials which allows to analyze these samples without environmental risks is an area of major concern.

A recognized method for the fabrication of sensors and biosensors for the determination of metal ions in industrial, environmental and biomedical applications is based on the screen-printing technology which permits production of numerous highly-reproducible single-use screenprinted electrodes (SPEs).

SPEs accessibility, low cost character, miniaturized size, and the possibility of connection to portable instrumentation make these devices very suitable for on-site determination of target analytes.

In this project the screen-printed electrodes are used as an alternative to determine metal ions concentrations in wastewaters without using mercury electrodes. This new working methodology has been implemented to determinate the nickel of stock solutions or real samples.

The composition of these real samples, provided by a metal electroplating company, was compared with the results by ICP (Parc Científic de Barcelona) method. The obtained results are very similar in both methods.
An alternative to the use of mercury electrode on the determination of metal ions in voltammetric techniques: Screen-Printed Electrodes

Summary

ABSTRACT

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1. Glossary

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<td>CSV</td>
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<tr>
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<td>SWP</td>
<td>Square Wave Polarography</td>
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<td>DME</td>
<td>Dropping Mercury Electrode</td>
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<td>STP / WWTP</td>
<td>Sewage Treatment Plant / Wastewater Treatment Plant</td>
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<td>HDME</td>
<td>Hanging Drop Mercury Electrode</td>
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<td>RDE</td>
<td>Rotating Disc Electrode</td>
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<td>SPE</td>
<td>Screen-Printed Electrode</td>
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<td>DMG</td>
<td>Dimethylglyoxime</td>
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2. Preface

2.1. Origin of the project

The present Degree Final Project is a contribution to these research projects:


“Síntesis verde de nanopartículas metálicas a partir de aguas ácidas de mina y extractos de residuos agroalimentarios” funded by Ministerio de Economía y Competitividad, Madrid, and FEDER funds, EU, 2016-2018. Project CTM2015-68859-C2-2-R (MINECO/FEDER)

2.2. Motivation

The main motivation of this project is to adjust the working conditions of the study with SPE to become as accurate as it is possible to determine metal concentrations and do it compatible with 797 VA Computrace.

The present Final Project Grade focuses its efforts on the use of voltammetry technique with SPE for analyzing water samples from industrial wastes in the purification of polluted effluents with heavy metals.
3. Introduction

3.1. Project objectives

The main objective of this project is to study the behaviour of a new working electrode called Screen-Printed Electrode (SPE) provided by Dropsens and check the reproducibility of measurements using hardware and software from Metrohm (797 VA Computrace) and analyzing standard or real samples of nickel in low concentrations (ppb).

A secondary objective is to compare different methodologies and perform them as precisely as possible to thereby obtain a sufficiently reliable values to replace the mercury electrode without losing effectiveness.

3.2. Project background

This project is based on previous studies carried out by Jordi Turmo and Xialei You, where monometallic copper determinations and multimetallic determinations of copper, zinc, cadmium and lead were studied by the voltammetric technique HDME using a mercury drop electrode in both cases. [1] [2]
4. Voltammetry

The electrochemical technologies include analytical methods based on the electrical properties of an analyte solution when comprises part of a electrochemical cell, which can be related directly or indirectly to the species of interest, usually measuring a parameter or electrical nature due to this change.

The electroanalytical methods have certain advantages over other general types of analytical procedures. Its specificity for a particular oxidation state of an element differentiating the concentration of each species in a mixture with some metals such as $M^{a+}/M^{b+}$, while other techniques only provide the total concentration of these.

They also can be used by economic instruments and easily miniaturizable which allows to carry out on-field measurements (i.e. glucose biosensors). In addition, some methods provide information regarding the activity of the species rather than concentration, which can be considered an advantage or a disadvantage depending on the situation; i.e. in physiological studies, measuring the activities of ions such as calcium or potassium provide more information.

There are a variety of electroanalytical methods, which are based on the experimental conditions and parameters measured that can be classified according to the scheme (Figure 4.1). Firstly, one can distinguish between interfacial methods based on phenomena that occur at the interface (these being the most used application) and methods within the solution based on events that take place within the solution (trying to avoid any interfacial effect). Within the first one can distinguish more categories according how the electrochemical cell operates: static and dynamic, i.e. in the absence or presence of current.

The static methods based on potentiometry measured in electrochemical potential of a solution which depends on the composition of particular analyte due to selectivity. Moreover, dynamic methods arise a new differentiation depending on the controlled applied potential and the intensity generated or a fixed value of intensity and other properties are measured such as the time required to react the analyte of interest.

Thus, since the particular technique used throughout this project has been the voltammetry, we will focus on this technique in the following paragraphs.
The voltammetry comprises a group of electroanalytical methods in which information about the analyte is extracted from the measurement of the current intensity depending on the applied potential, in conditions that favoured the polarization in the working electrode. The generation of this current comes from the application of an external potential capable of causing electron transfer between the working electrode and a species in solution, that can be oxidized or reduced.

In addition, this situation leads to other in which there is a minimum waste of analyte, which means minimal alteration or destruction of the sample.
4.1. Electrochemical cell

In order to apply the suitable potential while a current intensity is measured, it is essential to use a configuration of three electrodes in electrochemical cell design.

Therefore, the cell is formed by the following three electrodes:

![Electrode diagram](image)

**Fig. 4.2.** Electrode system in the cell. [2]

4.1.1. Working electrode

It is the most important electrode of the electrode system. It is where electrochemical reaction under study takes place on his surface. Figure 4.3 represents the working electrode used in the MME method. In this project SPE will be used as working electrode instead of the mercury electrode.
4.1.2. **Auxiliary/counter electrode**

Within the different types of auxiliary electrodes (Figure 4.4), platinum electrode is used to measure metal concentrations with the defined method. It is the most appropriate because it doesn’t react with any of the compounds present in the sample. They are used to close the connection between the electrolyte and the working electrode so that the current can be applied.

4.1.3. **Reference electrode (silver – silver chloride electrode)**

The reference electrode ensures that the potential applied is constant and the correct one so the electrochemical reaction takes place.
The standard reduction potential of AgCl | Ag is +0.222V at 25°C, which would be the potential of an electrode of silver - silver chloride if the chloride activity was the unit. But the activity of chloride in a saturated solution of KCl at 25°C is not the unity, so the potential of the electrode is +0.197 V with respect to the standard hydrogen electrode at 25°C.

In order to minimize the junction potential between the analyte and the KCl solution, double junction electrode is used. The disadvantage of this type of electrode is the possibility of clogging of the porous window, causing unstable and slow electrical responses.

![Scheme of a reference electrode](image)

Fig. 4.5. Scheme of a reference electrode. [1]

Thus, the potential of the working electrode is kept constant while the auxiliary electrode serves merely to allow the passage of electric current to or from the working electrode, depending on the applied potential. It is therefore interesting to note that depending on the applied potential our working electrode behaves as an anode or a cathode, so measurements can be used to determine voltammetry substances that present reduction and oxidation properties.
An alternative to the use of mercury electrode on the determination of metal ions in voltammetric techniques: Screen-Printed Electrodes

However, in systems where we want to apply a potential variation over time, we will take this variation in the potential of the working electrode with the aid of instrumentation, which will be responsible of reach the described situation by short increases in the applied potential (potential jump).

4.2. Excitation signals - Different voltammetry methods

As already mentioned, all potential-controlled techniques are based in the measurement of the current response to an applied potential (excitation signal, variable) at an electrode. The main difference between techniques is the applied potential excitation function. This can be a ramp, a series of potential steps, a differential pulse, a square wave, or even a combination of them. This section describes those techniques.

Therefore, depending on the type of excitation applied signal will get a characteristic intensity response in which the method is based; allowing to obtain different results in each case, therefore is a prerequisite to know the type of signal that we want to apply and the information we extract.

Figure 4.6 shows the four types of excitation signals commonly used in voltammetry:

![Excitation signals](image)

Fig. 4.6. (A) Sweep Linear, (B) Differential Pulse, (C) Square Wave, (D) Cyclic Voltammetry[6]
- **Sweep Linear**: where the potential DC applied to the cell linearly increasing function of time; the signal corresponds to the classic voltammetry.

- **Differential pulse**: derived from the above, where the excitation signal corresponds to the superposition of a series of regular pulses on the sweep linear measuring the difference in intensity before and after each pulse.

- **Square wave**: they apply to potential variations in the form of scale (a square wave is superimposed on potential sweep), measuring the differential current after each change of potential.

