New methods for the analytical control of a nickel electroplating bath. Application of chemometric techniques

Maider Vidal Postigo
phD thesis, 2010
New methods for the analytical control of a nickel electroplating bath. Application of chemometric techniques


Author: Maider Vidal Postigo

Supervisors: Carlos Ubide Sebastián

and: Miren Ostra Beldarrain
Index

1. Introduction 1

1.1. Metal electrodeposition 3
  1.1.1. Nickel electrodeposition 4
  1.1.2. The Hull Cell 11
  1.1.3. Analytical Techniques in Additive determination 13
  1.1.4. Physical parameters of the plated materials 16

1.2. Chemometrics as an analytical tool 17
  1.2.1. Classical least squares (CLS) 19
  1.2.2. Principal Component Regression (PCR) 19
  1.2.3. Partial least squares Regression (PLS-R) 24
  1.2.4. Number of factors or latent variables (LVs) 25
  1.2.5. Model evaluation 26
  1.2.6. Limit of detection (LOD) 26

1.3. New proposals in electroplating 27

1.4. References 28

2. Objectives 33

3. Nickel electroplating process. Control of Ni^{2+}, Cl, pH and T. 37

3.1. Introduction 39

3.2. Experimental 40
  3.2.1. Reagents 40
  3.2.2. Apparatus 40
  3.2.3. Software 41
  3.2.4. Procedures 41
    3.2.4.1. Nickel electrodeposition 41
    3.2.4.2. Nickel control 42
    3.2.4.3. Chloride control 43
    3.2.4.4. Temperature control 44
    3.2.4.5. pH control 44

3.3. Results and discussion 45
  3.3.1. Nickel concentration control 45
    3.3.1.1. Preliminary spectral study 46
5.2.4.2. Calibration 102
5.2.4.3. Additive determination in an electrolytic bath 103

5.3. Results and discussion 103
  5.3.1. NMR spectra 103
  5.3.2. Quantitation of additives 104
    5.3.2.1. Univariate linear regression 105
    5.3.2.2. Multivariate calibration methods 109
  5.3.3. Evaluation of the models 112
  5.3.4. Additive determination in a commercial electroplating nickel bath 112
    5.3.4.1. Degradation products 115

5.4. Conclusions 119

5.5. References 120

6. Physical parameters for nickel plated sheets 121
  6.1. Introduction 123
  6.2. Experimental 125
    6.2.1. Reagents 125
    6.2.2. Apparatus and material 125
    6.2.3. Software and data processing 126
    6.2.4. Procedures 126
      6.2.4.2. Measure of brightness 126
      6.2.4.3. Masure of specular reflectance (SR) 127
      6.2.4.4. Image Analysis 128
      6.2.4.5. Additive control 128
  6.3. Results and discussion 128
    6.3.1. Brightness evolution. SPB quantitation 128
    6.3.2. Exploring of sheets images through PCA 135
      6.3.2.1. Scanner stability 136
      6.3.2.2. Acquisition of the RGB image. Sheets scanning 138
      6.3.2.3. PCA of the sheets images 143
      6.3.2.4. Specular reflectance (SR) and critical evaluation 145
    6.3.3. Additive control by image analysis 147
      6.3.3.1. Mean colour value (MCV) 147
      6.3.3.2. Sheets classification and brightness quality assessment 150
      6.3.3.3. Calibration models for additives 152
6.3.3.4. Real-control and bath quality maintenance 153
6.3.3.5. Reference techniques 158
  6.3.3.5.1. UV-Vis spectrophotometry 158
  6.3.3.5.2. Brightness 160
6.4. Conclusions 161
6.5. References 163
7. Abstract and Conclusions 165
8. Resumen y conclusiones 169
  Appendix 173
1. Introduction
1.1. Metal electrodeposition

Metal electrodeposition is one of the most interesting electrochemical processes from both a theoretical and technological point of view. The electroplated metals have widespread uses. Among the most common, they are employed in¹:

1. Avoiding the corrosion, especially for iron and steel.
2. Improving the external appearance of diverse materials used for numerous purposes.
3. Metallic structures and engineering, where specific technological conditions must be obeyed.
4. Jewellery, costume and decoration.
5. Galvanization and cast replicates for electroerosion.
7. Electronic components and printed circuit tracks.

The electrodeposition process, in general, consists of the dissolution of a metal from an electrode, named anode, into a solution containing ions of the same metal, the passage of a continuous electric current along the solution and the subsequent electric discharge of the metal on an electrode surface, named cathode, in contact with the solution. The current is produced when a potential is applied between electrodes. One of the electrodes, the anode, is then charged positively and the other, the cathode, negatively. The positive metal ions in the solution, hence, move towards the negative electrode (the cathode) and the negative ions towards the positive electrode (the anode), producing the electric current (Figure 1).
In the electrodes, oxidation-reduction processes are then produced. The oxidation is caused in the anode while the reduction is caused in the cathode, and these reactions lead to a change in the metal oxidation state.

1.1.1. Nickel electrodeposition

In the case of nickel, the oxidation process in the anode is:

\[ \text{Ni}^0 \rightarrow \text{Ni}^{2+} + 2e^- \]  

(1)

On the other hand, in the cathode, the reduction reaction is:

\[ \text{Ni}^{2+} + 2e^- \rightarrow \text{Ni}^0 \]  

(2)
But together with this simple process, some other more complicated phenomena also appear, mainly related to the double electric layer: polarization, overtension, diffusion, etc.

Quite a lot of papers have been published studying the possible reaction mechanisms of the nickel electrodeposition. At the present time, the generally accepted mechanism involves, first of all, the formation of an adsorbed nickel complex and then, a subsequent two consecutive one-electron charge transfers.  

\[ \text{Ni}^{2+} + \text{X}^- \rightarrow \text{NiX}^+ \]  
\[ \text{NiX}^+ + e^- \rightarrow \text{NiX}_{\text{ads}} \]  
\[ \text{NiX}_{\text{ads}} + e^- \rightarrow \text{Ni}^{0} + \text{X}^- \]

It has been deduced that in a Watt-type bath, consisting of NiSO$_4$ + NiCl$_2$ and H$_3$BO$_3$ (see ahead for more details), the anion $X^-$ should be Cl$^-$ and the rate-determining step is reaction (4).

Nickel baths are widely used with decorative, engineering and electroforming purposes. Along the last 100 years, the annual nickel consumption for electroplating has gone from about 200 to 100 000 metric tonnes. This represents a large growth that summarizes the importance of nickel electroplating industry nowadays.

As it has been said, electroplating baths are frequently used in industry. The process involves covering inexpensive materials with metals in order to extend their applications that, otherwise, would have been too much costly. It takes the advantage that the process can be run at room temperature and pressure, it uses economically modest equipment and the process can be easily controlled. In Figure 2 a general sketch of a nickel electroplating bath can be seen.
Figure 2. Nickel electroplating bath used in this work. (a) vessel for nickel electrodeposition; (b) anodes of nickel; (c) cathode (steel sheet).
The interest in understanding the deposition phenomenon of these functional materials from aqueous media has increased in recent years. The electrochemistry of the deposition process has been studied by several analytical techniques which include voltammetry,\textsuperscript{5,6,7,8} impedance measurements\textsuperscript{9,10} or galvanostatic and potenciostatic pulse methods.\textsuperscript{11} Furthermore, attempts to study the deposits have been made by a wide variety of techniques, as X-ray diffractometry\textsuperscript{12} or scanning electron and optical microscopy.\textsuperscript{7} However, in spite of the numerous studies carried out, the phenomena or the processes affecting electroplating are not deeply known yet due to its complexity; the result can be a lack of quality of the obtained products.\textsuperscript{13}

Most nickel coatings are obtained by electrodeposition techniques from aqueous solutions which contain great quantities of nickel salts and small concentrations of organic compounds that are the main responsible for the final quality of the coatings.\textsuperscript{14} Also, electroless nickel plating is frequently used in different industrial applications; it involves an auto-catalytic reaction used to deposit a coating of nickel on a substrate.\textsuperscript{15} Unlike electroplating, it is not necessary to pass an electric current through the solution to form a deposit, but it needs a reduction agent so that the electrode reaction can be carried out. It is frequently used to avoid corrosion and wear. Apart from the fact that it does not need the use of electrical power, it provides homogeneous deposits regardless of work piece geometry or conductive surfaces. On the contrary, lifespan of chemicals is limited and waste treatments are expensive. The most common form of electroless nickel plating is used to produce nickel-phosphorus alloys.\textsuperscript{16}

One of the most used formulations for nickel electroplating baths was established by Oliver P. Watts in 1916 and it is know as Watts solution. It is composed by a combination of nickel sulphate, nickel chloride and boric acid and it is the basis of the majority of semibright and bright nickel baths.\textsuperscript{4} In the last few years, however, the need of finding more enviromentally friendly alternatives to boric acid has led scientist to test other acids in order to control the pH of the bath and at the same time to keep deposits smooth and ductile. Malic acid\textsuperscript{17} and citric acid\textsuperscript{18} have been proposed as alternatives.

It is very important to keep bath components within well defined values in order to maximize the deposit efficiency. Thus, the deposit is highly sensitive to the
concentration of hydrogen ions in the electrolyte and, therefore, pH should be tightly controlled. The usual pH in a bright nickel bath should ranges between 3.5 and 4.5. Higher pH values will lead to holes in the deposit and the formation of insoluble basic compounds of iron when the electroplating is carried on steel surfaces. The boric acid used in Watts-type baths acts as a buffer in the range of interest. In practice, however, pH tends to increase along the electrodeposition. That is the reason why some bath component supporters recommend adding frequently diluted sulphuric acid in order to maintain pH within the advised range. On the other hand, the industry experience has proven that it is also important to keep metals into established concentration ranges. In a similar way, nickel, iron or chloride concentrations must also be controlled and therefore monitored, to ensure a consistent alloy composition. Numerous troubleshooting charts of decorative nickel baths have been published. They usually collect a number of remedies based, in general, on experience to keep the bath under control through the identification of the problem source, when it is considered that the product obtained is not acceptable enough. Prevention is usually the simplest cure in most plating problems, but it is practically unavoidable that the bath gets ineffectual during electrodeposition. Metallic impurities coming from the pieces to plate, organic contaminants derived from the additives degradation, oils from the pump-systems, pollutants coming from the products used in the polishing operations as well as deficiencies in pH, boric acid or agitation can cause pitting (a form of extremely localized corrosion that leads to the creation of small holes in the metal), dullness (lack of brightness), high roughness (a measure of the texture of a surface) or non-adhesion affects in the final obtained deposits. Consequently, cleanliness control of nickel baths could reduce rejects or shutdowns. In nickel baths it is especially necessary to accomplish this task. Unlike alkaline cadmium, zinc or copper electrolytes that own cyanide nature and, therefore, possess intrinsic cleanliness properties, the Watts-type nickel bath is useless as a soft-cleaner. The treatments for bath cleanliness include filtration, electronic purification, carbon treatment, peroxide or permanganate treatment. Sometimes, the nickel anodes are introduced into bags to avoid the passage of small particles to the solution. The bags have been fabricated in diverse materials being canvas and nylon the most used materials.

In addition to the nickel baths cleanliness, the pieces to plate in a nickel bath must also be washed before the electroplating. Thus, the metallic surfaces should be
carefully degreased and afterwards they may be polished if a decorative plating is going to be accomplished. This polishment will depend on the future thickness of the nickel layer. The car bumpers, for example, only required being partially polished because they were covered with a thick nickel layer. The introduction of the bright nickel baths into the industry, however, has allowed to obtain highly bright platings with no need of previous polishment operations.

Additives

There is a wide variety in the formulation of the organic compounds or additives for nickel baths, which are the responsible of the final quality of the plating. Their use in aqueous electroplating solutions is extremely important due to the effect they have in the growth and structure of deposits.

Among their benefits, brightening the deposit, reducing grain size, reducing the tendency to tree-like structures or dendrites, increasing the current density range, promoting levelling, changing mechanical and physical properties, reducing stress, which is the amount of reversible work per unit area needed to elastically stretch a pre-existing surface, and reducing pitting can be cited. Preferences for additives would depend on the purpose the deposits will have. In fully bright nickel deposits, for example, sulphur-content additives are frequently added. They can be divided into Class I and Class II brighteners and are responsible for brightness and levelling.