- **Cyclic voltammetry**: the potential presents triangular shape, providing a cyclic potential variation between two values, increasing and decreasing between these two with the same speed.

### 4.2.1. Potential sweep techniques

Cyclic voltammetry (CV) is probably the most popular electrochemical technique. It is widely used in analytical chemistry for qualitative and quantitative determinations and by the physical-chemistry in the determination of thermodynamic and kinetic information of electrochemicals systems.

The technique consists in linearly scanning the potential using a ramp or a triangular potential waveform. It is recommended to begin the scan at a potential where no redox reaction occurs and sweep it in the direction where the reactions of interest take place. Eventually, the scan is reversed and the reverse process is registered. Depending on the technique, one partial cycle, a full cycle or a series of cycles can be performed. The resulting current-potential plot is termed cyclic voltammogram, and it is a complicated time-dependent function of a large number of physical and chemical parameters.

![Example of a cyclic voltammogram](image)

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**Fig. 4.7.** Example of a cyclic voltammogram [12]
Figures 4.6(E) and 4.7 illustrate the potential function of a cyclic voltammetry and the basic shape of a current response for a reversible redox couple during a single potential cycle. At the beginning of the experiment, the bulk solution contains only the reduced form of the redox couple. The potential is set more negative than the $E^0$, so only non-faradaic currents flow. As the electrode potential approaches $E^0$ the oxidation begins and a net anodic current appears. The surface concentration of the sample starts to decay, diffusion sets in and more redox couple will be carried in from the bulk, causing the current to increase until a maximum (peak current) is reached. After the peak current, the depletion of the diffusion layer takes over. Upon reversal of the scan, oxygen molecules (generated in the forward half cycle, and accumulated near the surface) are reduced back and a cathodic peak appears.

If a microelectrode is used instead of a macroelectrode, the cyclic voltammogram takes a sigmoidal shape because mass transport is dominated by radial instead of planar diffusion.

Going back to Figure 4.7, the peak current of a reversible voltammogram is described by the Randles-Sevcik expression:

$$I_p = 0.4463nFAC \sqrt{\frac{nFDv}{RT}}$$  \hspace{1cm} (Eqn. 4.1)

Where all the parameters take their usual meaning [5]:

- $I_p$ = current maximum [A].
- $n$ = number of electrons transferred in the redox event (usually 1).
- $A$ = electrode area [cm$^2$].
- $F$ = Faraday constant [C/mol]
- $D$ = diffusion coefficient [cm$^2$/s]
- $C$ = concentration in [mol/cm$^3$]
- $v$ = scan rate [V/s]
- $R$ = Gas constant $\left[ \frac{V\cdot C}{K\cdot mol} \right]
- T = temperature [K].$

Note that the current is directly proportional to concentration of electroactive species and increases with the square root of scan rate. The ratio of reverse-to-forward peak current ($I_{pc}/I_{pa}$) for reversible process should be close to one; however, chemical reactions coupled to the electrode process can significantly alter this ratio.
Other well defined characteristics of the V for the reversible electrochemical reactions are:

- That the formal redox potential is centred between the anodic peak potential and the cathodic peak potential.

\[ E^0 = \frac{E_{pa} + E_{pc}}{2} \]  
(Eqn. 4.2)

- That the number of electrons transferred in a reversible electrode reaction can be determined by the potential separation between peaks.

\[ \Delta E_p = E_{pa} - E_{pc} = 2.218 \frac{RT}{nF} \]  
(Eqn. 4.3)

The situation is really different in the presence of quasi-reversible or irreversible electrode kinetics. In these cases, cathodic and anodic potentials shift. The peak to peak separation is larger than predicted by Eqn (4.2). \( \Delta E_p \) grows larger as electron transfer kinetics become slower, as shown in Figure 4.8.

**Fig. 4.8.** Simulated cyclic voltammograms. System (A) shows reversible electron transfer kinetics whereas (B) presents slow electron transfer.[5]

However, electron transfer kinetics is not the only cause of shape alteration in voltammograms. If chemical reactions are coupled either before or after the electrochemical process, the primary measured parameter of the forward reaction (e.g. the peak current or
the peak potential, and the reversal parameters (e.g. $I_{pc}$, $I_{pa}$) are likely to be affected. For example, if we assume an homogeneous chemical reaction coupled to the electrochemical step, as shown in the Eqn (4.4 - 4.5), after the electrochemical step, Oxd freely reacts and, when the scan direction is reversed, Oxd is no longer present in the system to be reduced back (see Figure 4.9). The loss of peak current on the reverse scan is the most obvious indicator of a follow-up chemical reaction step.

\[ \text{Red} \leftrightarrow \text{Oxd} + e^- \quad \text{(Eqn. 4.4)} \]

\[ \text{Oxd} \leftrightarrow P \quad \text{(Eqn. 4.5)} \]

Savéant and coworkers introduced the concept of “zone diagrams” to describe the mechanistic behaviour of reactions. The variation of peak potential with experimental parameters such as the sweep rate and the initial concentration has been shown to be a valuable source of information in the elucidation of chemical kinetics.

![Simulated voltammogram of the unperturbed reversible redox reaction (dashed line) and a perturbed reversible system (solid line).][5]

Fig. 4.9. Simulated voltammogram of the unperturbed reversible redox reaction (dashed line) and a perturbed reversible system (solid line).[5]

Linear sweep voltammetry implementation is almost identical to cyclic voltammetry. The difference is that the potential is swept only in the forward direction while the cyclic method also includes a backward scan.
4.2.2. Potential step techniques

Chronoamperometry measures the transient current response to a potential jump. The potential is stepped from a value where no redox reaction occurs to a potential at which the desired electrochemical reaction takes place. This sequence is shown in the Figure 4.10 where the oxidized species are stable at $E_i$, but are reduced at a diffusion-limited rate at $E_f$.

A large initial current is recorded which decays rapidly as a result of growing diffusion layer and decreasing concentration gradients in the absence of convection. The equation that describes the theoretical behaviour of the current under planar diffusion conditions is known as Cottrell’s equations: (Eqn 4.6)

$$I(t) = \frac{nFACD^{1/2}}{\pi^{1/2}t^{1/2}} = kt^{-1/2}$$  \hspace{1cm} (Eqn. 4.6)

Note that “$t^{-1/2}$” takes a constant value which defines “Cottrellian behaviour”. Deviations from that behaviour can be observed at long times as a result of natural convection.
An alternative to the use of mercury electrode on the determination of metal ions in voltammetric techniques: Screen-Printed Electrodes

Chronoamperometry is often used for measuring the diffusion coefficient of electroactive species, provided that both their concentration and the number of electrons exchanged in the process are known. Multiple potential step techniques may be used to elucidate kinetic constant when the electrochemical step is coupled to a chemical reaction.

In order to increase speed and sensitivity, many forms of potential modulations (more complex than a simple staircase or a ramp) have been developed over the years.

Pulse voltammetry techniques are based on a sequence of potential steps (chronoamperometric measurements). Shortly after the pulse, a high capacitive current flows due the discharging of the double layer, which decreases faster than the faradaic current. For this reason, if the sampling time is chosen later in the pulse, it is possible to filter out non faradaic currents. In general, a pulse time of 50 ms is chosen. It is because 50 ms should be much larger than the constant cell time of most systems of interest and the non faradaic currents can be negligible. The cell time constant is calculated as 5 times the resistance plus the capacitance of the cell.

The difference between the various pulse voltammetric techniques is the excitation waveform and the current sample periods (Table 4.1 summaries the four most common pulse voltammetric techniques).

<table>
<thead>
<tr>
<th>Name</th>
<th>Potential waveform</th>
<th>Current response</th>
<th>Features</th>
</tr>
</thead>
</table>
| Normal Pulse Voltammetry (NPV) | ![Potential waveform](image) | ![Current response](image) | $t_p \sim 50 \text{ ms}$  
$\tau \sim 1 \text{ s}$  
$\Delta E_p \sim 2 \text{ mV} \cdot \text{s}^{-1}$  
$I_p = \frac{nFAD^{1/2}C}{\sqrt{\pi \tau_m}}$ |
Differential Pulse Voltammetry (DPV)

\[ \Delta I = I_2 - I_1 \]
\[ t_p \sim 50 \text{ ms} \]
\[ \tau \sim 1 \text{ s} \]
\[ \Delta E_p \sim 50 \text{ mV} \cdot \text{s}^{-1} \]
\[ \Delta E_p / \tau \sim 2 \text{ mV} \cdot \text{s}^{-1} \]

\[ I_p = \frac{nFAD^{1/2}C}{\sqrt{\pi t_m}} \left( \frac{1-\sigma}{1+\sigma} \right) \sigma \]
\[ = \exp \left( \frac{nF}{RT} \frac{\Delta E}{2} \right) \]

Square Wave Voltammetry (SWV)

\[ \Delta I = I_2 - I_1 \]
\[ \tau \sim 5 \text{ ms} \]
\[ \Delta E_p \sim 25 \text{ mV} \cdot \text{s}^{-1} \]
\[ \Delta E_s \sim 10 \text{ mV} \cdot \text{s}^{-1} \]

\[ I_p = \frac{nFAD^{1/2}C}{\sqrt{\pi t_p}} \Delta \psi_p \]

\[ \Delta \psi_p \text{ is dimensionless peak current.} \]

Alternating Current Voltammetry (ACV)

Amplitude: 10 – 20 mV
Frequency: 500 – 100 Hz

\[ I_p = \frac{n^2F^2Aw^{1/2}D^{1/2}C\Delta E}{4RT} \]

Table. 4.1. Comparison between the potential waveform and the current response between different pulse voltammetry techniques.[5]
4.2.3. Stripping techniques

The term of electrochemical stripping analysis is used for procedures involving a preconcentration of the analyte in solution over the working electrode, prior to its direct or indirect determination during its re-dissolution. Such combination, accumulation and stripping, results in very low detection limits and makes stripping analysis one of the most important techniques in metal trace analysis.

Different modes of stripping analysis can be employed depending upon the nature of the deposition and measurement steps. The most widely used one is anodic stripping voltammetry (ASV) at Hg electrodes. In this case, metals are preconcentrated by cathodic electrodeposition over a controlled time and potential. The metal ions reach the mercury electrode by diffusion and convection, where they are reduced and concentrated as amalgams:

\[ M^{n+} + ne^- + Hg \rightarrow M(Hg) \]  
(Eqn. 4.7)

At the end of the deposition step, the potential is scanned anodically, and the amalgamated metals are stripped out from the electrode producing characteristic peaks:

\[ M(Hg) \rightarrow M^{n+} + ne^- + Hg \]  
(Eqn. 4.8)

The potential time sequence used in ASV and the resulting stripping voltammogram is shown in Figure 4.11. The peak potential serves to identify the metals in the sample. The peak current depends upon various parameters of the deposition and stripping steps, as well as on electrode geometry and the characteristics of the metal ion, but in general it is proportional to the concentration of the latter.

Despite the high detection limits achieved with this technique, the presence of interferences can produce erroneous results. For instance:

1. Overlapping stripping peaks caused by a similarity in the oxidation potentials.
2. Formation of intermetallic compounds which affect peak shape, size and position.
3. The presence of surface organic compounds adsorbed on the mercury electrode which inhibit the metal deposition.
Considering the complexity of redox processes that can be carried out in electrochemical cells, there are many parameters that can be controlled to favour any particular process. These include the speed with which the potential varies over time (i.e. speed scanning), the potential difference between each measurement (i.e. the potential jump) and the amplitude potential on cases that variations or pulses are applied. Controlling these parameters we can get different voltamperograms for the same solution. One can predict with some assurance of success, such as initial conditions allow obtaining the desired results.

Among the methods described above, cyclic voltammetry is probably the most used, normally used as a tool for the characterization of substances and redox properties of the transducer used. Such voltammetry allows distinguishing redox pairs presenting reversibility in oxidation and reduction, as well as helps finding potential electroactive substances that have electrochemical reactivity. Therefore, the cyclic voltammetry is usually the first step in determining redox properties of substances unknown to the analyst or the characterization of new transducers.

Moreover, this is usually the first technique selected in the study of reaction rates and mechanisms of redox processes, particularly for organic and organometallic systems, as long as the system is treatable from electrochemical standpoint; being especially useful in the reaction intermediates.

![Anodic stripping voltammetry](image_url)
Along with cyclic voltammetry, differential pulse voltammetry can be considered as the next most widespread and popular method; usually related with methodologies for the determination of heavy metals and other substances that allow its deposition (accumulation) to the surface of the working electrode. In this case, they usually make use of anodic stripping, prior to the completion of the voltammetry measurement, in order to lower the detection limits thanks to the preconcentration achieved through its deposition.

Thus, voltammetry offers the ability to determine a wide range of substances at a relatively affordable price. However, today is hardly a technique that can move chromatography or mass spectrometry analysis of industrial systems.

4.3. Voltammograms

The cyclic voltammetry is a useful technique to characterize, in a wide range of potential, the electrochemical behaviour of the transducer and the electroactive species present in a given sample; turning it into a powerful technique for extracting information from both the sample and the transducer. However, the variation of this transducer can be used as a source for to get additional and complementary information on the sample.

As mentioned, this technique involves measuring the current intensity obtained from the linear variation of the applied potential versus time; In other words, when performing a potential sweep from a determined initial potential and then reversed the direction of the sweep to get back to the starting potential. The result of this record is called cyclic voltammogram (going back to Fig. 4.7, 4.8 and 4.9) and is the representation of the intensity of current (I) flowing between the working and the auxiliary electrode, depending on the applied potential at all times (E).

In positive potentials the electrode becomes an anode (oxidant) so if you initially have all the electroactive species in its reduced form, it is favouring oxidation on the surface of the electrode, which causes an increase in the anodic intensity. Considering that solution is not stirred, the intensity stops increasing once have been consumed all the species that are in contact with the electrode. Then the analyte comes only by diffusion so there is a decrease in the obtained signal and as a result, a peak intensity.

Then, reversed the sense of potential sweep and move towards negative potential, electrode becomes a cathode (reducer) causes the reduction of oxidized species that have accumulated during the previous process on surface (if the reaction is reversible) or other electroactive species present in the solution. This causes an increase in the cathodic intensity to a maximum value corresponding to the point where all the oxidized species
present on the surface of the electrode have been consumed, and therefore, the signal begins to decrease.

For a qualitative study of a particular redox system that are obtained from a cyclic voltammogram, the potential and the peak current are important parameters, both in the oxidation and in reduction ($E_{pc}$, $i_{pc}$; $E_{pa}$, $i_{pa}$), respectively.
5. Equipment and devices calibration

The most important and delicate part of the project is the calibration technique. Consequently, it has required a special attention. This technique uses several elements that will be shown in the following sections, which are equally important for the procedure.

5.1. 797 VA Computrace

VA Computrace is a PC controlled system for voltammetry, which consists of the following parts:

1. VA Computrace Stand with accessories (Figure 5.1).
2. Connecting Cable.
3. 797 VA Computrace Software.

The central element of this Stand is the Multi-Mode Electrode (MME), which combines the dropping mercury electrode (DME/SMDE) and the stationary hanging mercury drop electrode (HMDE) in a single construction. The rotating disk electrode (RDE) can also be used in the stand.

In our case mercury electrode will be replaced for Screen-Printed electrodes (SPE). So the computer will keep thinking that has connected a mercury electrode. Therefore, when configuring the parameters for determinations, it simply works in HMDE mode.
The 797 VA Computrace Stand is controlled with the PC-Software «797 VA Computrace Software». Parameters necessaries for the VA measurement are sent from the PC to the VA Computrace via USB connection. The data acquisition at the 797 VA Computrace Stand is started and controlled by the PC-Software «797 VA Computrace Software», which receives and stores the measurement data. At the end of the determination, the recorded data are sent back to the PC where they are evaluated and saved in a determination file. [8]

5.2. Cell

To proceed to use the cell, first of all has to be cleaned. This process consists of several stages, which should be followed methodically so as not to contaminate the sample that will be analyzed later:

i. Pour the contents of the cell in the corresponding waste container.
ii. Once spilled, rinse it twice with Milli Q water. Then, continue rinsing the cell with nitric acid diluted to eliminate the possible remains of pollution that Milli-Q water has not eliminated. The resulting acid to clean the cell has to be poured into the appropriate waste container for acids.
iii. Finally, rinse the cell again to clean up the remains of nitric acid with Milli-Q water three times.
iv. Reached this point, one can proceed to add the following sample.

5.3. Screen-Printed Electrodes (SPE)

Screen printing technology is a widely used technique for the fabrication of electrochemical sensors. This methodology consists to drive towards the miniaturized, sensitive and portable devices and has already established its route from “lab-to-market” for many sensors. The application of these sensors for analysis of environmental samples has been the major focus of research in this field.
For many years, mercury was used as the most suitable electrode material due to its very attractive behaviour and highly reproducible and renewable surface (Figure 4.3). These distinct properties of the mercury drop electrode carried Heyerovský the Nobel Prize in Chemistry awarded in 1959. Nevertheless the high toxicity and environmental hazard caused are increasingly making obsolete these electrodes because of the mercury.