Class I brighteners have two functions: to provide bright plating and to allow the second class of brighteners to be present over a wide range of concentrations. They include aromatic sulfonates, sulfonamides, sulfoimides, etc. as well as aliphatic or aromatic-aliphatic olefinically unsaturated sulfonates, sulfonamides, sulfonimides, etc. They can be used singly or in suitable combinations and specific examples of this type of additives are:

1. disodium 1,5-naphthalene disulfonate
2. trisodium 1,3,6-naphthalene trisulfonate
3. sodium benzene monosulfonate
Introduction

4. o-benzoyl sulfimide (saccharin)
5. dibenzene sulfonimide
6. sodium 3-chloro-2-butene-1-sulfonate
7. sodium β-styrene sulfonate
8. sodium allyl sulfonate
9. monoallyl sulfamide
10. diallyl sulfamide
11. allyl sulphonamide

The Class II brighteners are used to obtain mirror-like platings. Nevertheless, they can promote brightness and stress in the deposits in the absence of a first class brightener. They include products of epoxides with alpha-hydroxy acetylenic alcohol such as diethoxylated 2-butyne-1,4-diol N-heterocyclics, dye-stuffs, acetylenic amines, etc. Similarly to Class I brighteners, Class II can be used alone or in combination as well. Specific examples of such plating additives are:

1. 1,4-di-(β-hydroxyethoxy)-2-butyne
2. 1,4-di-(β-hydroxy-γ-chloropropoxy)-2-butyne
3. 1,4-di-(β,γ-epoxypropoxy)-2-butyne
4. 1,3-di-(β-hydroxy-γ-butoxy)-2-butyne
5. 1,4-di-(2’-hydroxy-4’-oxa-6’-heptenoxo)-2-butyne
6. N-(2,3-dichloro-2-propenyl)pyridinium chloride
7. 2,4,6-trimethyl N-propargyl pyridinium bromide
8. N-allylquininaldinium bromide
9. 2-butyne-1,4-diol
10. propargyl alcohol
11. 2-methyl-3-butyn-2-ol
12. quinaldyld-N-propanesulfonic acid betaine
13. butynoxy ethane sulfonic acids
14. propynoxy ethane sulfonic acids
15. quinaldine dimethyl sulphate
16. N-allylpyridinium bromide
17. isoquinaldyl-N-propanesulfonic acid betaine
18. isoquininaldine dimethyl sulphate
19. N-allylisoquinaldine bromide
20. 1,4-di-(β-sulfoethoxy)-2-butyne
21. 3-(β-hydroxyethoxy)-propyne
22. 3-(β-hydroxypropoxy)-propyne
23. 3-(β-sulfoethoxy)-propyne
24. phenosafranin
25. fuchsin
26. propargyl amine
27. 1-diehtylamino-2-methyl-3-pentyn-2-ol
28. 1-dimethylamino-2-pentyne
29. 1-dimethylamino-2-butyne

Anti-pitting or wetting agents are also used in bright nickel baths so that gas pitting is prevented or minimized in the baths. Furthermore, they may function to make the baths more compatible with contaminants, such as oil, grease, etc. by their emulsifying, dispersing, solubilising, etc. action on such contaminants, and thereby they promote sounder deposits. They include sodium lauryl sulphate, sodium lauryl ether-sulfate and sodium dialkylsulfosuccinates.\(^{24}\)

In general, these organic additives should be added in small amounts and frequently to maintain nickel plating quality, but there is not an established method to accomplish it in practice.\(^{13}\) In most cases, the experience of the operator is the subjective key which decide what agents and in which concentration should be added. Sometimes they are added after bath control is made, based on distillation and colorimetric, spectrophotometric or ion-chromatographic monitoring,\(^{21}\) but the preference seems to be the automatic addition based on the time of use of bath (ampere-hour).\(^{20,26}\) However, the brighteners concentration has often been controlled visually considering the final aspect of plated pieces or by the use of a Hull cell.

1.1.2. The Hull Cell

The Hull cell is an extremely powerful test tool capable of controlling several plating variables at the same time and it has probably been the tool that has contributed
in more extent to the development of electroplating. This Cell is a trapezoidal box of non-conducting material that in its standard size holds 267 mL of solution, (Figure 3). The anode is laid against the right angle and the cathode is laid against the sloping side. Thus, when a current is passed through the solution, the current along the sloping cathode varies in a known way. The cell shows the limits of acceptable current density ranges, detects the presence of impurities, degree of levelling or ability of electroplating process to deposit smooth uniform coating on a rough surface and throwing power or uniformity of the thickness of a coating deposited on irregularly shaped part. It also controls the morphology of the deposit, the alloy composition as a function of current density, agitation effects or the cathode average efficiency, that is, the ratio of the actual amount of the deposited material to the theoretical amount that should be deposited. It also evaluates the covering power of competitive electroplating systems, that is, the ability of an electroplating bath to produce a coating at a low current density electroplating range, the heat stability, life, compatibility, etc. and even it allows to make an estimation of the concentration of the compounds involved in electrodeposition.

Although the Hull cell has been an adequate tool, the increasing demand for process automation makes necessary the quantitative analytical control of organic additives. Moreover, the Hull cell can be misleading when it is used to evaluate high speed processes. Thus, parameters related to solution flow, solution geometry and current distribution are not always reproduced in the cell.
1.1.3. Analytical Techniques in additive determination

The lack of a reliable methodology to control the concentration of additives during an electroplating process leads to a percentage of samples rejected that varies between 2 and 4% annually; this means about 20-25 millions of nickel-covered materials removed per year in the industry. It is obvious, therefore, the necessity of a trustworthy methodology capable of controlling the concentration of additives, which is essential to maintain the quality of the nickel-covered samples. This methodology should be capable of dealing with problems arising from both the still huge ignorance of electrochemical processes and the high correlations between the variables affecting the processes.

Some of the most usual analytical techniques applied in bath electrochemistry have included voltammetry,\textsuperscript{29,30} UV-Vis spectrophotometry,\textsuperscript{31,32} or High Pressure Liquid Chromatography (HPLC)\textsuperscript{33,34} in order to separate and determine analytes. All these techniques are well known and widespread for analytical applications. Sulphur and carbon content of deposits has been also measured in order to experimentally evaluate the degree of additive decomposition, as additives with a high content in sulphur, like saccharine, or unsaturated carbon like 2-butyne-1,4-diol are frequently used.\textsuperscript{35} Nevertheless, some limitations are postponing the appearance of a common and conventional additive determination technique. Between the limitations for additive determination, they can be cited the low concentration of these compounds in the formulation, the lack of deep knowledge about its degradation mechanisms, the high number of variables involved in the process and specially the cross-effect of variables. Efforts, therefore, should be turn to new analysis procedures as well as to alternatives that permit a minimal consumption of time and a high frequency of analysis as automated flow methods. Chemometrics, besides, can show as an appropriate tool in order to deal with the high number of variables generated.

Nuclear Magnetic Resonance (NMR)

Recently, new techniques as Nuclear Magnetic Resonance (NMR) are reaching more demand among analytical chemists in quantitative determinations since it is a
unique and versatile spectroscopy method capable of measuring samples in solid, liquid and gas phases.  

The first quantitative measurements (qNMR) were made by Jungnickel and Forbes\textsuperscript{37} and Holes\textsuperscript{38} in 1963. During a long time there was a lack of acceptance of this technique as a precise tool, though it provides excellent results in quantification, but in recent years it is receiving major attention for the scientist community, especially due to the technical progress of modern NMR apparatus, that overcome problems of low sensitivity.

It allows to elucidate the structure of chemical compounds with no need of physical separation and, therefore, it has demonstrated to be precise and accurate, what makes it competitive with previous chromatographic methods, as these techniques need of more steps that increase the chance for systematic and randoms errors.\textsuperscript{39,40}

The applications of qNMR take place in many areas, including natural products,\textsuperscript{41} food,\textsuperscript{42} pharmacy\textsuperscript{43} or agriculture,\textsuperscript{44} showing excellent results.

**Flow analysis methods**

In the last few years, flow methods have developed thanks to the computer and electronic expansion. They were born in the fifties and they have become excellent tools in the analysis of aqueous samples ever since. They avoid the continuous presence of the analyst and allow to make faster analysis with minor sample manipulation.

The first flow technique was the Segmented Flow Analysis (SFA), proposed by Skeegs in 1957.\textsuperscript{45} It consists of a segmentation of the sample with air bubbles, which are followed by a washing-out solution in order to minimize the carryover from one sample to another. It implies both monochannel and multichannel designs and the latter is based on splitting the aspirated sample volume into several channels to analyze several parameters independently.\textsuperscript{46} The major drawback of this method comes from the use of the air bubbles which generate non-reproducibility and problems in the flow rate and in the shape of the signal. For these reasons, SFA has been gradually replaced by
continuous non-segmented techniques such as the Flow Injection Analysis (FIA). This method constituted an important innovation in the field of analytical chemistry because of its simplicity, economical instrumentation, straightforward operation and speed in the analysis. In conventional FIA manifolds, the sample is introduced into the stream and subsequently merged downstream with reagents. It allowed more reproducible timing and easier controllable dispersion of the analyte. In comparison with SFA, FIA needs smaller sample volumes, it allows higher sampling frequencies and avoids washing. Later on, another technique appeared; the Sequential Injection Analysis (SIA), proposed by Ruzicka et al., as an alternative to FIA. SI-system is composed by a selection valve whose central port is connected to a bidirectional syringe that works out as unit of liquid dispensary. The lateral ports of the valve are connected to the containers of sample, carrier and reagents (Figure 4). Now, precise volumes of sample and reagents are aspirated sequentially and dispensed into the reaction coil when the flow is reversed. It allows multiparametric determinations and a considerable saving of carrier, sample and reagents in comparison with FIA.

There are some papers dealing with flow analysis methods for analysis of electroplating baths. Thus, FIA has been used to determine fluoride with potentiometric detection, the content of chloride in a nickel bath with a silver tubular electrode as
detector,\textsuperscript{51} or the Ni\textsuperscript{2+}, Fe\textsuperscript{2+}, H\textsubscript{3}BO\textsubscript{3}, and Cl\textsuperscript{-} content with spectrophotometric detection.\textsuperscript{52} No additive control, however, has been found in literature using flow analysis methods.

1.1.4. Physical parameters of the plated materials

The analytical techniques applied to baths have been the most appealing to the chemists in order to study the behaviour of an electrodeposition process, but physical parameters of the plated materials should also be considered. Thus, a way of measuring the feasibility of a nickel coating can be found through some key parameters of plating properties. X-ray diffraction (XRD) has been used in order to study the crystalline structure of the different Ni electrodes,\textsuperscript{53} because it was proved that this crystalline structure is directly related to the surface morphology, as it is measured by scanning electron microscopy (SEM).\textsuperscript{54} Both techniques depend closely on pH and electroplating time as long as high pH values (> 5.0) and short times of deposition (≤ 10 min), support the growth of deposits with [111] Ni orientation, which facilitates the adsorption of H atoms on the deposit as well as the Ni(III)/Ni(II) transition. A good quality nickel deposit should be flat, smooth and ductile, but other properties, such as surface roughness, have also been measured. A surface roughness profilometer can be used with different additive compositions and concentrations in order to evaluate their suitability for electroplating\textsuperscript{55} and the data obtained can be correlated to the specular reflectivity of the coatings\textsuperscript{56,57} and brightness.\textsuperscript{25} Ductility is a mechanical property used to describe the extent to which materials can be plastically deformed without fracture. It may also be a discriminant factor of the suitability of nickel products. Thus, very bright nickel plates can be totally rejected by customers when cracking, peeling or popping occur upon subsequent fabrication. To test ductility, a daily bend or deformation examination is determined. Nonetheless, as ductility and stress are interrelated, the former can also be checked through stress measurements. X-ray fluorescence, optical microscopy dullness, adhesion or peeling effects, pitting, hardness or tensile strength of deposits are other physical parameters measured in order to detect possible imperfections in the deposits and they find its origin in the electroplating processes.\textsuperscript{58,59,60}
Because some of these properties, like brightness or ductility, are somewhat subjective properties, the quality threshold varies greatly from installation to installation.\textsuperscript{61}

Nonetheless, tools in order to cope with some of the problems coming from the high number of variables involved in most analytical processes are needed. The significant advance of chemometrics techniques is showing as a reliable and invaluable tool because they allow to solve both descriptive and predictive troubles in chemistry regardless they may come from highly complex and correlated systems. Sometimes this involves from hundreds to thousands of variables and hundreds to millions of cases or observations. Therefore, the application of chemometrics to chemical and physical signals in electroplating shows as a promising choice in order to extract useful information of the electrochemical processes. A new field of possibilities can then be open. On the other hand, the need of previous separations can sometimes be avoided.

1.2. Chemometrics as an analytical tool

Chemometrics is a collection of mathematical and statistical tools that, along the past 30 years, have successfully been applied to several instrumental signals coming from chemical systems with the aim of obtaining conclusions about the composition of samples or the chemistry of the involved processes. It also allows noise reduction in the signals or handling with interferences and outliers.\textsuperscript{62} Its development has been possible thanks to the improvement of the scientist instrumentation as well as computers increasingly exploited for scientific investigation. Its applications involve experimental design, multivariate classification and calibration, numerous quantitative predictive applications, signal processing etc.

In analytical chemistry, to be precise, many chemical problems and applications of chemometrics involve calibration. This implies finding a mathematical relationship between the analyte and the instrumental response obtained by measuring samples containing the analyte in known amounts. Unlike univariate calibration, that only affords the use of one instrumental response (one variable), multivariate calibration methods allow the use of multiple variables (e.g., the response at a range of potentials or wavelengths). That increases the amount of information that can be obtained.\textsuperscript{63} Over
Introduction

the past several decades, a wide variety of methods have been proposed in order to build
calibration models with spectral and other kind of data. Very well-known methods are
classical least squares (CLS)\textsuperscript{64} principal component regression (PCR)\textsuperscript{65} and partial least
squares regression (PLS-R)\textsuperscript{66}, which keep being the most popular methods in analytical
chemistry.\textsuperscript{67} PCR and PLS are based on variable reduction made through Principal
Components Analysis (PCA).\textsuperscript{68}

From the 1970s, many books and papers dealing with multivariate calibration in
analytical chemistry have been published.\textsuperscript{69,70,71,72} Moreover, numerous software
packages have been developed. Among them, Pirouette,\textsuperscript{73} Unscrambler,\textsuperscript{74} SIMCA\textsuperscript{75} or
MatLab.\textsuperscript{76} Their use depends on both the user’s experience and the type of data.\textsuperscript{77}

In general, the main aim of multivariate calibration is building a model able to predict
the value of the desired property in new unknown samples by measuring an
analytical signal. On the other hand, this analytical signal requires sometimes being
pretreated in order to minimize unwanted effects by removing or reducing irrelevant
sources of variation, random or systematic, which might come from the instrument, the
time passage, light scattering, turbidity in the samples, air bubbles, etc. It consists of
mathematical manipulation of the data prior to the main analysis and the choice will be
made based on the type of data or the concrete problem. For spectral data, they may
include: average, smoothness, derivatives, Fourier transforms or methods for scattering
correction as multiplicative scatter correction (MSC) or Standard Normal Variate
correction (SNV).\textsuperscript{78} Unfortunately, there is not a rule on which one is the most suitable
procedure to undertake and a particular treatment that can improve a particular model
for some data can, on the other hand, prejudice another model for other data.

Preprocessing, therefore, is very important in multivariate regression so that the
regression step can focus better on the important variability that must be modelled and
mostly, the best selection will be the one leading to the best prediction capabilities.
1.2.1. Classical least squares (CLS)

Classical linear regression (Classical Least Squares) is among the most used of the multiple linear regression (MLR) techniques. It is based on extending the Lambert-Beer law to all the compounds contributing to the experimental signal, e.g. the spectra. In this way, the spectrum of an unknown mixture is a linear combination of the individual spectra of the participating species and their corresponding concentrations:

\[ X = SC \]  \hspace{1cm} (6)

where:
- \( X \) = data matrix of the unknown mixture.
- \( S \) = pure spectra matrix.
- \( C \) = individual concentrations matrix.

For predicting new concentrations, the least-squares solution is sought:

\[ \hat{C} = (S^T S)^{-1} S^T X \]  \hspace{1cm} (7)

where:
- \( \hat{C} \) = estimated concentration matrix.

The superscript \(^T\) means the transpose.

In this method, it is assumed that the concentrations of the significant analytes are all known and the error is in the spectra. Therefore, its application to mixtures where there are unknown interferents can result in serious estimation errors.

1.2.2. Principal Component Regression (PCR)

Unlike CLS, PCR is based on assuming that the concentration is a function of the measured signal, e.g. the spectra and this is the equation to be solved:

\[ Y = XB + E \]  \hspace{1cm} (8)
where:

\[ Y = \text{concentrations matrix.} \]
\[ X = \text{spectra matrix.} \]
\[ B = \text{regression matrix.} \]
\[ E = \text{error matrix.} \]

Now, the least-squares solution for this equation is sought considering that the error is in the concentrations:

\[
\hat{B} = (X^T X)^{-1} X^T Y
\]  \hspace{1cm} (9)

where:

\[ \hat{B} = \text{estimated regression matrix.} \]

Although it is not necessary knowing all the species contributing to the absorbance, all the interferents must be included in every sample to be modelled.

Nevertheless, PCR does not use the whole set of independent variables measured. Thus, when absorbance spectra are measured, e.g., the whole set of wavelengths is not used. A reduction of variables will be made first, and afterwards the regression to estimate new concentrations.

This reduction of variables is made through Principal Components Analysis (PCA).

PCA

The method for reduction of variables is not normally applied over the raw data. They (\(X\)-matrix) are usually firstly centered and/or autoscaled.\(^8\)

Data centering supposes calculating the mean of each variable (columns of \(X\)-matrix) and subtracting that mean to each individual value of the column. The mean value represents the centre of the model and all the variables are now referred to that centre. Centering is used to avoid undesirable fluctuations.
Autoscaling supposes dividing each column of the $X$-matrix, after centering, into its standard deviation. The variance of each variable is then equal to 1. Autoscaling is used when original variables are in different units or their variances are very different.

PCA is an orthogonal linear transformation algorithm that may deal with a high volume of information, extracting the main source of variability of the considered data by visualizing and classifying the data. It is a data reduction technique that transforms a number of correlated variables into a smaller number of uncorrelated variables, called principal components (PCs). It enables to visualize all the information in a simple way and allows to detect sample patterns (like any particular grouping) and to quantify the amount of useful information contained in the data.

The concept behind PCA is to transform a matrix of many variables to a problem of some few principal components (PCs), which are linear combinations of the original variables. They are computed iteratively in such a way that the first PC, PC1, contains most of the information (statistically: the most explained variance), the second PC, PC2 that is orthogonal to PC1, contains the next most quantity of information and so on (Figure 5). It is mainly used in exploratory data analysis. The results of PCA are usually discussed in terms of component scores and loadings:

$$X = TP^T + E$$

where:
- $X$ = data matrix.
- $T$ = scores matrix.
- $P$ = loadings matrix.
- $E$ = error matrix.

The combination of the scores and loadings matrices are the structure part of the data. The error matrix represents the residuals or fraction of the variance in data that cannot be explained. When the result of PCA is interpreted, the focus is usually made on the structural part while the residual part is discarded. For doing this, however, residuals
must be negligible, although it is up to the operator decision to establish the limit. So, it is possible to calculate scores and loadings matrices as large as desired, provided that the “chosen” dimension is smaller than the original data matrix. The new dimension corresponds to the number of PCs taken.

![Diagram of PCA transformation](image)

*Figure 5. The original space transformation into a new orthogonal space where the axis are the Principal Components (PCs). It enables the sample grouping. In a general case, the new space can be extended to more than 3 dimensions whenever the number of original variables is larger. Taken from: M.Scholz Ph.D. Thesis. “Approaches to analyse and interpret biological profile data.” University of Potsdam, Germany. 2006.*

This dimensionality reduction is useful to reduce noise and to provide good orthogonal data for the regression.

After doing the variable reduction through PCA, a linear regression on the new variables is taken. For that, the PCs calculated by PCA are used instead the experimental values to build a calibration matrix:

\[
T = XP \tag{11}
\]

and the eq. (8) will stay as follows:

\[
Y = TB + E \tag{12}
\]
where:
\( \hat{B} = \text{estimated regression matrix.} \)

and \( \hat{B} \) is also calculated by the least-squares procedure by knowing \( Y \)-matrix:

\[
\hat{B} = (T^T T)^{-1} T^T Y
\] (13)

Once the model is built (calibration model) with known parameters, this is applied to a matrix of unknown spectra \( X^* \) for prediction, eq. (14) and (15):

\[
T^* = X^* P
\] (14)

where:
\( T^* \) = scores matrix for the samples in prediction.
\( X^* \) = unknown data matrix.
\( P \) = loadings matrix of the calibration model.

And therefore, the new predicted concentrations, \( Y^* \), will be obtained as follows:

\[
Y^* = T^* B
\] (15)

However, although PCR is a powerful tool against collinear \( X \)-data, it shows a weakness when it is used for prediction. There is not warranty that the PC-decomposition of the \( X \)-matrix produces a structure that can be correlated to the \( Y \)-matrix of concentrations. The reason is that it is not sure that the first PCs contain the information corresponding to the analyte concentration in samples. In fact, that transformation is unknown and it can be distributed within several PCs. A consequence is a serious tendency to keep a high number of PCs that lead to over-fitted models. In order to obtain better prediction ability by taking into account the \( Y \)-matrix in the \( X \)-decomposition, the PLS-R (Partial Least Squares Regression) approach was built.
1.2.3. Partial Least Squares regression (PLS-R)

PLS is an algorithm similar to PCR, but it uses the $Y$-data structure (the $Y$-variance) directly as a guiding hand to decompose the $X$-matrix, so that the outcome constitutes an optimal regression in the strict prediction (validation) sense. This is made by the search of the latent variables (LVs), similar to PCs in PCR, which describe the variance in the data in such a way that $Y$-data are related concentrations to $X$-matrix. Therefore, PLS reduces the probability that the $X$-variations do not correlate with $Y$ with respect to PCR.

There are two versions of PLS: PLS1, which models only one $Y$-variable and, therefore, the $Y$-data structure is a vector of the analyte concentrations, and PLS2, which models several $Y$-variables simultaneously, and therefore, $Y$-data structure is a matrix.

Chemometrics experience has demonstrated that similar or better prediction models are always obtained when using a series of PLS1 models on the pertinent set of $Y$-variables, instead a PLS2 model. The general equations of the algorithm are those summarized in the following:

\[
X = TP^T + E \tag{16}
\]
\[
Y = UQ^T + F \tag{17}
\]

where:
- $T =$ scores matrix for $X$.
- $P =$ loadings matrix for $X$.
- $U =$ scores matrix for $Y$.
- $Q =$ loadings matrix for $Y$.
- $E =$ residual matrix for $X$.
- $F =$ residual matrix for $Y$.

The goal of PLS is to model all the constituents forming $X$ and $Y$ so that the residuals $E$ and $F$ are approximately equal to zero. The vectors for both blocks, $X$ and
\(Y\), are calculated independently, but an inner relationship is established between them relating the scores of the \(X\)-block, \(T\), and the scores of the \(Y\)-block, \(U\):

\[
U = TW
\]  

(18)

The inner relation is improved by exchanging the scores, \(T\) and \(U\) in an iterative calculation. This allows information from one block to be used to adjust the orientation of the latent vectors in the other block and vice versa.

Once the complete model is calculated, the above equations can combine to give the regression matrix:

\[
\hat{B} = P(P^T P)^{-1} WQ^T
\]  

(19)

and \(Y\) will be calculated through:

\[
\hat{Y} = X\hat{B}
\]  

(20)

The values of matrices \(E\), \(F\) and \(B\) will depend on the LVs used in the model.

1.2.4. Number of factors or latent variables (LVs)

The choosing of the optimum number of latent variables (LVs) to be used with the PLS model is an important task for obtaining a model with a good prediction ability. If too many components are used, redundancy and noise in the \(X\)-matrix will be used and the solution will become overfitted. The use of too few components (underfitting) will also provide poor predictions because the model does not capture all the important variability in the data. To find the optimal number of LVs a previously established method was used. That is, the lowest number of LVs for which the validation (Cross-Validation) variance values does not differ significantly from the minimum one. An F-test with probability \(P = 0.25\) is chosen to compare variances.

Leave-one-out full Cross-Validation procedure has been applied to assess the robustness of the constructed models. It means to take as many sub-models as there are objects, leaving out just one of the objects each time and to use only this for the testing.
1.2.5. Model evaluation

To test the prediction capability of the developed models, the statistic relative error ($RE$) will be used:

$$RE = \frac{100}{\sum_{i=1}^{m} y_i^2} \sum_{i=1}^{m} (\hat{y}_i - y_i)^2$$

(21)

where:

$\hat{y}_i$ = estimated analyte concentration in the sample $i$.

$y_i$ = analyte concentration in the sample $i$.

$RE$ can be applied to the calibration ($RE_{cal}$) and the prediction ($RE_{val}$) sets. The calibration and prediction (validation) sets were always defined before any data processing and remained unchanged along the whole work.

The square of the differences between the predicted and the $y$-value (residuals) for the omitted sample are summed and averaged, giving the usual validation $Y$-variance.\(^85\)

1.2.6. Limit of detection (LOD)

The limit of detection is one the most important figures of merit of analytical methods. The calculation of the limit of detection in linear calibration is perfectly established and accepted through the $3s$ criteria\(^86\) and it is used for comparison of analytical methods obtained under the same or similar premises. Nevertheless, in the case of multivariate calibration methods there is not a generally accepted method for LOD determination. The *Found vs. added* plot\(^87\) and the *Multivariate Residuals Value (MR)*\(^88\) are two of the proposals for LOD calculation and both will be used throughout this work in multivariate calibration approaches. In short, the *Found vs. added* method
provides the LOD from the expression \( \frac{s_{y/x}}{m} \) applied to the plot that represents found concentrations vs. taken concentrations for standards, where \( s_{y/x} \) and \( m \) are the regression standard deviation and the regression slope respectively. The MR method uses the multivariate residuals from the model to calculate a standard deviation vector, \( s_{x/y} \), of the regression.

Chemometrics allows, therefore, to treat a great quantity of information and to extract precise and accurate conclusions from complex analytical signals. This can be extremely useful in electroplating bath analysis where there are numerous parameters related to each other (non-linearities) and where additives analysis is complex due to the small concentrations of these compounds in the bath. Multivariate methods require a great quantity of samples in order to follow the evolution of bath components. Furthermore, there is an increasing need of real-time control analysis in electroplating industry to follow the additives concentration on line. This allows to correct concentration deficiencies of additives, etc. and to reduce the percentage of rejected pieces.

1.3. New proposals in electroplating

In this work, a flow analysis method coupled to a diode-array spectrophotometer is used to extract sample aliquots periodically from the bath. Moreover, NMR is used as an alternative to traditional analytical techniques so that additives can be determined. Both techniques, however, imply invasive measuring procedures and therefore, choices able to extract information about additives without extracting samples from the bath are also tried. This is got through methodologies on the final plated products, which can provide valuable information on the bath composition. In this way, the enormous possibilities that chemometric techniques offer can be used to turn brightness, measured onto the electroplated surfaces, into a robust measuring method able to give priceless information. At the same time, the possibilities of image analysis on the electroplated products have been tested. Thus, the obtained images of the plated surfaces can be studied through chemometric tools, in order to get quantitative information of the bath composition and the quality of deposits.
1.4. References


73 http://www.infometrix.com/.  
74 http://www.camo.com/.  
75 http://www.umetrics.com/.  
76 http://www.eigenvector.com/.  
78 A. Gianguzza, E. Pelizzetti, S. Sammartano (Eds.), *Chemical Processes in Marine Environments*, Springer, Berlin, Germany, 2000, 389.  
2. Objectives
The main objective of this thesis is the application of different analytical techniques and chemometrics to the study and control the behaviour and performance of additives behaviour in a nickel electroplating bath, including major components, minor components (additives) and the product finish.