With the advancements in electro-analytical science, various non-mercury electrodes have also been examined. For example, bismuth and carbon electrodes started to be used in electroanalysis more than three decades ago due to their low background current, wide potential range, chemical inertness and suitability for various sensing and detection applications.

Recently, miniaturization of the solid electrodes was used to get several fundamental and practical advantages including such as a dramatic reduction in sample volume, portability and cost effectiveness.

Screen printing technology is a well established technique for the fabrication of economical, portable and disposable electrode systems. The whole electrode system, including reference, counter and working electrodes can be printed on the same substrate surface (Figure 5.2). However, in this project only the working electrode of the SPE will be used in determinations and the other two (reference and counter) will be the default electrodes provided from Metrohm to obtain greater quality and precision on measured samples. [Cristina Ariño and Núria Serrano, private communication, 2016]
Screen printed electrodes not only address the issue of cost effectiveness but also satisfy the requirement of portability, a progress towards decentralized analysis. The adaptability of SPE is of vital importance in the area of research, the ability to modify electrodes easily through different inks commercially available for the reference, counter and working electrode, allows for highly specific and finally calibrated electrodes to be produced for specific analytes.

As a result of the poor reproducibility of these electrodes which are devices for single use, many of them give poor response when analyzing the sample twice and they also lose precision. It is for this reason that the use of both references and auxiliary electrodes provided by SPE will be avoided in order to prevent possible experimental errors.

One of the possible reasons why the electrode can give a bad signal is from defects in the finish surface of carbon working electrode, as in the example of Figure 5.3 where one can see a small scratch in his surface.

![Defective Screen-Printed Electrode](image)

Fig. 5.3. Defective Screen-Printed Electrode (SPE Nº 2).

Many times it is possible to detect this type of defect simply reviewing the SPE prior to analysis. Others, they will not be so simple and a prior calibration should be performed in case of doubt.

A cyclic voltammetry with the pair ferrocyanide/ferricyanide will be used to check this, as mentioned in the section 5.7.
5.4. Reference electrode

This section describes the maintenance that must have the reference electrode during the determinations.

5.4.1. External part

First, in the reference electrode, one has the external part shown in Figure 5.4.

The maintenance of this piece is described below.

i. Remove the reference electrode from the cell: Unscrew the plug and remove the support cell. Then remove the top carefully because it is a very delicate piece (internal electrode).

ii. Empty the contents (trace residues of potassium chloride).

iii. Fill the electrode with 3M potassium chloride so that it does not exceed the horizontal electrode mark.

iv. Reassemble the electrode entering the internal electrode and placing it back into the cell.

To continue using the electrode once the outside part is prepared, must wait for 15 minutes to ensure that the electrode is stabilized and running normally again.

Note that this procedure can be performed every two or three days.

---

Fig. 5.4. External part of reference electrode.
5.4.2. Internal part

Instead, the internal electrode maintenance should not be carried out every day but have to do it every two weeks to ensure proper functioning (Figure 5.5).

i. Disassemble the reference electrode and carefully remove the outer.

ii. Remove the threaded pug carefully of the lower tip so the electrode remains invested. One has to be careful because it is a very small piece.

iii. Without turning the piece, fill of potassium chloride 3 M avoiding bubbles inside the electrode. Once full, the threaded part is screwed and will be ready to introduce it to the external electrode part.

iv. Put it back into the cell.

Fig. 5.5. Internal part of reference electrode.

5.5. Dosinos

The 800 Dosino is a versatile dosing drive which can be used with a number of different Metrohm dosing (Figure 5.7). The 800 Dosino and the 807 Dosing Unit associated with it are suitable as a buret for simple dosings, titrations and for complex automation and liquid handling tasks such as sample transfers or pipetting.

Thanks to various 807 Dosing Units with 2, 5, 10, 20 or 50 mL dosing cylinders, the 800 Dosino is suitable for flexible use as a buret (dosing drive and dosing unit) and for adaptation to a number of different kinds of applications. [9]
An alternative to the use of mercury electrode on the determination of metal ions in voltammetric techniques: Screen-Printed Electrodes

In the event of frequent changes of reagent, the dosing units can remain mounted on the reagent bottle. The dosing drive can be readily removed and set up on the next dosing unit in one manual step. This step is not necessary to carry out daily if SPE are continually used.

It can occur that the first sample to be analyzed presents an unexpected measure. For this reason it is advisable to perform the analysis of a sample known with Dosinos in order to check they are adding the correct volume.

To access the Dosino settings to configure the dosing unit, press the shortcut on the main menu:

Fig. 5.6. Direct access to the dosino control [1]

Once logged in, the window allows to access to the configuration. Two distinctions are made in order to reduce the error in the analysis of the samples, depending of the use of SPE.

Fig. 5.7. Dosinos.
a. Continued use of Computrace:

If you use it daily, his running is simple: In the box “Dose volume (ml)”, enter the value 0.5, corresponding to the units in millilitres; then press the “Dose ON”. In this process the Dosino adds 0.5 mL in a beaker. Thus, avoid small bubbles that the tubes might contain.

b. Not continued use of Computrace:

On the other hand, if Computrace is not used for three days or more, it is advised to press the “Prep ON” so that the Dosino automatically calibrate its start-up. This way, it is possible to eliminate any bubbles that may have formed inside the Dosino.

Finally, the Dosinos can be rinsed using Milli-Q water to clean the ends of the tubes from dosing unit as well as their inside too.

5.6. Nitrogen to purge the system

In order to proceed with the opening of the nitrogen cylinder, first the user must to access the following menu:

"Utility > Computrace control".

![Access to the menu “Computrace control”][1]

Before open the nitrogen cylinder without causing damage to the system, the system must be purged in order to have all the valves open. To proceed with the purge, select the working method, HMDE in this case. Then, enable the "Purge" option (Figure 5.9).
If the purge process is successful, the box at the right of the button "Purge" turns red during this.

![Computrace control menu](image1)

![Nitrogen gas cylinder](image2)

Fig. 5.9. Computrace control menu  
Fig. 5.10. Nitrogen gas cylinder.

It is also recommended to check the pressure indicated by the manometer (Figure 5.10) before to open the nitrogen cylinder, this value should be of 1 bar. Then open the bottle and the system will begin to bubble up when purge button remains activated. To complete the purge, press again the "Purge" button. If the purge is not activated before opening the stopcock of the cylinder it can cause damage to Computrace's valves.

### 5.7. Cyclic voltammetry of potassium ferricyanide/ferrocyanide

The electrical current through the electrochemical cell during cyclic voltammetry experiment is related, among others, to kinetic parameters (kinetic constants) and thermodynamic of the system under study. In this case, the process of reduction of ferricyanide to ferrocyanide on the working electrode will be studied. In a simplified outline of the process ferricyanide which is in solution will approach the working electrode where reduction takes place. Then, ferrocyanide will diffuse into the solution. The electric current at each moment is a measure of the speed of the overall process (Eqn 5.2).

Ferricyanide: \([Fe^{III}(CN)_6]^{3-}\) (Figure 5.12 – Right)

Ferrocyanide: \([Fe^{II}(CN)_6]^{4-}\) (Figure 5.12 – Left)
[Fe(CN)₆]³⁻ + 1e⁻ ⇌ [Fe(CN)₆]⁴⁻  \quad (Eqn. 5.1)

\[ i = n_e F A \left( \frac{dn_{Fe(CN)₆}^{3⁻}}{dt} \right)_{x=0} \]  \quad (Eqn. 5.2)

Where \( n_e = 1 \) and the derivate represents the moles of ferricyanide variation at time \( x = 0 \) (electrode surface). The kinetic constants of reduction and oxidation process depend exponentially on the applied potential, the reduction increase in cathodic sense and the oxidation in the anodic sense. Concentrations of ferricyanide and ferrocyanide in the \( x = 0 \) at depend each moment both of reaction rate and the diffusion rate in the solution.

Given all these factors (units mentioned in the Eqn 4.1 of the section 4.2.1), it is not possible to obtain an analytic expression for the intensity of current versus applied potential; however, it is possible to obtain expressions for the peak intensities and peak potentials depending on variables such as the concentration of the electroactive species within the solution, scan rate and diffusion coefficient. To do this, a first approximation can be considered that the system behaves reversibly. In electrochemistry, the reversible concept refers to the surface of the working electrode, where the relationship between the concentrations of reduced and oxidized species meets the Nernst equation (Eqn 5.3).

\( E^0 \) represents the formal potential of the process. Considering that the mentioned equation goes reversibly then the following expressions for the peak current \( i_{pc} \), peak potential \( E_{pc} \) and half-peak potential \( E_{pc/2} \) (Figure 5.11) are obtained:

\[ E = E^0 + \frac{RT}{nF} \ln \left( \frac{c_{Fe(CN)₆}^{3⁻}}{c_{Fe(CN)₆}^{4⁻}} \right) \]  \quad (Eqn. 5.3)

\[ i_{pc} \text{ (mA)} = (2.69 \cdot 10^5)AD^{1/2}Cv^{1/2} \]  \quad (Eqn. 5.4)

\[ E_{pc} = E_1 - 1,109 \frac{RT}{F} \]  \quad (Eqn. 5.5)

\[ E_{pc/2} = E_1 + 1,109 \frac{RT}{F} \]  \quad (Eqn. 5.6)
An alternative to the use of mercury electrode on the determination of metal ions in voltammetric techniques: Screen-Printed Electrodes

These figures (5.11 and 5.12) clearly show the oxidation of ferrocyanide to ferricyanide and the reduction of ferricyanide to ferrocyanide.

Fig. 5.11. Cyclic voltammetry of ferrocyanide and ferricyanide [11]

Fig. 5.12. Potassium ferrocyanide (left) and potassium ferricyanide (right).
5.7.1. Experimental conditions

A stock solution of ferricyanide/ferrocyanide 2 mM in a phosphate 100 mM (sodium phosphate dibasic dehydrate) buffer solution at pH 7.4 was prepared.

To prepare the buffer the solution an amount of HCl was added and the pH was controlled by the pH meter under magnetic stirring.

Once the solution was obtained, 20mL were pipetted in the cell and preceded to the determination.

The following parameters were entered into the software for analyzing the sample in the optimal working conditions (view Figure 5.13 and 5.14).

![Working method specifications](image)

Fig. 5.13. Computrace control menu
An alternative to the use of mercury electrode on the determination of metal ions in voltammetric techniques: Screen-Printed Electrodes

Finally, the determination was performed obtaining the following voltammograms.

As can be seen in the image above (Figure 5.15), the electrode responds correctly when the peaks are proportional and are obtained in a specific potential. Also, there is an overlap between the first determination and its replica so that it can ensure a minimum of precision and stability. This is because the SPE was used in determinations for the first time.

The Figure 5.16 shows the same situation. The difference is that in this case, the SPE was used more times and probably it was not as precise. Even so, the determination and its replica are still having the same values.

Instead, in the third image (Figure 5.17) can be seen as the oxidation and reduction peaks are slightly offset and the graphic loses accuracy owning a defective electrode. In this case the electrode cannot be used for subsequent determination of Nickel.
Fig. 5.15. Cyclic voltammetry using SPE Nº40 for the first time in Computrace (2 mM solution)

Fig. 5.16. Cyclic voltammetry with SPE Nº3 in Computrace (2 mM solution)
Fig. 5.17. Example of a defective voltammogram, SPE Nº2. (2 mM solution), where the oxidation and reduction peaks are slightly offset.
6. Experimental procedure

6.1. Preparation of solutions

Prior to the implementation of the experimental procedure, a series of solutions has been prepared. They are all mentioned below:

- Dimethylglyoxime (DMG) 0,1 M in 95% methanol.
- Antimony (III) solution 50 mM containing HCl 0,01 M
- Amonia buffer solution 0,1 M (pH 9,2)
- Nickel samples with known concentration

Ultrapure water (Milli-Q, Millipore) was used in all experiments.

In the “batch” working process, six standard solutions (0,25; 0,5; 1; 2; 3; 4 and 5 ppm) were prepared.

For the process of standard addition, two real samples were properly diluted and used. These samples were provided by a metal electroplating company.

- Bany Niquel.
- Níquel Wood.

The annex includes all calculations related to each of the above solutions.

6.2. Mounting SPE

The procedure for assembly the SPE as working electrode consists in the following steps.

First, an electrode workable was selected, i.e., having a carbon surface well polished and without scratches (as commented in section ¡Error! No se encuentra el origen de la referencia..).

Once selected the electrode, it was properly connected in the cable connector (Figure 6.2) also provided by DropSens. This cable links the electrode and the VA Computrace.

Fig. 6.1. SPE protected by parafilm
An alternative to the use of mercury electrode on the determination of metal ions in voltammetric techniques: Screen-Printed Electrodes

Each electrode connected to the cable will be covered with parafilm (Figure 6.1), as a precaution, to avoid any contact with the solution in the cell.

Then 20 mL of antimony solution were pipetted in the cell for the antimony deposition on the SPE. This step was made to obtain a better analyte signal during the analysis.

![Cable connection for SPE](image)

**Fig. 6.2.** Cable connection for SPE.

The following parameters were entered during this deposition and were performed by ex-situ process.

![Working parameters of the antimony ex-situ deposition](image)

**Fig. 6.3.** Working parameters of the antimony ex-situ deposition.
A purge with nitrogen was held for 10 minutes for the deaeration of the system in order to avoid any other signal during deposition time.

After deaeration of the solution, an \( E_d \) of -0.5 V was applied during 300 s under stirring, followed by a rest period (without stirring) of 20 s (Figure 6.3). Once the antimony film was deposited, all electrodes were rinsed carefully with water and the Sb(III) solution was replaced in the cell by the one to be measured. [13]

6.3. Analysis of the sample

To analyze the sample, first 20 mL of an ammonium buffer solution \( \text{pH} = 9.2 \) were pipetted in the cell.

After that, 10 µL of DMG were pipetted in order to obtain a concentration in the cell that must be of \( 5 \cdot 10^{-5} \) M.

Depending on the working method (Figure 6.4) a certain volume of nickel sample can be manually or automatically added to perform the analysis. In the case where the nickel will be manually added, one can select the manual addition mode in the working method specifications.

Otherwise, if the nickel will be automatically added, one can select the automatic addition. Then the software will be configured so that Dosinos will automatically add the sample for analyze the desired concentration.

![Fig. 6.4. Working parameters of nickel determination (I).](image-url)
Once initialized the working method, the sample was deaerated with pure nitrogen for 15 minutes, to avoid the effect of oxygen in the voltammetric measurements. In case of calibration by standard addition, some aliquots of Ni(II) standard solution were further added and the respective voltammograms were recorded. All solutions were deaerated and mechanically stirred for 30 s after standard addition. (Figure 6.5)

It is important to remind that before each measurement on an ex-situ Sb SPE a cleaning step was performed by keeping the working electrode at -1.25 V for 30 s. [13]
6.4. Signal treatment (OriginPro 9.0)

To create the baseline two different methods that are described below can be chosen.

First, once the data is obtained by VA Computrace software, the intervals can be manually entered in the function to automatically calculate a baseline and then reporting an area or a peak height (depending on the choice), as shown in section B.1 of the annex.

The problem is in this procedure, although it is very intuitive because all calculations are carried out by default, when the software has a replica of a peak (i.e., at same concentration during the determination) and both of them are different from each other the intervals cannot be configured individually.

Likewise, it is also possible that the signal obtained is slightly pronounced due to a low concentration in the cell. When this happens, the software will not recognize any peak and therefore, the baseline will not be displayed and its interval cannot be edited. Thus, the software will not report any height nor area.

For this reason, the baseline is calculated manually using complementary software called OriginPro 9.0. By the following steps the program would be able to report, not only the area or peak height, but also each the the baseline points.

![Peak Analyzer of OriginPro 9.0](image)

Fig. 6.6. Peak analyzer of OriginPro 9.0.
An alternative to the use of mercury electrode on the determination of metal ions in voltammetric techniques: Screen-Printed Electrodes

Steps to create the baseline:

- Click the menu Analysis > Peaks and Baselines > Peak analyzer > Open dialog in the Menu bar.
- Then the window of the Figure 6.6 will be open up and choose the “Integrate Peaks” option to define a baseline, find and integrate peaks.
- In the baseline mode select the user defined option and then the program connects each points of the baseline shown by a default interpolation or gives us the option to add and modify them. Also selecting the interpolation method, in this case “Spline” or “Bspline” were selected to do the calculations. (Figure 6.7)
- Finally the program gives us the option to auto Subtract Baseline which means that the function is rescaled setting the baseline as abscissa axis. Thus, the interval of the desired area can be easily changed as shown in Figure 6.8.