The control of parameters not involving additives (Ni$^{2+}$ concentration, Cl$^-$ concentration, pH or temperature) will be studied in a nickel plating bath, in Section 3. Well-known analytical procedures including volumetric titration, UV-Vis spectrophotometry or pH measurements will be carried out with that purpose.

Then, analytical techniques such as UV-Vis spectrophotometry and Nuclear Magnetic Resonance (NMR), will applied to bath samples in order to study the behaviour of the additives in the electroplating bath. These additives are the main responsible for the final quality of the coating. Automation of measurements (Sequential injection analysis, SIA) will be also proposed for sample dilution and measure. The fundamentals and results of both procedures are explained in detail in Sections 4 and 5 of this thesis.

Finally, in Section 6, physical parameters of the electroplated sheets will be assessed by the use of techniques as brightness, specular reflectance and image analysis. They could be considered as a relevant source of information of the state of the bath. The results obtained from the final electroplated product will be related to the chemical composition of the bath.

The use of chemometrics tools as Principal Components Analysis (PCA), classical least squares (CLS) or partial least squares (PLS) will be considered throughout in order to deal with the huge number of variables and data extracted from the analysis of the bath additives and from the physical parameters.
3. Nickel electroplating process. Control of $\text{Ni}^{2+}$, $\text{Cl}$, pH and T.
3.1. Introduction

There is no doubt that additives are probably the most important ingredients of electroplating baths, but the industrial experience has proven the necessity of keeping all the chemical bath components into well defined concentration ranges in order to assure an effective plating. Variations in their concentrations could lead to significant physical modifications on the plated coatings. Thus, although the initial conditions are well known, the bath components can be gradually run out with their use; therefore, a regular control of the parameters along the passage of current should be carried out.

The determination of nickel(II) can rely on the absorbance of the hydrated ion that shows a maximum at 395 nm. An absorbance probe allows to register absorbance spectra in a rapid and simple manner. The path length of the probe can be modified through washers that can be coupled to the probe; as a result, high concentrated analytes can be measured with the probe with no need of a previous sample dilution procedure, more awkward and time consuming. That is the case of nickel in a bright nickel bath, where nickel concentration is quite high and sample dilution would be necessary in order to real-time control of this major constituent of the bath.

On the other hand, chloride helps to promote anode corrosion. It increases the conductivity and allows to work at lower voltages, therefore it is important to guarantee that its concentration keeps approximately constant during the process. A low chloride concentration will generate a low current density affecting the bright of plates and some properties of the bath; consequently, nickel chloride should be added in this case. Volumetric methods with silver ion have been traditionally used to follow the chloride concentration during electroplating.

Although the operating temperature range in a nickel bath can be quite wide, (from 54 to 76°C), the most recommended temperature is between 60 and 70°C. The specific optimum temperature will vary from different processes and will also depend upon the degree of bath agitation. At too low temperatures, dull deposits would be obtained, so continuous temperature checking should be made in the bath. Automatic temperature control equipments are frequently used with this purpose.
The control of pH is also essential in order to assure good quality platings. It should be maintained between 3.5 and 4.5. A pH < 3.0 promotes the decrease in bright throwing power and pH > 4.5 leads to the formation of insoluble basic iron compounds, when electroplating is carried on steel surfaces and can produce dark plates since the basic nickel salts will plate out.\textsuperscript{5,6}

3.2. Experimental

3.2.1. Reagents

A volume of 1.8 L of a commercial nickel bath (Supreme Plus brilliant, Atotech formulation) was used with the following composition: NiSO\textsubscript{4}·6H\textsubscript{2}O (250 g L\textsuperscript{-1}), NiCl\textsubscript{2}·6H\textsubscript{2}O (50 g L\textsuperscript{-1}) and H\textsubscript{3}BO\textsubscript{3} (45 g L\textsuperscript{-1}) as non-additive solution; SA-1 (2.6 ml L\textsuperscript{-1}), A-5(2X) (20 ml L\textsuperscript{-1}), NPA (2 ml L\textsuperscript{-1}) and Supreme Plus Brightner (SPB) (1 ml L\textsuperscript{-1}) as additives (additives from Atotech, Berlin, Germany). The chemical composition of additive solution is unknown. The final pH was 4 and it was maintained constant along the process with addition of either NiCO\textsubscript{3} or H\textsubscript{2}SO\textsubscript{4} as required. Solutions of 0.1M AgNO\textsubscript{3} and 10\% K\textsubscript{2}CrO\textsubscript{4} analytical reagent grade were also used. Non-additive chemicals were also of analytical reagent grade (Panreac or Fluka) and used without further purification. Additives were obtained from Atotech S.A. and used as received. Doubly distilled water was used throughout.

3.2.2. Apparatus

The following instrumentation was used (Figure 1): an electrodeposition vessel with a water jacket (Afora, Barcelona, Spain) for the nickel bath; a sensor probe, PEEK, 300 micron SR, UV with adjustable path (2-10 mm) PEEK tip TP300-UV/VIS, a DT_MINI-2_GS UV-VIS-NIR light source and a USB4000 CCD spectrophotometer, all from OceanOptics (Dunedin, FL, USA), for spectra acquisition (during the work, a diode-array spectrophotometer Hewlett Packard (HP) 8452A (Avondale, PA, USA) was also used instead); a Crison 501 pH meter (Alella, Spain); a Haake water bath thermostat controlled by an external probe dipped into the nickel bath for Tº control; a rectifier ± 20A / 30V from HQ Power (Nedis BV, The Netherlands) (model no. PS...
3020) for electrodeposition; A 25ml blue Brand burette was used for Cl⁻ titration and micropipettes Brand (Wertheim, Germany) or Eppendorf (Hamburg, Germany) were used throughout.

3.2.3. Software

Spectral data were acquired with a computer coupled to either the HP 8452A or the USB4000 CCD spectrophotometer. OOIBase32 software was used for USB4000 spectra acquisition. Afterwards, spectra were handled with the UNSCRAMBLER v. 9.7 (Camo A/S, Trondheim, 2007) software package in order to correct baseline drifts.

3.2.4. Procedures

3.2.4.1. Nickel electrodeposition

Nickel electrodeposits were obtained galvanostatically in a glass cylindrical vessel (10.5 cm inner diameter, 21 cm height) of approximately 2 L of capacity (Figure 1) with a lid that minimized heat and solvent losses. The electrodeposition was carried out on both sides of 16.5 x 3 cm commercial steel sheets at a temperature of 65 °C with mechanic stirring under 4 A·dm⁻² current density for 15 min. Prior to each electrodeposition, the steel sample was cleaned with soap and water, then degreased with calcium carbonate, and finally etched with hydrochloric acid/Beizentfetter solution for 30 s and rinsed with water. Two 20 x 3 cm Ni pieces were used as anodes. An amount of 53 steel sheets were nickel plated along the bath life. After that, the bath was considered to be run out.
Nickel electroplating process. Control of Ni\(^{2+}\), Cl\(^-\), pH and T

3.2.4.2. Nickel control

The Ni\(^{2+}\) concentration in the bath along the electrodeposition process was measured using an absorbance sensor probe, which was introduced into the nickel bath vessel after each plating process (Figure 2). A nickel calibration curve was built measuring NiSO\(_4\)·6H\(_2\)O standards at different concentrations. The Ni\(^{2+}\) concentration levels were: 0, 10.2, 30.7, 51.1, 68.2, 81.8, and 102.3 g L\(^{-1}\) and they were prepared by

---

Assembly for nickel electrodeposition

---

Figure 1. Manifold for process analysis of nickel electroplating. a, vessel for electrodeposition; b, anodes; c, cathode; d, absorbance sensor probe; e, temperature probe; f, magnetic stirrer; g, current source; h, light source; i, spectrophotometer; j, burette; k, pH-meter; l, water bath thermostat, m, computer.
Nickel electroplating process. Control of Ni\(^{2+}\), Cl\(^{-}\), pH, T

dissolving NiSO\(_4\)·6H\(_2\)O in water. The absorbance at the 395 nm absorption maximum was used. Finally, an integration time of 1s was chosen and the signal was averaged to a value of 1.

*Figure 2. Manifold for nickel control. (a) light source; (b) spectrophotometer; (c) absorbance sensor probe; (d) , computer for spectra recording.*

**3.2.4.3. Chloride control**

Chloride was determined at three stages of the bath life: 0, 16.7 and 28.9 A·h/L. Argentometric titrations were followed by the Mohr method using indicator paper to maintain the pH solution between 5 and 10.
Nickel electroplating process. Control of Ni$^{2+}$, Cl$^-$, pH and T

1mL of the nickel bath was taken out at each of the three stages and diluted 250 times. Afterwards, it was titrated with 0.1 M AgNO$_3$ and 2ml 10% K$_2$CrO$_4$ as indicator.

3.2.4.4. Temperature control

The nickel bath temperature was automatically controlled with a water bath thermostat through the vessel water jacket (65±3 ºC). (Figure 3).

Figure 3. Water bath thermostat used during the procedure. Temperature must be strictly controlled.

3.2.4.5. pH control

The value of pH was periodically measured with a Ag/AgCl glass electrode as a reference (Figure 4); it was calibrated daily. To maintain the bath into the adequate range of pH either 1M H$_2$SO$_4$ or solid NiCO$_3$·3Ni(OH)$_2$·4H$_2$O was added.
3.3. Results and discussion

3.3.1. Nickel concentration control

It was firstly checked that no other bath components showed absorbance at the chosen wavelength. The optical path of the probe was previously adjusted through different washers, which can be coupled to the probe in order to assure that the spectrophotometric signals would not saturate the measuring system. According to the Lambert-Beer’s law:

\[ A = \varepsilon l c \]  

(1)

where:
Nickel electroplating process. Control of Ni$^{2+}$, Cl$^-$, pH and T

\[ A = \text{Absorbance} \]
\[ \varepsilon = \text{molar absorptivity} \]
\[ \ell = \text{optical path} \]
\[ c = \text{molar concentration} \]

Equation (1) represents a limiting law and absorbance tends to break down at high concentrations, especially if the material is highly scattering. The experimental signal, \( A \), can be modified by choosing a proper path length. In practice, the path length can be modified from 0.1 to 1.0 cm, to get \( A \) values within the range where equation (1) is obeyed (usually between 0 and 1.0-2.0).

For optimization, a sample with the same formulation as the initial nickel bath was measured with the probe at three different path lengths: without washer, with a 1 mm. washer and with a 2 mm. washer. The optimum integration time has also to be optimized. The integration time is the interval of time over which the measurement is taken at the selected bandwidth. It is usually chosen as the longer time that not saturate detector because longer times allow to filter out background noise and to boost the signal-to-noise ratio in more extent.

3.3.1.1. Preliminary spectral study

Both, nickel hexahydrated sulphate and nickel hexahydrated chloride dissociate in water giving the hydrated Ni(II) ion, which is the responsible of the green-coloured bath solutions. The UV-visible spectrum for both salts in water solution, at the same concentration as they are in a nickel bath is depicted in Figure 5. The spectrum of an aliquot of nickel bath at its standard formulation is also depicted. This bath sample has been diluted with water (1:10). The spectra were registered in a diode-array HP 8452A spectrophotometer.
Nickel electroplating process. Control of Ni$^{2+}$, Cl$^-$, pH, T

As it can be seen from Figure 5, the maximum at 395 nm and the broad band from 570 to 800 nm in the nickel bath spectrum match the nickel salts spectrum as long as no other bath component interferes at those wavelengths. The nickel control during electrodeposition can, therefore, be made through the evolution of the absorbance at 395 nm.

3.3.1.2. Optimization and spectra correction

Spectra registered at different optical paths with the absorbance sensor probe of a CCD spectrophotometer detector are shown in Figure 6. As expected, the absorbance increases when the path is enlarged. Considering that the absorbance value at 395 nm gets saturated at the largest paths, no washers were used for standards and samples.

The value of the path length can be evaluated by applying the following equations derived from the Lambert-Beer law:
Nickel electroplating process. Control of Ni\(^{2+}\), Cl\(^{-}\), pH and T

\[
\frac{A_2(395\text{nm})}{A_1(395\text{nm})} = \frac{\text{path}_2}{\text{path}_1}
\]  \hspace{1cm} (2)

\[
\text{path}_2 = \text{path}_1 + \text{washer length}
\]  \hspace{1cm} (3)

In this case, the optical path was found to be 1.40 mm.

![Figure 6. Effect of washers on the absorbance registered by an optical probe. 1, (blue line), bath nickel spectrum measured without washer; 2, (pink line), 1 mm washer; 3, (green line), 2mm washer. The nickel bath sample is the same in all the three cases. Integration time = 1000 ms. Average =1. USB 2000 Ocean Optics CCD spectrophotometer.](image)

The spectra were corrected for baseline drifts. This was made applying the baseline linear correction tool of Umscrambler, taking to 0 the absorbance values registered at 320.12 nm and at 520.73 nm, where the nickel bath is supposed not to show absorbance.

3.3.1.3. Calibration

Once the measuring parameters have been optimized, the nickel calibration standards were measured with the probe and then baseline-corrected.
The spectra of nickel standards with the optimized parameters, as well as the calibration line are in Figure 7.

Figure 7. (a) Spectra of standard nickel solutions, obtained with an optical probe for calibration. NiSO$_4$·6H$_2$O (g/L$^{-1}$): 1) 0; 2) 37.5; 3) 112.5; 4) 187.5; 5) 250; 6) 300; 7) 375. NiCl$_2$·6H$_2$O (g/L$^{-1}$): 1) 0; 2) 7.5; 3) 22.5; 4) 37.5; 5) 50; 6) 60; 7) 75. H$_3$BO$_3$ (g/L$^{-1}$): 1-7). The concentration of the nickel salts is the same as the one in the plating bath. (b) Calibration line. Measuring conditions as in Figure 2.