![Fig. 6.7. Creating the baseline with OriginPro 9.0](image)

![Fig. 6.8. Editing the function area](image)
7. Results

The main objective of this project is to determine and evaluate whether voltammetry technique by using SPE is viable or not to calculate unknown concentrations of metals in a sample.

The following studies have focused on the determination of nickel (II).

Once oriented the results, the next step is to obtain these and try to explain the research findings. Then the data obtained from each of the different methodologies are discussed and finally, a real sample will be tested to compare whether the values obtained are reliable.

About 60 SPE were used throughout this project to obtain all these determinations. In the Figure 7.1 most of them can be seen.
7.1. External addition

7.1.1. One stock solution

First, an external calibration method was used by manually adding standard solution to the cell in each determination. So, higher signal obtained in the electrode would be proportional to the concentration of nickel in the cell.

As can be seen in the Figure 7.2, the peaks obtained are not referenced on the abscissa (logical value obtained in the hypothetical case that the cell does not contain analyte concentration) nor on a constant signal value. Instead of this an increasing polynominal baseline is obtained. This is the first problem when trying to obtain a correlation between each determination due this curve can vary in every concentration and even in each replicate.

It is also reflected a small signal increase for each determination start done with the same SPE, probably because of its character of “single use”. This problem will be further discussed in the section 7.2.

For example, in the Figure 7.2, the concentrations of 160 ppb and 180 ppb seem that the highest concentration presents a more significant peak signal. However, the baseline is also displaced and this affects the value that one chooses to perform the calibration line and both concentrations represent values roughly equivalent.

The significant values that have been carried out to perform the calibration line have been the peak area and peak height. Values that will always be referenced on the baseline provided by the software of Metrohm or with external programs that makes a better approximation automatically as Origin 9.0.

These values, once edited the baseline intervals, are also recalculated where the peak height is the distance between the maximum nickel peak obtained and the baseline in the same potential. Analogously, the area is the region between the start and end of the peak to the baseline.

Thus the following graphics are obtained:
It can be seen as both have significantly linear behaviour between 20 and 100 ppb (Figures 7.3) and then the function stops growing as it passes from the linearity limit interval. In this case the best linearity range has not been obtained.

The real sample determinations with standard addition (that will be seen in section 7.3) will be made in a similar range to avoid errors.

**Fig. 7.2.** Nickel determination by external addition I. (SPE Nº28)
An alternative to the use of mercury electrode on the determination of metal ions in voltammetric techniques: Screen-Printed Electrodes

7.1.2. **Multiple stock solutions**

In this section the methodology used was similar to the previous one with the difference that multiple stock solutions were used and a constant volume was added in each determination as mentioned in the experimental procedure (Section 6.1).

Emphasize again that during this process a special care was considered and very careful procedure with the washing of the cell between each determination in order to avoid contaminations of the sample.

---

**Fig. 7.3.** Nickel determination by external addition II. (SPE Nº28)

---

**Fig. 7.4.** Nickel determination with multiple stock solutions I. (SPE Nº29)
In Figures 7.5 one can see the good linearity between concentrations of 20-200 ppb and this range coincides with the literature [13].

Both the peak area and peak height referenced from the baseline give very linear values except when the 200 ppb are passed, where the electrode loses accuracy and does not report any logical value.

![Graphs showing linear relationship between concentration and area/height](image)

**Fig. 7.5.** Nickel determination with multiple stock solutions II. (SPE Nº 29)

### 7.2. Lifetime

Another process carried out during the project was to determine the behaviour of the SPE in different determinations during all the operational lifetime.

Thus a single SPE was used for 1 week (5 days) to observe the reproducibility of the measurements and see how obtained current values changed during the week obtaining the following graphics. (Figure 7.6)

During the first day the peaks obtained were uniform and well defined so, a correlation in function of the cell concentration can be clearly seen. From the second day a lower accuracy can be observed as a lost of definition in the peak, which generally involves lower peak area and peak height.
This effect was multiplied throughout the days and the reproducibility of the experiment was completely lost. Note that during the fifth day, it gives the feeling that all the peaks and areas are identical and no distinction was observed even though the cell had more or less concentration.
7.3. Standard addition

7.3.1. Nickel Wood sample

In both samples Nickel Wood and Bany Nickel, the Dosinos were configured to add a certain volume to the cell. As shown in the Figure 7.7, the determination did not work well because the second replica of 40 ppb moved considerably at the end of the peak. Therefore the value of the desired concentration was not accurately obtained.

![Standard Addition Niquel wood (SPE Nº45)](image)

Fig. 7.7. Determination of Nickel Wood by standard addition. (SPE Nº45)

So, as discussed in the section 7.1.1, both the sample concentration and the Dosinos added volume were decreased trying not to exceed the limit of linearity. The dilution factor in the flask was also varied from 1:1000 mL to 1:100 mL to reduce possible errors.

Results were much more accurate and the standard deviation was considerably reduced for each determination, obtaining this way the corresponding data shown in Figure 7.8.
An alternative to the use of mercury electrode on the determination of metal ions in voltammetric techniques: Screen-Printed Electrodes

Fig. 7.8. Determination of Nickel Wood by standard addition. (A) Area, (B) Height - (SPE Nº54)

Keeping in mind that each replicate and each addition has its own baseline, in the graphic can be seen how the peak area (Figure 7.8-A) and peak height (figure 7.8-B) were represented.

Fig. 7.9. Standard addition of Nickel Wood (SPE Nº54). Points of OriginLab baseline.
<table>
<thead>
<tr>
<th>Area</th>
<th>Peak Height</th>
</tr>
</thead>
<tbody>
<tr>
<td>OriginLab 9.0:</td>
<td>$C_{Ni\text{Wood}} = 21,75 \text{ ppb}$</td>
</tr>
<tr>
<td>Computrace:</td>
<td>$C_{Ni\text{Wood}} = 20,2 \pm 0,6 \text{ ppb}$</td>
</tr>
</tbody>
</table>

Table 7.1. Comparison between OriginLab 9.0 and Computrace of Nickel Wood determinations.

These are the calculated values by determining Nickel Wood samples.

### 7.3.2. Bany Nickel sample

In the Bany Nickel sample determination the results are very similar to those obtained previously, thus a linear correlation between concentration and the obtained signal can be seen.

![Standard Addition Niquel bany (SPE Nº57)](image)

Fig. 7.10. Determination of Bany Nickel by standard addition. (SPE Nº57)
In order to observe this relationship, the graph of the Figure 7.11 is taken as an example of the rescaled signal thanks to the baseline points obtained with OriginPro.

![Standard Addition Niquel bany (SPE Nº57)](image)

**Fig. 7.11.** Rescaled obtained function.

Again, a linear regression is obtained using the standard addition method (Figures 7.12). Then, the sample concentration can be calculated and compared.

![Standard Addition Niquel bany (SPE Nº57) - Area](image) ![Standard Addition Niquel bany (SPE Nº57) - Height](image)

**Fig. 7.12.** Standard addition of Bany Nickel (SPE Nº57). (OriginLab baseline)

Comparing these values with those obtained by Metrohm software (Figures 7.13, 7.14), one can observe a slight decrease in the sample concentration results, perhaps because the baseline of OriginLab is less accurate as it is estimated manually. Anyway, this software has been used in order to avoid the problem discussed in section 6.4.

The calculated values of Bany Nickel are shown below in Table 7.2.
Fig. 7.12. Standard addition of Bany Nickel (SPE Nº57) – Area (VA Computrace baseline)

Fig. 7.12. Standard addition of Bany Nickel (SPE Nº57) – Peak height. (VA Computrace baseline)

<table>
<thead>
<tr>
<th></th>
<th>Area</th>
<th>Peak height</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>OriginLab 9.0:</strong></td>
<td>$C_{\text{Bany Ni}} = 26.6 \text{ ppb}$</td>
<td>$C_{\text{Bany Ni}} = 24.05 \text{ ppb}$</td>
</tr>
<tr>
<td><strong>Computrace:</strong></td>
<td>$C_{\text{Bany Ni}} = 21.9 \pm 0.7 \text{ ppb}$</td>
<td>$C_{\text{Bany Ni}} = 20 \pm 1 \text{ ppb}$</td>
</tr>
</tbody>
</table>

Table. 7.2. Comparison between OriginLab 9.0 and Computrace of Bany Nickel determinations.
An alternative to the use of mercury electrode on the determination of metal ions in voltammetric techniques: Screen-Printed Electrodes

7.4. ICP Determinations

Once done the nickel determinations, the diluted samples of Nickel Wood and Bany Nickel were analyzed by ICP-MS in the Barcelona Science Park to make sure that the obtained values were correct.

As mentioned in the Annex, two dilutions (C₁ and C₂) were prepared for each nickel sample. These were the analyzed samples so the ICP values of the table 7.3 and 7.4 show the real concentration in these dilutions. Notice the differences between the theoretically calculated values (row 1) and those given by ICP (row 4).

The first step was to recalculate the dilution in cell. Then one can compare the results more accurately.

- Nickel Wood sample

<table>
<thead>
<tr>
<th></th>
<th>C&lt;sub&gt;real&lt;/sub&gt; [ppm]</th>
<th>C₁ [ppm]</th>
<th>C₂ [ppm]</th>
<th>C&lt;sub&gt;cell&lt;/sub&gt; [ppb]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel Wood (Sample)</td>
<td>54.604,04</td>
<td>546,04</td>
<td>5,46</td>
<td>13,6</td>
</tr>
<tr>
<td>OriginPro 9.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Area</td>
<td>87.261</td>
<td>872,61</td>
<td>8,72</td>
<td>21,75</td>
</tr>
<tr>
<td>Peak Height</td>
<td>90.150</td>
<td>901,5</td>
<td>9,01</td>
<td>22,47</td>
</tr>
<tr>
<td>Computrace</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Area</td>
<td>80.918</td>
<td>809,18</td>
<td>8,09</td>
<td>20,169</td>
</tr>
<tr>
<td>Peak Height</td>
<td>81.809</td>
<td>818,1</td>
<td>8,18</td>
<td>20,391</td>
</tr>
<tr>
<td>ICP</td>
<td>-</td>
<td>708,66</td>
<td>6,89</td>
<td>17,17 (*)</td>
</tr>
</tbody>
</table>

Table. 7.3. Nickel Wood results.

V<sub>cell</sub> = 20,06 mL.

A volume of 50 µL of the second dilution (C₂) was added to the cell to perform the determination.
**Bany Nickel sample**

<table>
<thead>
<tr>
<th></th>
<th>$C_{\text{real}}$ [ppm]</th>
<th>$C_1$ [ppm]</th>
<th>$C_2$ [ppm]</th>
<th>$C_{\text{cell}}$ [ppb]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bany Nickel (Sample)</td>
<td>6.180,32</td>
<td>61,8</td>
<td>0,61</td>
<td>10</td>
</tr>
<tr>
<td>OriginPro 9.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Area</td>
<td>15,920</td>
<td>159,2</td>
<td>1,59</td>
<td>26,6</td>
</tr>
<tr>
<td>Peak Height</td>
<td>14,394</td>
<td>143,95</td>
<td>1,43</td>
<td>24,05</td>
</tr>
<tr>
<td>Computrace</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Area</td>
<td>13,147</td>
<td>131,47</td>
<td>1,31</td>
<td>21,966</td>
</tr>
<tr>
<td>Peak Height</td>
<td>12,442</td>
<td>124,4</td>
<td>1,24</td>
<td>20,788</td>
</tr>
<tr>
<td>ICP</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>66,07</td>
<td>0,84</td>
<td>14,03 (**)</td>
</tr>
</tbody>
</table>

Table. 7.4. Bany Nickel results.

$V_{\text{cell}} = 20,350$ mL.

A volume of 340 µL of the second dilution ($C_2$) was added to the cell to perform the determination.

Thanks to the values obtained by ICP, the concentrations determined in the cell were much closer than the theoretically calculated. As can be seen, Nickel Wood determination by Computrace was the most accurate.

The rest of determinations made under the same condition gave similar values. They are all in annex.

In conclusion, it can be confirmed that the method using SPE is very accurate and that the values differ only in a few ppb's units.

(**) These values were manually calculated.
8. Economic study

In this section, all the resources used throughout the project were calculated. Thus, the equipment and laboratory equipment, the reagents, the personnel and other were included.

- **Equipment**

The cost of the used equipment was calculated based on the amortization costs and not the total cost of the instrument according to Eqn.8.1.

\[
Amortization = \frac{\text{Equipment cost}}{\text{Service life}} \cdot \text{Total time used}
\]

(Eqn. 8.1)

Note that in the realization of this project, other equipments such as the computer for data acquisition, two stirrers and an analytical balance have been used, but they are already amortized. Therefore they are not included in this economic study.

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Cost [€]</th>
<th>Lifetime [years]</th>
<th>Total time used [years]</th>
<th>Amortization [€]</th>
</tr>
</thead>
<tbody>
<tr>
<td>797 VA Computrace</td>
<td>19.600</td>
<td>5</td>
<td>0.3</td>
<td>1176</td>
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</tbody>
</table>

Subtotal

1176

- **Lab’s material**

<table>
<thead>
<tr>
<th>Lab’s Material</th>
<th>Uds</th>
<th>Unit cost [€]</th>
<th>Total cost [€]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPE (C110)</td>
<td>60</td>
<td>1,95</td>
<td>117</td>
</tr>
<tr>
<td>Cable connector for SPE</td>
<td>1</td>
<td>75</td>
<td>75</td>
</tr>
<tr>
<td>Waste bin</td>
<td>7</td>
<td>3</td>
<td>21</td>
</tr>
<tr>
<td>Magnet bar</td>
<td>2</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Volumetric flask 1000 mL</td>
<td>2</td>
<td>13,5</td>
<td>27</td>
</tr>
<tr>
<td>-------------------------</td>
<td>---------</td>
<td>------</td>
<td>-----</td>
</tr>
<tr>
<td>Volumetric flask 500 mL</td>
<td>2</td>
<td>7,5</td>
<td>15</td>
</tr>
<tr>
<td>Volumetric flask 250 mL</td>
<td>1</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>Volumetric flask 100 mL</td>
<td>4</td>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td>Volumetric flask 50 mL</td>
<td>10</td>
<td>4,2</td>
<td>42</td>
</tr>
<tr>
<td>Spatula</td>
<td>1</td>
<td>2,2</td>
<td>2,2</td>
</tr>
<tr>
<td>Parafilm</td>
<td>1</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Beakers</td>
<td>10</td>
<td>2,5</td>
<td>25</td>
</tr>
</tbody>
</table>

**Subtotal** 365,2

- **Reagents**

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Uds</th>
<th>Unit cost</th>
<th>Total cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>HNO$_3$ 69% (1 dm$^3$)</td>
<td>1</td>
<td>48,90</td>
<td>48,90</td>
</tr>
<tr>
<td>KCl 3 M</td>
<td>1</td>
<td>15,90</td>
<td>15,90</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>1</td>
<td>57,96</td>
<td>57,96</td>
</tr>
<tr>
<td>Potassium hexacyanoferrate (III) (500 g)</td>
<td>1</td>
<td>77,40</td>
<td>77,40</td>
</tr>
<tr>
<td>Potassium hexacyanoferrate (II) trihydrate (500 g)</td>
<td>1</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>di-sodium hydrogenphosphate 2-hydrate (1 kg)</td>
<td>1</td>
<td>47,30</td>
<td>47,30</td>
</tr>
<tr>
<td>Sb 1000 mg/L in nitric acid (250 mL)</td>
<td>2</td>
<td>23,20</td>
<td>46,40</td>
</tr>
<tr>
<td>Dimethylglyoxime</td>
<td>1</td>
<td>97,6</td>
<td>97,6</td>
</tr>
</tbody>
</table>
An alternative to the use of mercury electrode on the determination of metal ions in voltammetric techniques: Screen-Printed Electrodes

Methanol (1000 mL) 1 25,26 25,26

Milli Q water 20(1) 1 20

Subtotal 476,72

- Personal

<table>
<thead>
<tr>
<th>Personal</th>
<th>Nº of Hours</th>
<th>Salary [€/h][2]</th>
<th>Total cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Waste management</td>
<td>4</td>
<td>20</td>
<td>80</td>
</tr>
<tr>
<td>Experimentation</td>
<td>400</td>
<td>15</td>
<td>6.000</td>
</tr>
<tr>
<td>Data analyzer</td>
<td>150</td>
<td>30</td>
<td>4.500</td>
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</table>

Subtotal 10.580

- Others

<table>
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<tr>
<th>Concept</th>
<th>Uds</th>
<th>Unit cost [€]</th>
<th>Total cost [€]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water and electricity</td>
<td>500</td>
<td></td>
<td>500</td>
</tr>
<tr>
<td>Gloves (100 ud/box)</td>
<td>2</td>
<td>9,50</td>
<td>19</td>
</tr>
<tr>
<td>Micropipette tips (2-20 μL)</td>
<td>50</td>
<td>0,05</td>
<td>2,5</td>
</tr>
<tr>
<td>Micropipette tips (2-200 μL)</td>
<td>10</td>
<td>0,01</td>
<td>0,1</td>
</tr>
</tbody>
</table>