3.3.1.4. Nickel evolution during electrodeposition

The absorbance probe was introduced into the bath after the plating of each steel sheet and the obtained spectrum for nickel was registered. The baseline correction was made in the same way as for standards and the result of this procedure is shown in Figure 8, where it can be seen how the baseline drift in the spectra has largely been corrected.
Nickel electroplating process. Control of Ni$^{2+}$, Cl$^-$, pH and T

Figure 8. Spectra for the plating bath solution during the electroplating process. (a) Uncorrected. (b) after linear baseline correction.

As for standards, the absorbance values at 320.12 and 520.73 nm were taken as zero and the nickel concentration was calculated from the calibration line in Figure 7 (b).

Figure 9 shows the evolution of the Ni$^{2+}$ concentration in the bath along the electroplating process until the bath was considered to be run out.

Figure 9. Ni$^{2+}$ concentration evolution during the electroplating process.
From Figure 9, it can be concluded that the Ni$^{2+}$ concentration keeps approximately constant during the plating procedure, as it could be expected. That means that the amount of nickel that settles down onto the surface of the sheets is practically the same as the amount of nickel that goes into solution from the anodes.

### 3.3.2. Chloride concentration

The Mohr method is a direct titration of chloride with silver ions (silver nitrate as primary standard) using a soluble chromate salt as indicator. The value of pH must be ranged between 5 and 10. At pH < 5, CrO$_4^{2-}$ ion dimerizes and the end point is not visible; if pH >10, Ag$_2$O(s) is formed. The volumetric process involves two reactions:

\[
\text{Titration reaction} \quad \text{Ag}^+ + Cl^- \rightarrow \text{AgCl(s)} \tag{4}
\]

\[
\text{Indicator reaction} \quad 2\text{Ag}^+ + \text{CrO}_4^{2-} \leftrightarrow \text{Ag}_2\text{CrO}_4(s) \tag{5}
\]

The order of precipitation depends on the solubility products. Thus, after the most of chloride has been precipitated as silver chloride, a brown-red precipitate of Ag$_2$CrO$_4$ appears and it can be considered the end point of titration.

Table 1 summarizes the results obtained at the three stages of the bath life. Figure 10 depicts the Cl$^-$ concentration found along the electrodeposition. As it happened with Ni$^{2+}$, the chloride level maintains constant along the electrodeposition, as expected.

<table>
<thead>
<tr>
<th>Current (A·h/L)</th>
<th>AgNO$_3$ 0.1N added (ml)</th>
<th>Cl$^-$ concentration found (g L$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.72</td>
<td>56.1</td>
</tr>
<tr>
<td>16.7</td>
<td>4.68</td>
<td>55.6</td>
</tr>
<tr>
<td>28.9</td>
<td>4.78</td>
<td>56.8</td>
</tr>
</tbody>
</table>

*Table 1. Argentometric titration of chloride ion along the bath life. Titrant (AgNO$_3$) volume added in each titration and Cl$^-$ concentrations found in each case.*
3.3.3. pH and temperature control

The value of pH was periodically checked along the electrodeposition. It increases slightly with the passage of current and whenever it reached a value of 4.5, 1M H$_2$SO$_4$ was added to return it to 3.5.

An external control of temperature checked that the water bath temperature permanently kept between 60º and 70ºC during the whole process. The circulating water bath was controlled by the T probe sunk in the nickel bath.

3.4. Conclusions

The behaviour of the nickel bath parameters that are not the additives have been checked along the electroplating process. The concentrations of Ni$^{2+}$ and Cl$^-$ keep constant during the whole bath life. The value of pH slightly increases during the process, but it can be maintained around 4.5 with the addition of H$_2$SO$_4$. On the other hand, the water bath keeps the temperature stable within the 60-70ºC range. The behaviour of the substances used as additives deserves a different chapter.
3.5. References

3 K.E. Langford, Análisis de baños electrolíticos, Aguilar, Madrid, Spain, 1963, 103.
5 N.V. Mandich, H. Geduld, Metal Finishing, 2002, 100(6), 74-83.
4. Quantitative determination of additives in a commercial electroplating nickel bath by spectrophotometry and multivariate analysis
4.1. Introduction

The previous chapter deals with the behaviour of the bath parameters that do not involve additives. From now on, the work attempts the control of the compounds that are the main responsible for the final quality of the coatings; that is, the additives. The additive control has frequently been accomplished in an empirical way, due to the lack of rapid and accurate analytical methods. Therefore, monitoring techniques can be very useful in order to follow the behaviour of additives during the electroplating process. Thus, although usual analytical techniques have been tested in electroplating, some limitations are postponing the appearance of straight forward additive determination procedures and only a few references have been found dealing with additive monitoring.\textsuperscript{1,2} One of these constraints is the highly complex chemical composition of baths, what makes difficult the additive control.

A-5(2X) and Supreme Plus Brightener (SPB) are the commercial names of two organic additives for nickel electroplating baths that show UV absorption bands. A sequential injection analysis (SIA) system has been configurated in order to carry out the control of both nickel bath additives during an electroplating process. The optimization process and fundamentals of the configurated SI-system will be described in this chapter as well as the results obtained for A-5(2X) and SPB additive determination.

Most of flow designed systems are used in the quantitative determination of different species of interest. These flow systems show major advantages for the analytical community as automation of sample preparation, increased throughput and precision, less consumption of reagents and generation of waste as well as multi-species determinations.\textsuperscript{3} Sequential injection (SI), specifically, has been frequently used in food,\textsuperscript{4} water,\textsuperscript{5} or soils\textsuperscript{6,7} analysis. It usually requires a previous optimization process of the variables affecting the flow. On the other hand, the number of detectors associated to SIA can be numerous, as chromatographs, amperometers, fluorimetric spectrophotometers or UV-Vis diode-array spectrophotometers; the latter has been used in the present study. Diode-array spectrophotometers provide second-order data, that is, a matrix of data absorbance-wavelength-time for every sample, so they are especially
useful in kinetic studies (systems in evolution) where spectra are continuously registered along the period required to carry out a complete analysis. Reaction rates and mechanisms can be studied in this way. Usually, however, the generated complex matrices will require the use of chemometric tools to obtain both qualitative and quantitative information about the analytes in the presence of interferents. Nevertheless, in spite of their great application in kinetics, flow systems have been also used in sample pretreatments, in qualitative analysis of samples to detect the presence of certain substances or just to lead the sample to detector after a proper dilution. The aim of the SI-system here, is an example of the latter. Nickel bath samples should be diluted before measuring and this procedure was made through a SI-system, which had to be previously optimized.

In general, the sample is mixed with the reagents/carrier through the phenomenon of dispersion, either axial or radial and the time required to carry out a determination will be the sum of the reaction, the dilution, and the measurement period together with the time required to aspirate the different solutions. During the time the analysis is running, therefore, well defined segments of samples and reagents disperse and penetrate mutually and an overlapping reproducible zone is obtained. The type of data obtained by SIA, consequently, will depend on the extent of overlapping between analyte and reagents, and this can be controlled by both the reversal and the volumetric flow rate of the mixture to the detector, once the SI-system has been set up.

The optimization of a SI-system is not a simple task and the procedure followed will be explained along this chapter. The results obtained in the resolution of A-5(2X) and SPB additive mixtures in an electroplating process will be compared to those obtained by a manual procedure. In the manual procedure, the extraction of aliquots from the nickel bath, the dilution and the measuring process were carried out by the operator. This manual procedure will be used as a reference method.

As it has been said, both, A-5(2X) and SPB show UV absorption bands. Nevertheless, their spectra are strongly overlapped, making it impossible to determine their concentration in a simple manner. The joint use of UV-Vis-NIR spectrophotometry and multivariate calibration algorithms has gained acceptance to resolve mixed signals and it can be an excellent alternative to the classical
Multivariate calibration methods applied to spectral data are being increasingly used for biomedical and pharmaceutical analysis. They can use the whole spectra for the resolution of complex mixtures of analytes containing some interferences, for noise reduction, for outlier control etc. In this study, two very well-known multivariate models have been applied to UV data and compared: namely, Partial Least Squares (PLS) regression and Classical Least Squares (CLS).

PLS, as a low-rank calibration method, discards irrelevant and unstable information contained in the data set (the $X$-matrix) and finds a linear combination between the $X$-matrix and the known concentration of the standards (the $Y$-matrix) as it was previously explained in the Section 1.2.3 of the Introduction. Once the model has been established, it can be used to predict concentrations of sample mixtures. This variable reduction procedure affords improved prediction results, although sometimes PLS is a time-consuming method because it requires the building of a calibration model through standards, high enough in number. On the other hand, it is an accurate and robust method. It is especially appealing for analyte determination in complex matrices with three or more components; moreover, it allows to handle interferences whenever they are included in the calibration set samples.

CLS is a simpler, fast and rigid method. It does not need calibration standards because it only uses for calibration the pure spectra of absorbing species (analytes). As counterpart, the Lambert-Beer’s law must be strictly obeyed as it was said in the Section 1.2.1. of the Introduction. Complex matrices may easily generate errors because of deviations of the Beer’s law. Hence, CLS is not able to model hidden compounds or effects in the mixture (i.e. non-linearities or possible interferences).

At first sight, interactions and non-linearities are not expected in the case of the electroplating nickel baths. Consequently, the use of CLS looks attractive because of its simplicity; however, electroplating baths are complex matrices with several compounds at very high concentrations. This justifies the attempt of a softer algorithm such as PLS. The optimization process included signal pretreatment and variable selection in order to obtain the best results in the determination of additives concentration. The calibration
model chosen proved to be robust enough to cope with changes occurring along time (eight months) including the change of the measuring instrument.

4.2. Experimental

4.2.1 Reagents

A volume of 1.8 L of a commercial nickel bath (Supreme Plus, Atotech formulation) was used. The bath formulation as well as the description of the used reagents are explained in detail in Section 3.2.1.

4.2.2. Apparatus

The following instrumentation was used (Figure 1): an electrodeposition vessel with a water jacket (Afora, Barcelona, Spain) for the nickel bath (65°C); a Crison 501 pH meter (Alella, Spain); a Haake water bath thermostat controlled by an external probe dipped into the nickel bath; a rectifier (± 20A / 30V) from HQ Power (Nedis BV, The Netherlands, model no. PS 3020) for electrodeposition and a diode-array spectrophotometer Hewlett Packard (Avondale, PA, USA) 8452A (during the work, an Agilent 8453 spectrophotometer (Santa Clara, CA, USA) was also used instead). A sequential injection (SI) set-up was also used to take the solution from the bath to the spectrophotometer and back to the bath; it included a multiburette 4S, a port selection valve VA+1 from Crison (Alella, Spain), a holding and reactor coil and a solenoid valve. Micropipettes Brand (Wertheim, Germany) or Eppendorf (Hamburg, Germany) were used throughout.
Figure 1. Manifold for process analysis of nickel electroplating with the SI system emphasized. 
a, nickel bath vessel; b, anodes; c, catode; d, pH double electrode; e, temperature probe; f, magnetic stirrer; g, pH-meter; h, current source; i, water bath thermostate; j, carrier vessel; k, multiburette manifold; l, holding coil; m, selection valve; n, water vessel; o, waste vessel; p, reaction coil; q, diode-array spectrophotometer; r, solenoid valve; s, waste vessel; t, computer.

4.2.3. Software and data processing

Experimental data were acquired with a computer coupled to the spectrophotometer. The SI-system was controlled with a commercial programme (AutoAnalysis, Sciware, Mallorca, Spain). Absorbance spectra were treated with the UNSCRAMBLER v. 9.7 (Camo A/S, Trondheim, Norway, 2007) software package.
which allowed the application of PLS; Matlab 7.4.0 software (The Mathworks Inc., Natick, USA) with PLS_Toolbox (Eigenvector Research Inc, USA) was also used for CLS. The Savitzky–Golay derivative transformation, with a three-point filter width and polynomial order two was used when necessary for background and base-line correction. To test the prediction capability of the developed models, the statistic relative error \( RE \), see Introduction, Section 1.2.5.\) was used. The calibration and prediction (validation) sets were defined before any data processing and remained unchanged along the work. Leave-one-out full Cross-Validation procedure was used to assess the robustness of the constructed models. The selection of the optimum number of factors (LVs) to be used with the PLS model was made through the method explained in Section 1.2.4. of the Introduction.

4.2.4. Procedures

**Nickel electrodeposition**

The nickel electrodeposition process was carried out as it is explained in detail in Section 3.2.4.1. An amount of 53 steel sheets were nickel plated along a bath life. Afterwards, the bath was considered to have run out.

4.2.4.1. SI-system for additive determination in nickel baths

A SI-system was configurated and optimized in order to follow automatically the concentration of A-5(2X) and SPB additives in a nickel bath during the electrodeposition process. Spectrophotometric measurements were carried out in an automatic way by a SI system (Figure 1 and 2). The strength of a SI system lies on the ability to perform highly reproducible and automated sample manipulations (sample clean-up, chemical reactions prior to spectrum acquisition, etc.) and it has been successfully applied in the simultaneous determination of analytes with a diode-array spectrophotometric detector. The SI-system was configured to extract 25\(\mu\)l of sample from the bath and then it was diluted approximately 70 times with distilled water and taken to detector with a very high precision. The first daily measurement carried out
with the SI system was always removed because it was unstable. The spectra were acquired between 248 and 320 nm every 2 nm.

Figure 2. Manifold for nickel electrodeposition and additives measurement by SI-system. (a) Vessel for nickel; (b) current source; (c) multiburette manifold; (d) selection valve; (e) diode-array spectrophotometer; (f) solenoid valve.
Calibration stage for the SI-system

A calibration matrix for mixtures of the two additives under study was built. Standard baths were prepared containing different additive concentrations. The concentration levels for A-5(2X) were 4, 8, 12, 16, 20 and 24 ml L\(^{-1}\) and the concentration levels for brightener (SPB) were 0.14, 0.18, 0.20, 0.60, 1.00 and 1.40 ml L\(^{-1}\). The concentration levels for the other bath components were the standard for a nickel bath, (Section 3.2.1). The initial calibration matrix was supplemented by additional mixtures along six months to cope with variations coming from the use of two spectrophotometers and variations from the day by day measurement. The whole matrix contained 64 samples (Figure 3); the calibration set contained 38 samples, including 17 replicates; the validation set contained 26 mixtures, including 11 replicates. Replicates were always kept in the same set, (Figure 3). It should be noted that no electric current went through the bath samples used for calibration or validation.

![Figure 3. Concentration matrix for SPB and A-5(2X) mixtures. Circles, calibration; squares, validation. Filled marks are replicates.](image)

To make a study on accuracy and precision, five bath samples at several fixed Supreme Plus Brightener and A-5(2X) concentration levels were randomly measured five times each.
4.2.4.2. Manual procedure for additive determination in nickel baths

The procedure was similar to the automatic process but now 100 µl of sample from the bath were manually taken out, diluted 100 fold with distilled water and measured in the detector (a HP8452A UV-Vis spectrophotometer). This technique is used as a reference method for the automatic results. Spectra were also acquired between 248 and 320 nm every 2 nm.

Calibration stage for the manual procedure

A calibration matrix of the two additives under study was built. The concentration levels for A-5(2X) were 6, 10, 20, 40 and 60 ml L\(^{-1}\); the concentration levels for SPB were 0.05, 0.3, 0.6, 1, 2 and 3 ml L\(^{-1}\). The concentration for the other bath components was the standard for a nickel bath, (Section 3.2.1.). The samples required to be diluted 100 times with distilled water before measuring. The whole matrix contained 45 samples (Figure 4), including 30 from the calibration set, (7 of them were replicates) and 15 from the validation set (6 of them were replicates). Replicates were always kept in the same set (Figure 4). Not electric current went through the calibration and validation samples. It is also important to point out that this calibration matrix for the manual procedure is not the same as the one used for the automatic procedure (see above).
To make a study on accuracy and precision, five bath samples at several fixed Supreme Plus Brightener and A-5(2X) concentration levels were randomly measured five times each.

4.3. Results and discussion

The UV-Visible spectra of bath components are all depicted in Figure 5 together with the nickel bath spectrum. The additives A-5(2X) and SPB show UV absorbance in the 248 - 320 nm region, where no other bath component shows UV signal. The spectra of both additives are totally overlapped, but there is not interference from other material in the bath.
Figure 5. (a), UV-Vis spectra of nickel bath components: (1, light blue), SPB; (2, red), A-5(2X); (3, green), nickel bath; (4, dark blue) NiSO$_4$·6H$_2$O; (5, pink), NiCl$_2$·6H$_2$O; (6-8), H$_3$BO$_3$, SA-1 and, NPA. The conditions for all of them are the same as the nickel bath. (b), enlarged range from 248 to 320 nm after 1:25 dilution of solutions in (a).

4.3.1 Bath stability

The UV spectra for the A-5(2X) and SPB mixture did not show appreciable changes along a 5 month period for neither a diluted bath sample nor an original standard sample (Figure 6). The absorbance value at the maximum of the peak, 266 nm, (Figure 6a and c) is depicted along time (Figures 6b and d) showing that there is no remarkable trend in the spectral variation. The standard deviations calculated between absorbance measurements at 266 nm are 4.7% for the diluted sample and 3.9% for the standard sample. These variations can be due to baseline drifts and measurement uncertainties coming from both the apparatus and the dilution process.
Determination of additives. Spectrophotometry

Figure 6. Stability of the nickel bath along a 5 month period. (a) and (b), 1:100 diluted nickel bath; (c) and (d), nickel bath at standard concentration diluted 1:100 at the measuring time. (a) and (c), spectra in the 248-320 nm range. (b) and (d), absorbance at 266 nm.

4.3.2. Automatic data acquisition

The measuring cycle of the SI technique comprises the following operations: (1) aspiration of the carrier, (2) aspiration of the sample, (3) aspiration of reagent solution (water in this case), (4) injection of the interdispersed sample/reagent zone through the reactor into the detector, (5) a stopped flow period for spectrum monitoring and (6) rejection of the sample and reagent from the valve and from the flow channel. These operations have to be carried out in such a way that a desired degree of penetration of sample and reagent zones is achieved, within an adequate resident time and a satisfactory sampling frequency. Therefore, an optimization procedure will be accomplished. This procedure, in general, is not a simple task since it involves several
steps that depend on what is exactly desired.\textsuperscript{26,27} In this case, there is no reaction, so there is no reagent solution which is substituted by water as dilution solvent.

In Figure 1 it is depicted the SI-system configurated for the spectrophotometric analysis of the A-5(2X) and SPB additives in a nickel plating bath. In Table 1 the program configurated to carry out the measurement for each UV-Vis spectrum with the software AutoAnalysis has been detailed. This program will be performed in loop in order to carry out the necessary 53 measurements along a complete electroplating process. The complete system works automatically and is controlled by a computer.

The whole system is interconnected by Teflon tubes, whose length or diameter are usually optimized in order to get the desirable signal in the detector at the measuring time. The volume and geometry of the coils or reactors should be also optimized. In general, the longer the tubes are, the higher is the dispersion since the flow takes more time to reach the detector.\textsuperscript{28} Therefore, to assure a proper dilution of the nickel bath with water, a long reactor coil will be preferred provided that measuring time is not long. Tubes of 0.8 mm. i.d., frequently used in SIA, have been used throughout, except for the tube connecting the water vessel (i) with the syringe which had a diameter of 1.5 mm. i.d. In general, differences in flow dispersion with the tube diameter are very small.\textsuperscript{29}

First of all, the order in which the components are aspirated through the valves and the amount of aspirated volumes should be selected. In the built system, water will be used as carrier and it will be stored in (i). The flow will be controlled by the syringe (j), connected to the carrier when syringe valve [head-2] is set to the OFF position and to the holding coil (k) when the syringe is set to the ON position. The holding coil, in turn, is joined to the central port of the selection valve (m) and it will be always filled with the carrier, water in this case. One lateral port of the valve (l) is connected to the sample, the nickel bath, in (a); another port (3) is connected to a vessel of water in (n), the dilution agent, an other port (4) is connected to the reaction coil in (p) and finally the port (8) is connected to a waste vessel in (o). It is important to point out that regardless the procedure programmed in AutoAnalysis$^\text{\textregistered}$, syringes, by default, will be positioned at the bottom and set to OFF at the beginning of any procedure. In this case, therefore, the syringe (2.5mL) will be always filled with water from (i) before starting any method.
Usually, the syringe aspirates initially the carrier/washing solution to the holding coil and then, the sample and the reagents. Therefore, the first step for the additives determination by the SI-system is to guarantee that both the holding coil and the reaction coil are filled with the carrier. The first three orders of the program will guarantee that it is fulfilled. Action \( \text{I} \) will move the valve to port (4) in such a way that the holding and the reaction coils are linked and then, a 2 seconds wait it is introduced by order \( \text{II} \). The inclusion of this stabilization time will be carried out every time the valve is moved from a port to another, after aspiration of the sample and reagents by the propulsion device and when the flow is led to the detector to avoid a rise in pressure. Action \( \text{III} \) will dispense the water stored in the syringe towards the system so that it is filled with the carrier. Afterwards, blank is measured, orders \( \text{IV} \) and \( \text{V} \). Because there is no other bath component that absorbs in the UV-Vis region considered apart from A-5(2X) and SPB (Figure 5), blank is measured with water in the detector cell to simplify the problem. Then, the sample will be aspirated through the valve. In general, it is preferable to aspirate a reduced volume of sample, the nickel bath here, in an exact and reproducible manner in such a way that an appropriated and not saturated absorbance spectrophotometric signal is obtained. If a small volume is taken, a high sampling frequency can be obtained as the measuring time is reduced. In Figure 7 the influence of the aspirated sample volume in the SIAgram profile is depicted. A SIAgram represents the evolution of the signal in the detector along as the flow travels through the SI-system.
Determination of additives. Spectrophotometry

Table 1. Program configuration in AutoAnalysis for automatic spectrum measurement.

<table>
<thead>
<tr>
<th>ORDER</th>
<th>ACTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Valve A move to position 4.</td>
</tr>
<tr>
<td>2</td>
<td>Wait 2 seconds.</td>
</tr>
<tr>
<td>3</td>
<td>Priming in dispense with heads [2-ON, 8-OFF]. Exclusive Mode.</td>
</tr>
<tr>
<td>4</td>
<td>Wait 2 seconds.</td>
</tr>
<tr>
<td>5</td>
<td>Wait: measure Blank.</td>
</tr>
<tr>
<td>6</td>
<td>Valve A move to position 1.</td>
</tr>
<tr>
<td>7</td>
<td>Wait 2 seconds.</td>
</tr>
<tr>
<td>8</td>
<td>Pickup 0.200 mL [Buret-1] at 0.500 mL/min with heads [2-ON,8-OFF].</td>
</tr>
<tr>
<td>9</td>
<td>Wait 2 seconds.</td>
</tr>
<tr>
<td>10</td>
<td>Priming in pickup with heads [2-OFF]. Exclusive Mode.</td>
</tr>
<tr>
<td>11</td>
<td>Valve A move to position 8.</td>
</tr>
<tr>
<td>12</td>
<td>Wait 2 seconds.</td>
</tr>
<tr>
<td>13</td>
<td>Dispense 0.500 mL [Buret-1] at 7.500 mL/min with heads [2-ON,8-OFF]. Exclusive Mode.</td>
</tr>
<tr>
<td>14</td>
<td>Valve A move to position 1.</td>
</tr>
<tr>
<td>15</td>
<td>Wait 2 seconds.</td>
</tr>
<tr>
<td>16</td>
<td>Pickup 0.025 mL [Buret-1] at 0.500 mL/min with heads [2-ON, 8-OFF]. Exclusive Mode.</td>
</tr>
<tr>
<td>17</td>
<td>Wait 2 seconds.</td>
</tr>
<tr>
<td>18</td>
<td>Valve A move to position 3.</td>
</tr>
<tr>
<td>19</td>
<td>Wait 2 seconds.</td>
</tr>
<tr>
<td>20</td>
<td>Pickup 0.450 mL [Buret-1] at 2.500 mL/min with heads [2-ON, 8-OFF]. Exclusive Mode.</td>
</tr>
<tr>
<td>21</td>
<td>Wait 2 seconds.</td>
</tr>
<tr>
<td>22</td>
<td>Priming in pickup with heads [2-OFF]. Exclusive Mode.</td>
</tr>
<tr>
<td>23</td>
<td>Valve A move to position 4.</td>
</tr>
<tr>
<td>24</td>
<td>Wait 2 seconds.</td>
</tr>
<tr>
<td>25</td>
<td>Dispense 0.700 mL [Buret-1] at 0.500 mL/min with heads [2-ON, 8-OFF]. Exclusive Mode.</td>
</tr>
<tr>
<td>26</td>
<td>Dispense 0.800 mL [Buret-1] at 0.500 mL/min with heads [2-ON, 8-ON]. Exclusive Mode.</td>
</tr>
<tr>
<td>27</td>
<td>Wait 10 seconds.</td>
</tr>
<tr>
<td>28</td>
<td>Wait: measure nickel bath spectrum.</td>
</tr>
<tr>
<td>29</td>
<td>Dispense 0.600 mL [Buret-1] at 7.500 mL/min with heads [2-ON, 8-ON]. Exclusive Mode.</td>
</tr>
<tr>
<td>30</td>
<td>Valve A move to position 2.</td>
</tr>
<tr>
<td>31</td>
<td>Wait 2 seconds.</td>
</tr>
<tr>
<td>32</td>
<td>Dispense 0.400 mL [Buret-1] at 7.500 mL/min with heads [2-ON,8-OFF]. Exclusive Mode.</td>
</tr>
</tbody>
</table>
It can be seen in Figure 7 that the starting point of the curve does not depend on the aspirated volume. In this case, volumes higher than 10-15 µl lead to saturated signals; also the increase of the aspirated volume displaces the maximum of the peak to longer times. That is because the higher the aspirated volume, the wider the peak. Moreover, the dispersion is higher when the volume increases. The sample aspiration is given by orders from 6 to 15. The order number 6 moves the valve to port (1), where there is the nickel bath, and 7 stops the system for 2 seconds. Before aspirating a certain volume of sample, there is a need to assure that the sampling tube is filled with the sample. To get that, orders 8 and 9 are introduced. Because the sampling tube has a size of 0.5 mL, a volume of 0.200 mL of the nickel bath will be aspirated through the port (1) to assure the sampling tube is filled properly with the nickel solution. Small flow rates are generally preferred when sample and reagents are aspirated to minimize undesired effects of flow cavitation. A rate of 0.500 mL/min was chosen. Figure 8 shows the multiburette and the valve commands configuration for order 8. Syringe 2, (Figure 8a), is turn ON so that sample from the nickel bath can be aspirated. A volume

![Figure 7. Influence of the sample volume on the SIA peaks profile. (1, blue), 25 µl; (2, pink), 50 µl; (3, green) 100 µl; (4, light blue) 225 µl. SIAgrams were not obtained at the final conditions.](image-url)
of 0.200 mL will be aspirated at 0.500 mL/min. Valvule position, in Figure 8b, is connected to port (1); that is, to the bath nickel sample.