Subtotal 521,6
- **Total cost of the project**

<table>
<thead>
<tr>
<th>Concept</th>
<th>Cost [€]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equipment</td>
<td>1176</td>
</tr>
<tr>
<td>Lab’s material</td>
<td>365.2</td>
</tr>
<tr>
<td>Reagents</td>
<td>476.72</td>
</tr>
<tr>
<td>Personal</td>
<td>10.580</td>
</tr>
<tr>
<td>Others</td>
<td>521.6</td>
</tr>
<tr>
<td><strong>Gross total cost</strong></td>
<td><strong>13.119.52</strong></td>
</tr>
<tr>
<td>I.V.A (21%)</td>
<td>2.755</td>
</tr>
<tr>
<td><strong>Total net cost</strong></td>
<td><strong>15.874.62</strong></td>
</tr>
</tbody>
</table>

(1) Volumetric units [dm³].  
(2) Dataset based on Xialei’s project [2].
9. Waste Management

During the realization of this project, different chemical wastes were generated. Aqueous solutions of nickel, antimony, methanol, ammonia, acids and bases, as well as mercury and solid wastes must be differently handled, as it is explained in more detail below.

Acetone and ethanol were also used in cleaning tasks.

9.1. Metals in solution and solid waste

Liquid effluents with metals in solution containing nickel, copper, cadmium, zinc and lead at low concentrations, but still above the provisions of the regional legislation [14]. These solutions were stored in waste bins for further processing.

The generated solid wastes were broken and contaminated pasteur pipettes or used gloves. These were stored in a special container for further treatment.

9.2. Mercury management

The mercury handled during the task of cleaning the old working electrode of the VA Computrace should be treated also with special care. The remaining amount was deposited in a special container due mercury requires specific treatment and is strongly regulated.

It is important to ensure that no traces of mercury within the electrode or in the tray that has to be used for security. If it happens, it will be collected with the corresponding tool.

9.3. Acids and bases

Acids and bases wastes are mainly nitric acid and ammonia buffer used for the preparation of electrolyte and they were discharged into an acid-base waste bin for further treatment.

In the case of determined samples with nitric acid or ammonia, they also may contain heavy metals. Since these metals are more harmful to the environment than acids or bases, these are thrown into the metal waste container.
10. Environmental Impact

10.1. Impact generated in the experimentation

All chemical are toxic potential pollutants, with a damaging impact on both the environment and in the workplace. Therefore, it is necessary to know their properties, effects that cause and how to reduce their harmful impact. The annex contains the law "20/86 14 May 1986" [15]. It is the basic law of toxic and hazardous waste.

For this reason, a separation of toxic waste according to whether it can be recycled or stored for further processing or collection is performed. All chemical waste must have been recovered, processed or removed.

An environmental impact improvement was carried out in this project replacing mercury electrode from the working method. The SPE are easier to manage due they are solid wastes.

The following sections describe the main environmental disadvantages of mercury and nickel in general.

10.1.1. Mercury

The mercury impact is very important because it is highly toxic, it must be managed correctly to avoid any accident. As previously discussed (section 9.2), there is an exclusive waste bins for it.

Various forms of human activity release mercury directly into soil or water, as the application of fertilizers in agriculture and industrial wastewater discharges. All mercury that is released to the environment will eventually end up in soils or surface waters.

Compared to other mercury compounds the elimination of methyl mercury from fish is very slow, for example. In certain species of fish, mercury concentration tends to increase with age due to the methyl mercury can accumulate in fish and in the food chains.

The effects that mercury has on animals are kidneys damage, stomach disruption, damage to intestines, reproductive failure and DNA alteration.
Mercury has also a number of harmful effects on humans that can all of them be simplified into the following main effects:

- Disruption of the nervous system.
- Damage to brain functions.
- DNA damage and chromosomal damage.
- Allergic reactions, resulting in skin rashes, tiredness and headaches.
- Negative reproductive effects, such as sperm damage, birth defects.

Damaged brain functions can cause degradation of learning abilities, personality changes, tremors, vision changes, deafness, muscle incoordination and memory loss. Chromosomal damage is known to cause mongolism [10].

10.1.2. Nickel

Nickel is a compound that occurs in the environment only at very low levels. Humans use nickel for many different applications. The most common application of nickel is the use as an ingredient of steal and other metal products. It can be found in common metal products.

Foodstuffs naturally contain small amounts of nickel. Chocolate and fats are known to contain high quantities. Nickel uptake will boost when people eat large quantities of vegetables from polluted soils. Plants are known to accumulate nickel and as a result the nickel uptake from vegetables will be imminent. Smokers have a higher nickel uptake through their lungs. Finally, nickel can be found in detergents.

Humans may be exposed to nickel by breathing air, drinking water, eating food or smoking cigarettes. Skin contact with nickel-contaminated soil or water may also result in nickel exposure. In small quantities nickel is essential, but when the uptake is too high it can be a danger to human health.

An uptake of too large quantities of nickel has the following consequences:

- Sickness and dizziness after exposure to nickel gas.
- Lung embolism.
- Respiratory failure.
- Birth defects.
- Asthma and chronic bronchitis.
- Allergic reactions such as skin rashes.
- Heart disorders.
Nickel fumes are respiratory irritants and may cause pneumonitis. Exposure to nickel and its compounds may result in the development of a dermatitis known as “nickel itch” in sensitized individuals. The first symptom is usually itching, which occurs up to 7 days before skin eruption occurs. The primary skin eruption is erythematous, or follicular, which may be followed by skin ulceration. Nickel sensitivity, once acquired, appears to persist indefinitely.

Nickel is released into the air by power plants and trash incinerators. It will then settle to the ground or fall down after reactions with raindrops. It usually takes a long time for nickel to be removed from air. Nickel can also end up in surface water when it is a part of wastewater streams.

The larger part of all nickel compounds that are released to the environment will adsorb to sediment or soil particles and become immobile as a result. In acidic ground however, nickel is bound to become more mobile and it will often rinse out to the groundwater.

For animals nickel is an essential foodstuff in small amounts. But nickel is not only favourable as an essential element; it can also be dangerous when the maximum tolerable amounts are exceeded. This can cause various kinds of cancer on different sites within the bodies of animals, mainly of those that live near refineries.
Conclusions

- SPE works along with the different hardwares and softwares from Metrohm.

- Experiments have demonstrated that the voltammetric technique is very sensitive and can measure analyte concentrations in ppb's range. Thanks to the antimony coating, the signals obtained are better defined and are more amplified.

- The standard sample has been optimized and also the potential range has been chosen to determine concentrations in the ppb levels.

- It has been found that it is not possible to use SPE over more than a determination because peaks and areas lose proportionality due to the wear.

- The linearity found in the most general working conditions ranged from 20 to 100 ppb. However, if the SPE works within optimum conditions during analysis, a linearity up to 200 ppb can be obtained in some cases.

- A maintenance procedure and handling of the instrument SPEs and 797 VA Computrace has been defined to work under optimal conditions allowing accurate and reproducible measurements.

- Origin Pro 9.0 facilitates the identification of areas and peak heights through the baseline.

- The results were compared with analysis by the ICP - Parc Cientific de Barcelona it can be confirmed that the method using SPE is very accurate and that the values differ only in a few units.

- The SPE are environmentally less polluting than mercury drop electrode.
Acknowledgements

I would like to especially thank Professor Antonio Florido, I really appreciate the effort to carry out this difficult project. Thanks to all his support, advices and patience during these months.

I would also thank the help of the members of the Department of Chemical Engineering. As well, this project would have been impossible without the support of the Members of Electroanalysis from UB, especially Núria Serrano and Cristina Ariño.

Thanks to my family. My parents, Antonio and Maite, and my brother Quim for helping me so hard during these years.

Thanks to Inma for her dedicated love everyday and her sister Elena for correcting my English in the last moment.

Thanks to my lab partners for the shared moments: Carlos for his patience. Adrian for supporting me on the mornings. Finally, Eli and Anabel for their support in the afternoons.
Bibliography

References


[10] Lennetech [online]. Available from:


[15] Ministerio de la Presidencia

Additional references


**An alternative to the use of mercury electrode on the determination of metal ions in voltammetric techniques: Screen-Printed Electrodes**