Figure 8. (a) Multiburette command software configuration and (b) valvule command software configuration for order 8.
Then, the syringe is led to bottom to be filled in with water from (i), 10. The extra volume of nickel bath that has been stored in the holding coil has now to be taken to waste. Thus, the valve is moved to port 8 by order 11 and after a waiting time of 2 seconds, 12, a volume of 0.500 mL will be dispensed to waste, order 13. The holding coil volume must be larger than the syringe volume. Otherwise, the sample can accidentally go into the syringe during aspiration. Here, a holding coil of 2.6 mL was used. After the washing step, a reduced volume of sample, 25 µl in this case, is aspirated by the syringe and it is stored into the holding coil, orders from 14 to 17. Afterwards, the reagent, water in this case in (n), will be aspirated through the dilution tube through port (3). Orders from 18 to 20. Unlike the conventional flow injection, FIA, where the sample zone is injected directly into the carrier stream, in the sequential injection (SI), the sample is first aspirated and then the reagent, by using a selector valve. Consequently, a stack of well-defined zones towards the detector is obtained. The flow reversal, as a result of the injection step, creates a composite zone in which the sample and reagent zones penetrate to each other due to a combined axial and radial dispersion. A more effective dilution process is achieved in this way. 32,33 Thus, order 18 moves the valve to port 3, where there is the water vessel and after the 2 seconds waiting time, 19, 0.500mL of dilution agent will be aspirated through the dilution tube, which has a capacity of 0.20 mL, 20. Then, the system pressure has to get stabilized again, 21. After leading the syringe down again by order 22, valve is move to position 4, towards the detector, 22 and 24. The reaction coil (p) has 3 mL of capacity. As it has been already said, in general, the longer the tubes, the higher the dispersion, since the flow takes more time to reach the detector. 34 In this case, a long reaction coil was used to make the path to the spectrophotometer long enough and to assure proper dilution of the sample. The flow is pushed to the detector (q) at a certain rate, 25 to 26. The flow rate chosen to lead the sample to the detector was 0.500 mL because it has also influence on the sample dispersion. In general, the higher the flow, the smaller the dispersion. 35 In this case, the flow rate chosen assured a suitable dilution step. 25 leads the flow to waste, since it is mainly carrier solution step. 26, however, leads the flow back to the nickel bath, in (a), because it is mainly diluted nickel bath. This action will be controlled by the solenoid valve in (q) [head-8]. Thus, the OFF position leads the flow to waste, in (s) and the ON position back to the bath (a). Nickel bath losses are
minimized in this way. When it is considered that the sample, conveniently diluted, has reached the detector, the absorbance spectrum in the range 248 - 320 nm is registered. When the sample reaches the detector, it is better to select the tail of the SI profile to stop the flow and to measure the spectrum, once the maximum of the SIAgram has been reached, because the ascending part is very stepped and the higher the slope the worse. 36,37 (Figure 7). The maximum of the SI profile provides the highest sensitivity but precision is poorer. This precision, in general, improves as the slope of SIAgram decreases. Therefore, the measuring point will be set after the SI maximum. Nevertheless, the finally chosen position to stop the flow must be a balance between precision, sensitivity and time. It was noticed, in this particular case, that a better precision in the signal was obtained if the flow was stopped. In Figure 9 there are several SIAgrams depicted, each of them shows the signal obtained when the flow is stopped at a different time. After stopping the flow, there are small flow variations along the time; therefore, it is important to measure the spectrum at a fixed time previously established to get reproducible results. A small stabilization time of about 2 seconds is essential to avoid irregularities in the flow pattern immediately after the pump stops; afterwards, there should be a fixed period of time so that the spectra registered along time are comparable. Even though the flow is stopped, high absorbance variations during a reasonably short interval of time have been previously reported38 and this phenomenon can be also appreciated in this case (Figure 9). The flow was stopped at different times and the absorbance evolution was observed along a 30 second interval. A small absorbance variation is appreciated. This kind of variation is shown in Figure 10, where several spectra have been registered at different times after stopping the flow at 110s from the beginning of the SI procedure. The change in a nickel bath spectrum shape between 248 and 320 nm is plotted in Figure 10a, whereas the absorbance evolution at the maximum of the absorbance peak (266 nm) and at the foot of the absorption band, 320 nm, are represented in Figure 10b. There is a slight increase in absorbance at 266nm and there is a slight decrease in absorbance at 320nm. Therefore, it is essential to control tightly the stopping time and the waiting time after stopping the flow.
Figure 9. Influence of the flow stopping time in the SI signal evolution at 266 nm. SIAgrams were not obtained at the final conditions.

Figure 10. (a) Spectrum evolution after the flow stopping at 110s. (b) Absorbance evolution at 266 nm and 320 nm.

In this case, the spectrum was always registered 10 seconds after stopping the flow (orders 27 and 28). Altogether, the UV-Vis spectrum was finally acquired 205s after the beginning of the process. The chosen conditions proved to give reproducible
spectra as long as the repeatability between several responses acquired along five days was quite high (Figure 11a and 11b). The standard deviation was measured at 266nm and 205 seconds to study the uncertainty between responses. A 2.2% of relative standard deviation was obtained among these measurements. This value can be considered satisfactory, demonstrating that the chosen conditions to acquire spectra by the SI-system were suitable for the automatic determination of A-5(2X) and SPB in the nickel bath.

Once the spectrum has been registered, sample leftovers have to be expelled (steps 29 - 32). Step 29 leads the diluted nickel bath from the detector back to the nickel bath, and after moving the valve to port (1) (28 and 29) step 30 dispenses the stored nickel bath into the sample tube, back to the bath to minimize bath losses. Together with the nickel bath, a certain volume of water will be also expelled to the bath. This is made to compensate somehow the loss of water in the bath by heating. In spite of that, extra periodical additions of water were strictly necessary to keep the volume of bath approximately constant during the electrodeposition process.

![Graphs showing absorbance over time](image)

**Figure 11.** (a) SIA profiles of a nickel bath sample at the finally chosen conditions along a five day time. (b) Absorbance signal at 205 seconds.
4.3.3. Data pretreatment and variable selection

The variability of the collected spectra due to the use of different measuring apparatus or to the time passage is a problem to deal with. In this case, the spectrum of an amount of 64 standard samples with the same bath composition of non-additive components, SA-1 and NPA, but different concentration of A-5(2X) and SPB was measured. The first few measurements were carried out with a Hewlett Packard 8452A spectrophotometer, but due to an equipment renewal, the spectrophotometer was changed to an Agilent 8453A. Furthermore, measurements of standards were performed along an eight-month period and all of these measurements were kept and used. This allowed the building of a more robust calibration model, able to cope with unforeseen variations in the bath samples.
Figure 12. (a) Raw data. (b) First derivative data. (c) Residuals of CLS model using raw data. (d) Residuals of CLS model using first derivative data. (— red). Data acquired with Hewlett Packard 8452A. (--> blue). Data acquired with Agilent 8453 (early measurements). (·•, black) Data acquired with Agilent 8453 (late measurements).

In Figure 12a some standard spectra are depicted. An instrumental drift can be appreciated between data acquired with spectrophotometer Hewlett Packard 8452A (—) and those obtained with the spectrophotometer Agilent 8453, regardless of whether early data (·••·) or late data (••••) are considered. A slight drift can also be appreciated between early and late data (Figure 12a, zoomed top-right box). These differences, however, can be minimized through both a spectral pretreatment and a variable selection. Common spectral pretreatments include Standard Normal Variate method (SNV), Multiplicative Scatter Correction method (MSC) or the use of derivative signals. For instance, SNV and MSC have been successfully applied in Raman or infrared spectroscopy; calibration models based on derivative spectral data are used
to reduce scatter effects. A first derivative removes an additive baseline and a second derivative removes a linear baseline.\(^{20}\) These methods have successfully been applied to the multicomponent analysis of mixtures by UV-Vis spectrophotometry.\(^{44}\) In this work, first-derivative with a Savitzky-Golay approach (three-point filter width and polynomial order two) was used. The choice of the window size is a trade-off between noise reduction and distortion of the spectrum; window sizes of five- or seven-point filter are generally used,\(^{45}\) but in this case a three-point filter was used because a larger window size resulted in higher errors, probably due to spectrum distortion. This pretreatment minimized both the instrumental and time drifts (Figure 12b, zoomed bottom-left box).

An enlarged view of drifts in spectra can be seen when residuals of CLS models are plotted vs. wavelength. CLS residuals represent the difference between the recovered spectra of standards and those of the pure species.\(^{46}\) The higher the residuals are, the larger the difference between the pure spectra and the standard spectra. In our measured spectra, residuals are very high for long wavelengths when raw data are used (Figure 12c), but they are negligible for first derivative spectra (Figure 12d).

Variable selection can sometimes be useful for improving multivariate calibration models by removing variables that do not contain useful information.\(^{47,48}\) In this case, different ranges were tested and the region 256-296 nm was confirmed to give the best results, as it could be expected from Figure 12(b). Therefore, this region was used for building the calibration models. In any case, both raw and first derivative data were always used to make PLS and CLS calibration models and results were compared.

A model with only 12 samples for the calibration set, all of them measured with the same spectrophotometer, HP8453, was also tested as calibration set, but poor results were obtained and so the model was not included.

4.3.4. Calibration models

Table 2 summarizes the results obtained for the calibration of mixtures of SPB and A-5(2X) additives in nickel electroplating bath matrices. The Figures of merit obtained for the models are included. The Limit of detection (LOD) was deduced from Found vs. added plot\(^{49}\) and according to the Multivariate Residuals Value (MR) method\(^{50}\) (see Introduction, Section 1.2.6.) The number of LVs ranged between 3 and 5.
which shows that there are sources of variance different from the concentration of analytes (additives). Some part of the extra variance might come from the drift of spectra along time and from the change of instrument (Figure 12). This is the reason why when first derivative data is used, the number of LVs is lower (Table 2). There is still some extra unexplained variance that PLS was able to model using an additional LV. On the contrary, CLS had some difficulties to accomplish it. The consequence is that mean errors with PLS keep always under 10% (Table 2), regardless if raw or first derivative data are used. Similar errors are obtained for both additives, even though SPB contribution to the experimental signal is very low (Figure 5 (b)). On the contrary, mean errors obtained with CLS are much higher (between 9.2 and 23%) showing that CLS always provides poor results. This is probably due to the presence of a complex matrix. The CLS model for SPB (the lower signal contribution) is much worse (15 – 23% mean errors) than the CLS model for A-5(2X) (the higher signal contribution, 9 – 12% mean errors). The lower random errors obtained for SPB using PLS gave lower detection limit compared to those obtained with CLS. In the case of A-5(2X), errors are not so different for both algorithms and consequently they are the limits of detection.

Table 2. Relative errors found in the resolution of binary mixtures of additives SPB and A-5(2X) in nickel electroplating bath matrices. Spectral Range, 256-296 nm (every 2nm).

<table>
<thead>
<tr>
<th>Additive</th>
<th>algorithm</th>
<th>Pretreatment</th>
<th>LVs</th>
<th>Calibration</th>
<th>Validation</th>
<th>LOD Found vs. added (mL L⁻¹)</th>
<th>LOD MR (mL L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPB</td>
<td>PLS</td>
<td>No&lt;sup&gt;a&lt;/sup&gt;</td>
<td>5</td>
<td>5.3</td>
<td>7.6</td>
<td>0.12</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Yes&lt;sup&gt;b&lt;/sup&gt;</td>
<td>4</td>
<td>4.7</td>
<td>5.8</td>
<td>0.11</td>
<td>0.09</td>
</tr>
<tr>
<td>CLS</td>
<td>No&lt;sup&gt;a&lt;/sup&gt;</td>
<td>17.4</td>
<td>23.0</td>
<td>0.31</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Yes&lt;sup&gt;b&lt;/sup&gt;</td>
<td>15.3</td>
<td>20.3</td>
<td>0.21</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A-5(2X)</td>
<td>PLS</td>
<td>No&lt;sup&gt;a&lt;/sup&gt;</td>
<td>4</td>
<td>5.2</td>
<td>7.3</td>
<td>2.7</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Yes&lt;sup&gt;b&lt;/sup&gt;</td>
<td>3</td>
<td>5.8</td>
<td>8.1</td>
<td>3.0</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td>CLS</td>
<td>No&lt;sup&gt;a&lt;/sup&gt;</td>
<td>9.6</td>
<td>13.4</td>
<td>3.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Yes&lt;sup&gt;b&lt;/sup&gt;</td>
<td>9.2</td>
<td>12.4</td>
<td>3.9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> Raw data. <sup>b</sup> First derivative data.
4.3.5. Accuracy and precision

Table 3 shows the mean precision for SPB and A-5(2X) in the whole range of concentrations shown in Figure 3. Different and independent empirical estimation could be obtained for each additive using several replicates at fixed concentration levels. The concentration ratio range: A-5(2X)/SPB was set between 2.8 and 60. These measurements were considered as an external test set and were collected several months after the measurement of the main part of the calibration samples. Results are given in Table 3. Some slight systematic errors (just above 10%) were found for SPB and A-5(2X) when the PLS model was used. CLS models, however, gave higher systematic errors for low A-5(2X) concentrations (up to 40%). Precision was better than 5% in 90% of individual cases for A-5(2X) and 60% for SPB. Nonetheless, low concentrations of SPB were determined with less precision (11-16%) when PLS and raw data were used. In general, PLS provides better results than CLS and the use of first derivative data always furnishes similar or slightly better (but not much) errors than raw data. If there is only a need for checking the evolution of the additive at the first stage of the bath life, when the quality could be still considered acceptable, not very fine results are needed and CLS could well be used, otherwise, PLS is strictly necessary to obtain fine
Table 3. Accuracy and Precision in the determination of SPB and A-5(2X) in nickel electroplating bath matrices. Concentrations are in mL additive/L bath.

<table>
<thead>
<tr>
<th>Algorithm</th>
<th>Experimental data</th>
<th>SPB Added</th>
<th>Found</th>
<th>Error (%)</th>
<th>RSD (%)</th>
<th>A-5(2X) Added</th>
<th>Found</th>
<th>Error (%)</th>
<th>RSD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLS</td>
<td>raw</td>
<td>0.14</td>
<td>0.12</td>
<td>-14</td>
<td>13</td>
<td>4.0</td>
<td>3.9</td>
<td>-2.5</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.15</td>
<td>7</td>
<td>11</td>
<td>24</td>
<td>26</td>
<td>8</td>
<td>3.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.20</td>
<td>0.19</td>
<td>-7</td>
<td>16</td>
<td>12</td>
<td>13</td>
<td>8</td>
<td>8.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.40</td>
<td>1.59</td>
<td>14</td>
<td>1.3</td>
<td>4.0</td>
<td>4.4</td>
<td>10</td>
<td>3.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.55</td>
<td>11</td>
<td>1.4</td>
<td>24</td>
<td>27</td>
<td>12</td>
<td>8</td>
<td>2.2</td>
</tr>
<tr>
<td>1st derivative</td>
<td></td>
<td>0.14</td>
<td>0.13</td>
<td>14</td>
<td>9.8</td>
<td>4.0</td>
<td>4.3</td>
<td>7.5</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.13</td>
<td>-7</td>
<td>5.0</td>
<td>24</td>
<td>27</td>
<td>12</td>
<td>5.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.20</td>
<td>0.20</td>
<td>16</td>
<td>12</td>
<td>14</td>
<td>17</td>
<td>5.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.40</td>
<td>1.55</td>
<td>11</td>
<td>2.0</td>
<td>4.0</td>
<td>3.9</td>
<td>-2.5</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.46</td>
<td>1.45</td>
<td>1.6</td>
<td>24</td>
<td>26</td>
<td>8</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>CLS</td>
<td>raw</td>
<td>1.40</td>
<td>1.21</td>
<td>-13</td>
<td>1.6</td>
<td>4.0</td>
<td>5.6</td>
<td>40</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.47</td>
<td>5.0</td>
<td>1.2</td>
<td>24</td>
<td>26</td>
<td>8</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>1st derivative</td>
<td></td>
<td>0.2</td>
<td>0.2</td>
<td></td>
<td>11</td>
<td>12</td>
<td>13</td>
<td>9</td>
<td>5.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.40</td>
<td>1.34</td>
<td>-4.1</td>
<td>1.8</td>
<td>4.0</td>
<td>4.8</td>
<td>20</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.30</td>
<td>-7.5</td>
<td>1.7</td>
<td>24</td>
<td>26</td>
<td>8</td>
<td>1.1</td>
<td></td>
</tr>
</tbody>
</table>

4.3.6. Additive determination in a commercial electroplating nickel bath

An electroplating nickel bath was prepared according to a commercial formulation (Section 3.2.1.) and used to plate steel sheets in the way explained in the nickel electrodeposition (Section 3.2.4.1.). The concentrations of SPB and A-5(2X) could then be monitored over the time by an on-line interfacing that automatically sampled one aliquot by the SI-system and measured the UV spectrum. A total of 53 aliquots were measured in order to determine A-5(2X) and SPB concentrations. The results obtained for SPB and A-5(2X) along the bath life, after using PLS and CLS models previously developed (Table 2), can be seen in Figure 13. Concentrations found
under LOD values given in Table 2 are represented by open marks and are included with informative purposes exclusively. The lower LOD values corresponding to PLS method can clearly be seen for SPB additive.

Results obtained with both algorithms, PLS and CLS, were not much different. Moreover, it made little difference whether raw (Figure 13a and 13b) or first derivative data (Figure 13c and 13d) were used. However, when pretreatment was made, differences were still smaller. The higher precision of PLS can be appreciated in Figure 13a and 13c, where smoother concentration curves were obtained. The lower limit of detection with PLS is also appreciated. All this, as well as the lower $RE(\%)$ values found for calibration and validation, made the PLS models with first derivative data as the most suitable for both additives, because more precise predictions with lower errors were obtained.
Figure 13. SPB ((a) and (c)) and A-5(2X)((b) and (d)) concentrations in the bath along the electrodeposition process. (a) and (b,) raw data; (c) and (d), first derivative data. Wavelengths from 256 to 296 in every case. (Rhombs, PLS; triangles, CLS. Open marks, values under the detection limits given in Table 1).

The concentration of A-5(2X) does not change appreciably along the bath life but the concentration of SPB decreases as electroplating proceeds. This decay follows a first order law as it can be seen in Figure 14, where the logarithmic plot is straight for at least three half-lives. The pseudo-first order constant obtained from the slope of the logarithmic plot can be used to evaluate the rate of consumption of SPB additive. In this case, the value of the rate constant, when PLS and first derivate data were used, was $0.137 \pm 0.005 \text{ (A·h/L)}^{-1}$. The decomposition products of SPB brightener do not show
UV-vis absorption and they were not identified by any other experimental technique; in any case, the chemical composition of the additive is unknown and neither do we have any hypothesis about the decomposition reaction path, nor have we found in the literature any related references. However, literature is abundant in references on decomposition of saccharin\textsuperscript{14,51} (probably the main component of A-5(2X) additive), but it keeps stable along time in the present case (Figure 13b and 13d). On the other hand, no explicit information has been found on decomposition of the other additives (SA-1 and NPA) and because they do not show UV-Vis absorption, they were not studied further.

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{figure14.png}
\caption{First order kinetic plot for SPB decay in the electroplating bath when PLS model is applied to first derivative data.}
\end{figure}

4.3.7. Validation of the automated method

Because of baseline shifts, the manual data also required some pretreatment and variable selection as it was made in the automatic procedure. The PLS regression of the first derivative original spectra demonstrated to give the best prediction results and, this method was chosen to report the results by the manual procedure, as it happened with the automatic one. Thus, the first-derivative with a Savitzky-Golay approach (three-
point filter and polynomial order two) was used so that the spectra drifts could be minimized. The region from 256 to 296 nm was chosen because shorter and longer wavelengths showed to be usefulness as they do not contain relevant information.

Table 4 summarizes the results of the PLS calibration model for mixtures of A-5(2X) and SPB additives (Figure 4) in nickel electroplating bath matrices by the manual procedure. The limit of detection (LOD) was calculated with two different methods; one of them the Found vs. added plot\textsuperscript{52} and the other, the Multivariate Residuals Value (MR)\textsuperscript{53}, (see Section 1.2.6. of the Introduction). The number of LVs was 3 for A-5(2X) and 5 for SPB and the mean errors are always under 3% for both calibration and validation, which means an excellent precision. Because the only sources of variability expected are the concentration of both additives, the extra LVs should probably be due to some outliers (disarrangements in the sample preparation, etc.) that will affect more to the analyte that show a lower absorbance (SPB).

\textit{Table 4. Relative errors found in the resolution of binary mixtures of additives SPB and A-5(2X) in bath matrices by the manual procedure. First derivative data. Spectral range, 256-296 nm (every 2 nm). PLS model.}

<table>
<thead>
<tr>
<th>Additive</th>
<th>LVs</th>
<th>Calibration</th>
<th>Validation</th>
<th>LOD \textit{Found vs. added} (mL L\textsuperscript{-1})</th>
<th>LOD \textit{MR} (mL L\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPB</td>
<td>5</td>
<td>1.0</td>
<td>2.9</td>
<td>0.05</td>
<td>0.01</td>
</tr>
<tr>
<td>A-5(2X)</td>
<td>3</td>
<td>2.0</td>
<td>1.1</td>
<td>2.2</td>
<td>0.6</td>
</tr>
</tbody>
</table>
Table 5. Accuracy and precision in the determination of SPB and A-5(2X) by the manual procedure in nickel electroplating bath matrices. Concentrations are in mL additive/L bath. First derivative data. Spectral range, 256-296 nm (every 2 nm). PLS model.

Table 5 summarizes the results obtained by the manual procedure in the prediction of several replicates at fixed concentration levels. The concentration ratio: A-5(2X)/SPB was set between 2 and 1200. These measurements were considered as an external test set and were collected several months after the calibration set was measured. The whole of samples in Table 5 were measured in a random way along 7 days.

In general, very good prediction results were obtained regardless A-5(2X) or SPB is considered. A systematic error up to 30% (and 75% relative error) was found for SPB at the lowest level, but it can probably be explained due to the fact that concentration level, 0.05mL/L, is the LOD value for that additive or may be the sample was an outlier. For A-5(2X) accuracy results below 12% were obtained in all the cases. Precision was always better than 2.3% for A-5(2X) and better than 2.2% for SPB whenever concentrations were higher than the LOD value.

Table 6 summarizes the results of regression of the PLS calibration model obtained for both, manual and automatic procedures and compares them.
Determination of additives. Spectrophotometry

Table 6. Relative errors found in the resolution of binary mixtures of additives SPB and A-5(2X) in the bath matrices by both manual and automatic procedures. Derivated data. Spectral range, 256-296 nm (every 2nm).

<table>
<thead>
<tr>
<th>Calibration method</th>
<th>Additive</th>
<th>Concentration range (ml L⁻¹)</th>
<th>LVs</th>
<th>RE(%)</th>
<th>LOD (mL L⁻¹)</th>
<th>Found vs. added</th>
<th>MR</th>
</tr>
</thead>
<tbody>
<tr>
<td>manual</td>
<td>SPB</td>
<td>0.05-3</td>
<td>5</td>
<td>1.0</td>
<td>2.9</td>
<td>0.05</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>A-5(2X)</td>
<td>6-60</td>
<td>3</td>
<td>2.0</td>
<td>1.1</td>
<td>2.2</td>
<td>0.6</td>
</tr>
<tr>
<td>automatic</td>
<td>SPB</td>
<td>0.14-1.40</td>
<td>4</td>
<td>4.7</td>
<td>5.8</td>
<td>0.11</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td>A-5(2X)</td>
<td>4-24</td>
<td>3</td>
<td>5.8</td>
<td>8.1</td>
<td>3.0</td>
<td>0.20</td>
</tr>
</tbody>
</table>

No evidence of systematic errors were found in any case for A-5(2X) and SPB in nickel bath matrices, but random errors are significantly lower in the manual method and so is the limit of detection. The concentration matrices used for the calibration models in both cases (manual and automatic methods) were different, but it can, certainly, be concluded that the manual method provided better results for A-5(2X) and SPB additives both for the calibration and validation sets. The reason can be the simpler handling of the sample with the manual procedure. However, things changed when both methods were used for the monitoring of additives along a nickel bath life, especially in the case of SPB (Figure 15). The automatic method provides a more uniform and steady decay curve of concentration for SPB, whereas the manual method provides more disperse results. Perhaps the influence of the operator when taking samples after each plating process may account for it. Along the life of the bath, the SI system automatically takes reproducible aliquots from the bath and the dilution process is made by the system with a high reproducibility and no handling from the operator.
Figure 15. Additives evolutions along the electroplating process. (a) SPB; (b) A-5(2X). Automatic (squares) and manual (circles) results are compared. PLS results with first derivated data. Wavelengths from 256 to 296 nm in every case. Open marks, values under the detection limits. According to the Found vs. added plot method.

4.4. Conclusions

UV-Vis spectrophotometry has proven to be a suitable technique to follow the evolution of A-5(2X) and SPB additive concentrations in a nickel bath. The automatic bath sampling procedure for determination of additives (SPB and A-5(2X)) in a nickel electroplating bath through a SI-system has been reported. A manual procedure was used as reference. The implementation of the SI-system is easy and neither expensive nor sophisticated apparatus are needed. This can be very interesting from an industrial point of view. Multivariate methods of calibration have been applied because of the spectral overlapping. Both PLS and CLS models can be used for monitoring the additive degradation along the life of the bath, but best prediction results are obtained by using PLS with first derivative experimental data. No systematic errors were found in the determination of both additives. A good precision was obtained in any case, showing that additives can be monitored along the whole bath life without the need of an operator. The level of SPB in the bath follows a first-order decay model. The proposed method can be considered a process analysis that can be implemented at a close-to-real time. This can allow to keep constant the additive (SPB) concentration and, consequently, the bath performance.
4.5. References.


28. V. Cerdà, *Introducción a los métodos de análisis en flujo*. SCIWARE, Palma de Mallorca, Spain, 2006, 45-46.

29. V. Cerdà, *Introducción a los métodos de análisis en flujo*. SCIWARE, Palma de Mallorca, Spain, 2006, 47.


34. V. Cerdà, *Introducción a los métodos de análisis en flujo*. SCIWARE, Palma de Mallorca, Spain, 2006, 45-46.

35. V. Cerdà, *Introducción a los métodos de análisis en flujo*. SCIWARE, Palma de Mallorca, Spain, 2006, 47.


